EXHIBIT A-31

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USGS
science for a changing world

Naturally Occurring Radioactive Materials (NORM) in Produced Water and Oil-Field Equipment—An Issue for the Energy Industry

Introduction

Naturally occurring radioactive elements such as uranium, radium, and radon are dissolved in very low concentrations during normal reactions between water and rock or soil. Ground water that coexists with deposits of oil can have unusually high concentrations of dissolved constituents that build up during prolonged periods of water/rock contact. Many oil-field waters are particularly rich in chloride, and this enhances the solubility of other elements including the radioactive element radium. Some of this saline, radium-bearing water is unavoidably brought to the Earth's surface with the oil and must be separated and then disposed, usually by return to depth in an injection well. At some oil-field sites the pipes and tanks that handle large volumes of this "produced water" can become coated with scale deposits that contain radium. Radium-bearing scale is the type of "diffuse NORM waste" that occurs in the oil industry. Radium accumulation in oil-field equipment in the United States first became apparent in the 1980's when scrap metal dealers began to routinely detect unacceptable levels of radioactivity in shipments of oil-field pipe. Since that time the oil and gas industry has sought to better define the extent of the oil-field NORM problem, and to develop techniques for the prediction, prevention, remediation, and disposal of oil-field NORM. In parallel efforts, State and Federal regulatory agencies have worked to develop guidelines for the control of NORM that will adequately protect public health and the environment. This report summarizes current understanding of the composition and mode of occurrence of oil-field NORM in the United States, briefly reviews the status of NORM regulations, and identifies some health and environmental issues associated with oil-field NORM.

Location of Oil-Field NORM in the United States

Deposits of oil are found in 30 States, but the vast majority (86 percent) of onshore oil production is concentrated in Texas, Oklahoma, Louisiana, Wyoming, California, Kansas, and New Mexico (fig. 1*A*). In 1989 the American Petroleum Institute sponsored a preliminary nationwide reconnaissance of measurable radioactivity at the exterior surfaces of oil-field equipment (Otto, 1989). The results of this nonstatistical sampling indicated that gamma-ray radiation levels exceeded natural background radiation levels at 42 percent of the sites. Radiation levels greater than five times the median background of all sites were found at approximately 10 percent of the sites. Most of the sites with markedly higher radioactivity were concentrated in specific geographical areas, such as the Gulf Coast, northeast Texas, southeast Illinois, and south-central Kansas (fig. 1*B*). Additional surveys by some State agencies identified radioactive oil-field equipment in northern Michigan and eastern Kentucky. Pipe, casing, fittings, and tanks that have an extended history of contact with produced water are more likely to contain radioactive deposits than other parts of the plumbing system at oil-field production

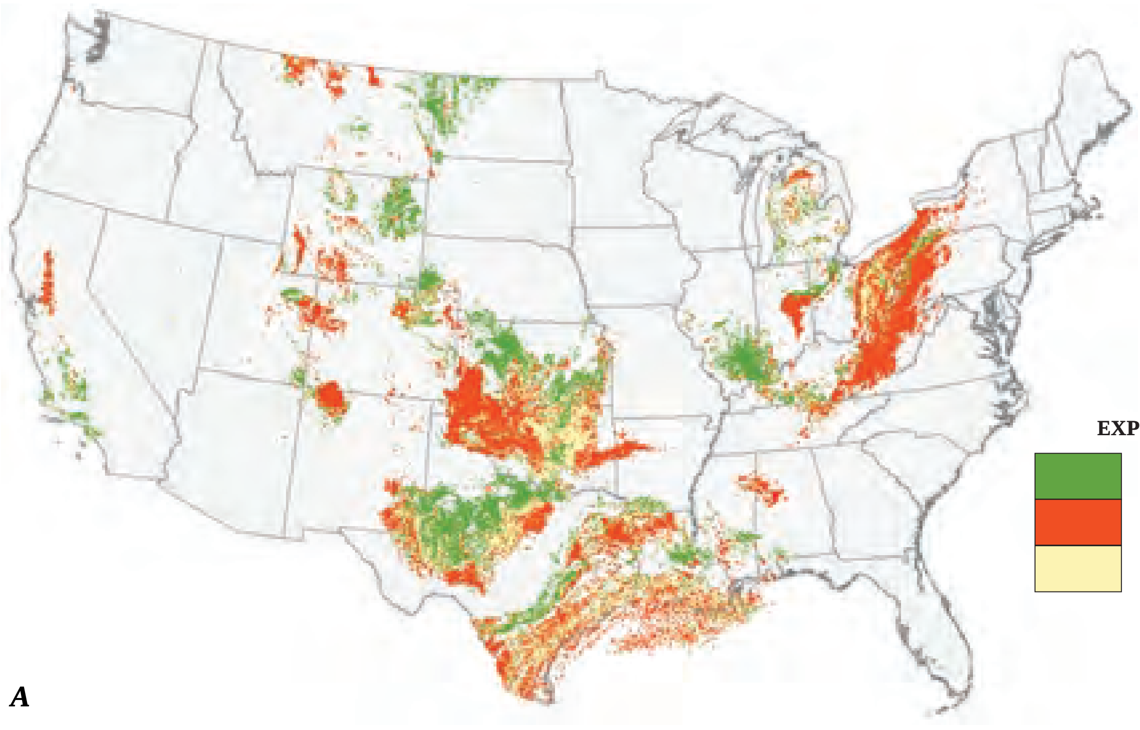

Figure 1 (left and next page). Areal distribution in conterminous United States of *A*, producing oil and gas wells through 1994, and *B*, radioactive oil-field equipment (next page). *A*, from Mast and others, 1998. *B*, modified from Otto, 1989. Reprinted courtesy of the American Petroleum Institute—based on original API figure, modified by U.S. Geological Survey.

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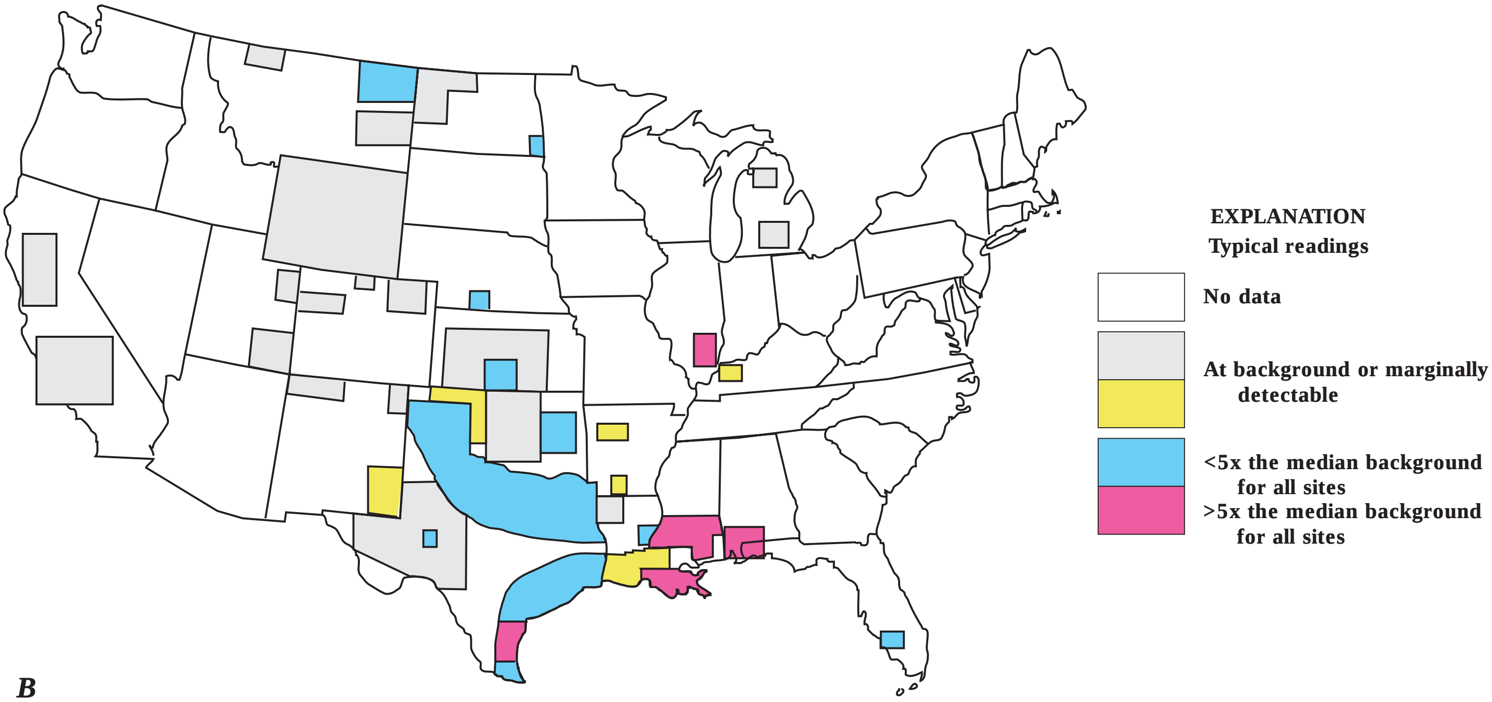


sites. Soil in the immediate vicinity of production sites may be unusually radioactive if affected by spills or leakage of produced water, or if contaminated by scale removed during pipe or tank cleaning operations. Handling of used pipe at pipe storage yards may also contaminate soil with radioactive scale. Although not discussed herein, some equipment used to process and transport natural gas may contain small amounts of radioactive decay products of radon gas.

Form of Oil-Field NORM

Oil-field equipment can contain radioactive scale and scale-bearing sludge, both of which form as coatings or sediments. The scale precipitates from produced water in response to changes in temperature, pressure, and salinity as the water is brought to the surface and is processed to separate coexisting crude oil. The scale is typically a mixture of carbonate and sulfate minerals. One of these sulfate minerals is barite (barium sulfate), which is known to readily incorporate radium (Ra) in its structure. Many studies of radioactive scale from oil-field equipment have documented that barite is the primary host of oil-field NORM and that the radioactivity is from isotopes of radium and their decay products. The two radium isotopes present in produced water and barite scale are ^{226}Ra (half-life =1,600 years) and ^{228}Ra (half-life =5.8 years). These two isotopes are produced by radioactive decay of uranium and thorium present in rocks of the oil-producing formations. The concentration of dissolved radium is therefore influenced by the abundance of uranium and thorium in reservoir rock and by the accessibility of water to the sites containing uranium and thorium. When radium is brought to the surface in produced water, the concentration of radium that is incorporated in barite scale is largely a function of (1) the concentration of dissolved radium and (2) the amount of produced water that moves past the site of barite precipitation.

Ongoing studies by USGS scientists are documenting variations in the mineralogy, chemistry, and radium concentration of in-place scale deposits. Better understanding of the specific location and texture of the most radioactive barite scale should contribute to more cost-effective strategies for its removal. Figure 2*A* illustrates some of the textural and mineralogical variability in a sample of scale from an old section of above-ground oil-field pipe. Lighter colored barite is present along with variable amounts of darker iron oxides. Barite occurs as intact layers as well as fragments of former layers that were transported and recemented with iron oxides. A corresponding image of radioactivity in this sample (fig. 2*B*) is recorded on a special film and illustrates the variable concentration of radium and its radioactive decay products in these layers.

Abundance of Radium in Oil-Field NORM

Measurement of total radioactivity with a hand-held radiation detection instrument permits rapid assessment of a site for NORM contamination, but site cleanup criteria and waste disposal options are based on actual concentrations of radium isotopes. Some specialized field instruments permit rapid estimates of the concentration of radium isotopes, but such estimates require confirmation by careful laboratory analysis of selected subsets of samples. Radium concentrations are generally reported as picocuries/gram (pCi/g) of solid material or picocuries/liter (pCi/L) of water or air. A picocurie equals 2.22 disintegrations-per-minute (dpm). Figure 3*A* illustrates the distribution of total radium concentration (^{226}Ra and ^{228}Ra) in barrels of oil-field NORM waste stored in Louisiana in 1992 (Wascom, 1994). The maximum radium concentration in this waste and in most reported oil-field scale from the U.S. is several thousand pCi/g, although very small quantities of scale have been reported with as much as 400,000 pCi/g of radium. For comparison, most natural soils and rocks contain approximately 0.5–5 pCi/g of total radium. A uranium ore sample containing 1 weight percent uranium has approximately 3,300 pCi/g of ^{226}Ra. Most of the radium in older oil-field scale is ^{226}Ra, because the shorter lived ^{228}Ra decays with a half-life of 5.8 years.

Figure 3*B* illustrates the distribution of dissolved ^{226}Ra concentration in 215 samples of produced water from seven major oil-producing areas (Fisher, 1998). Radium tends to be more abundant in the more saline and chloride-rich varieties of these produced waters. The maximum concentration of dissolved ^{226}Ra in this limited data set is several thousand pCi/L, but concentrations above 10,000 pCi/L have been reported in the U.S. Produced water also contains dissolved ^{228}Ra, which is typically one-half to twice the concentration of ^{226}Ra. For comparison, the U.S. EPA maximum contaminant level for drinking water is 5 pCi/L for total dissolved radium.

Regulations for the Control of Oil-Field NORM

There currently exist no Federal regulations that specifically address the handling and disposal of oil-field NORM wastes. States that have enacted specific NORM regulations include some important oil producers such as Texas, Louisiana, New Mexico, and Mississippi. New NORM regulations or modifications to general radiation protection statutes are under consideration in other major oil-producing States such as California, Kansas, and Oklahoma. Standards for cleanup of radium-contaminated soils that typically appear in enacted or proposed NORM regulations call for an average concentration of less than 5 pCi/g in the upper 15 cm (centimeters) of soil and an average of less than 15 pCi/g in deeper increments of 15 cm. Some States allow an average of as much as 30 pCi/g of radium in the upper 15 cm of soil. For oil-field equipment, typical standards for release for other uses or for recycling require that radioactivity at the surface should not exceed some low multiple of natural background radioactivity.

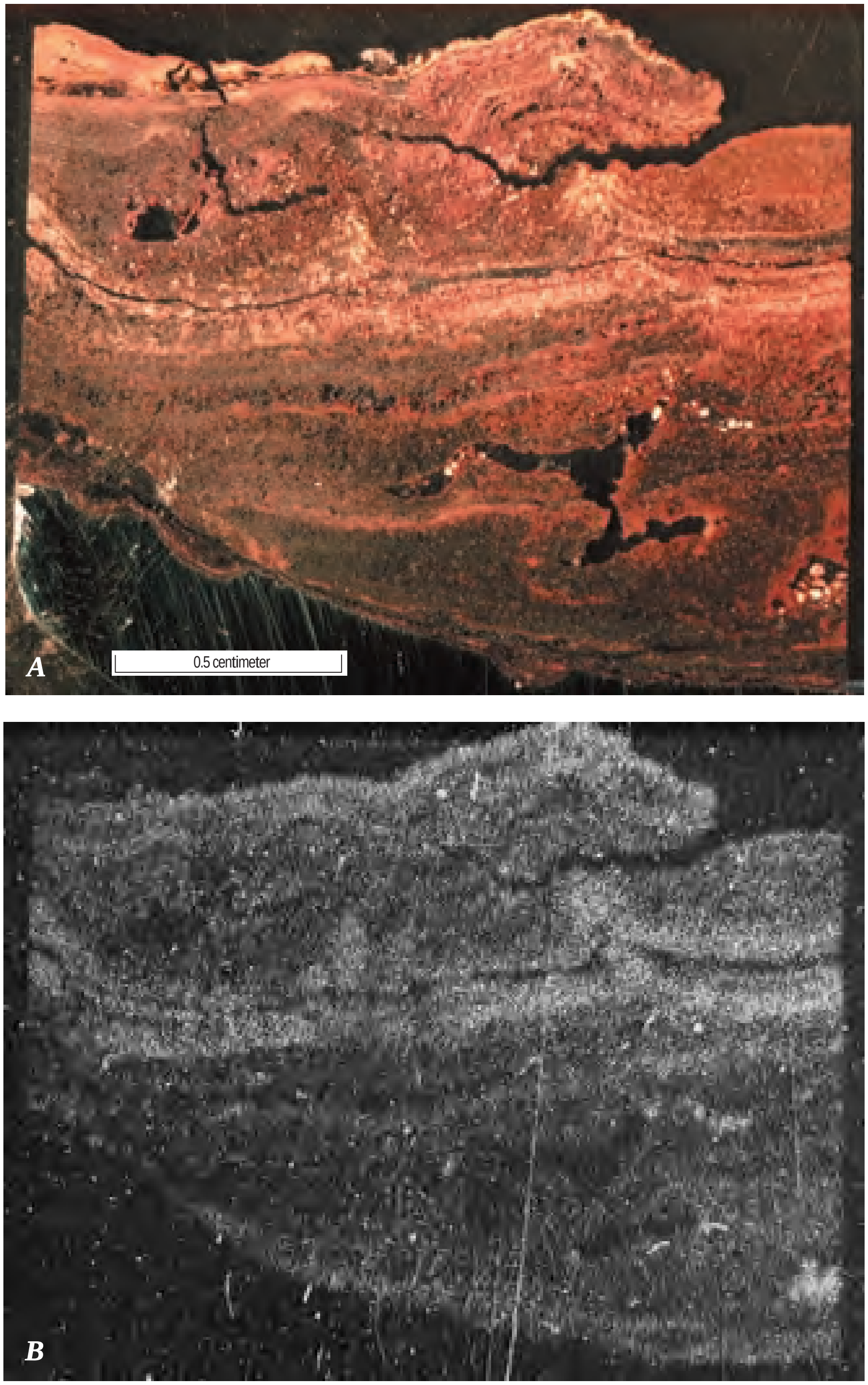


Figure 2. Radioactive scale deposits inside oil-field pipe (*A*) and the distribution of alpha-particle-emitting radium and radium decay products in the same sample (*B*). Brighter regions on the alpha emission image indicate areas of scale with higher concentrations of radioactive elements.

Health and Environmental Issues of Oil-Field NORM

Once formed, barite is a very insoluble mineral. One liter of water at the Earth's surface dissolves only 0.0025 grams of barite. Efficient removal of barite deposits from oil-field equipment requires special chemicals or vigorous mechanical methods. The process of barite removal and disposal is complicated by the need to minimize radiation dose to workers and the general public. Radiation exposure pathways include external gamma radiation (major), ingestion (minor), and inhalation of particulates and radon gas (major).

Figure 4 illustrates the relative isolation of NORM waste from the general public for a variety of possible disposal options. As degree of isolation increases so does the capability for disposing of higher radium concentrations. Currently most oil-field NORM waste is stored at production sites awaiting disposal in specially designated and permitted landfills, disposal wells, or injection wells (fig. 4). Surface spreading and dilution of low-level NORM waste (fig. 4) is a past practice that is now disallowed by most States with NORM regulations. A preliminary radiological dose assessment was reported for a scenario in which individuals live on a NORM-amended soil and consume local water, livestock, and food crops (Smith and others, 1996). For soils amended with radium to the highest concentration under regulatory consideration (30 pCi/g) the additional annual radiation dose by all pathways was equivalent to the average annual background dose to the U.S. population. Current limits set by the Nuclear Regulatory Commission require that the total of such additional doses to the general public be limited to about 30 percent of the average annual background dose.

Prior to 1970 the regulations governing disposal of produced water and scale were less restrictive, and thus older oil-field production sites are more likely to have above-background concentrations of NORM in nearby soils and stream sediments. Several studies, including some by USGS researchers, have documented the presence of barite in soils contaminated with oil-field NORM.

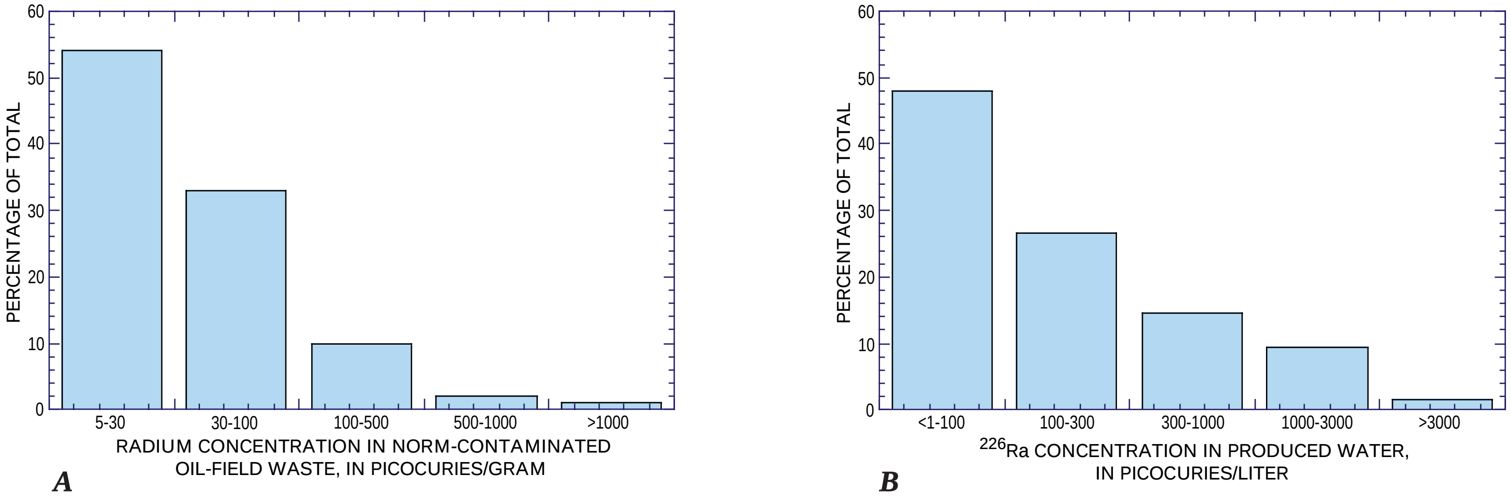
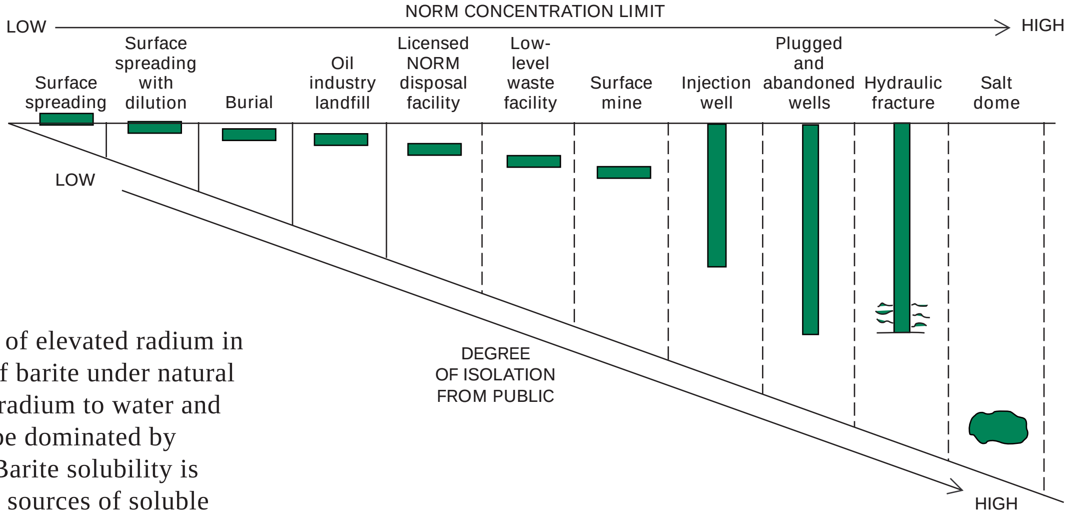


Figure 3. Estimated distribution of radium concentration in *A*, solid oil-field waste and *B*, produced water.

Figure 4. Disposal alternatives for NORM wastes. Disposal of more concentrated wastes requires greater isolation of waste from the general public. Modified from American Petroleum Institute (1992). Reprinted courtesy of the American Petroleum Institute—based on original API figure, modified by U.S. Geological Survey.



Barite scale is the most likely host of elevated radium in these soils. The extreme insolubility of barite under natural conditions limits the rate of release of radium to water and suggests that dispersal of radium will be dominated by physical transport of barite particles. Barite solubility is lowest in oxidized soils that are rich in sources of soluble sulfate such as gypsum. In organic-rich soils barite solubility is increased by the action of sulfate-consuming bacteria. The average age of formation of barite scale can be estimated based on the different rates of decay of ^{226}Ra and ^{228}Ra, or based on the buildup of radioactive decay products of these radium isotopes. Such information is useful for determining the sources and history of contamination at a site and for assigning possible liability.

Current Status and Future Direction of the Oil-Field NORM Issue

The magnitude of the oil-field NORM problem in the U.S. has been estimated, but it remains to be completely assessed. Increased industry awareness and understanding of the problem coupled with government regulatory efforts have provided much better control of oil-field NORM wastes and have reduced the radiation exposure to workers and the public. Management of the present inventory of stored oil-field NORM waste and options for its disposal are designed to reduce radiation hazard to the general public. The challenge to the oil and gas industry will be to develop safer and more cost-effective methods to minimize, process, and dispose of future oil-field NORM. An additional challenge to industry and government is to identify, remediate, and if necessary, remove NORM contamination that remains at old or abandoned petroleum production sites.

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EXHIBIT A-36

Management of Exploration, Development and Production Wastes: Factors Informing a Decision on the Need for Regulatory Action

Management of Exploration, Development and Production Wastes:

Factors Informing a Decision on the Need for Regulatory Action

April 2019

United States Environmental Protection Agency
Office of Land and Emergency Management
Office of Resource Conservation and Recovery

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Definitions

Definitions of certain terms drawn from the *Report to Congress: Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy* (U.S. EPA, 1987a,b,c):

Acidize: To treat oil-bearing limestone or other formations, using a chemical reaction with acid, to increase production. Hydrochloric or other acid is injected into the formation under pressure. The acid etches the rock, enlarging the pore spaces and passage through which the reservoir fluids flow.

Additive: A substance or compound added in small amounts to a larger volume of another substance to change some characteristic of the latter. In the oil industry, additives are used in lubricating oil, fuel, drilling mud, and cement for cementing casing.

Annulus or Annular Space: The space around a pipe in a wellbore, the outer wall of which may be the wall of either the borehole or the casing.

Blow Out: To suddenly expel oil-well fluids from the borehole with great velocity.

Borehole: The wellbore; the hole made by drilling or boring.

Burn Pit: An earthen pit in which waste oil and other materials are burned.

Casing: Steel pipe placed in an oil or gas well as drilling progresses to prevent the wall of the well from caving in during drilling and to provide a means of extracting petroleum if the well is productive.

Centralized Brine Disposal Pit: An excavated or above-grade earthen impoundment located away from the oil or gas operations from which it receives produced fluids (brine). Centralized pits usually receive fluids from many wells, leases, or fields.

Centralized Combined Mud/Brine Disposal Pit: An -excavated or above-grade earthen impoundment located away from the oil or gas operations from which it receives produced fluids (brine) and drilling fluids. Centralized pits usually receive fluids from many wells, leases, or fields.

Centralized Mud Disposal Pit: An excavated or above-grade earthen impoundment located away from the drilling operations from which it receives drilling muds. Centralized pits usually receive fluids from many drilling sites.

Centralized Treatment Facility (Mud or Brine): Any facility accepting drilling fluids or produced fluids for processing. This definition encompasses municipal treatment plants, private treatment facilities, or publicly owned treatment works for treatment of drilling fluids or produced fluids. These facilities usually accept a spectrum of wastes from a number of oil, gas, or geothermal sites, or in combination with wastes from other sources.

Completion Fluid: A special drilling mud used when a well is being completed. It is selected not only for its ability to control formation pressure, but also for its properties that minimize formation damage.

Completion Operations: Work performed in an oil or gas well after the well has been drilled to the point at which the production string of casing is to be set. This work includes setting the casing, perforating, artificial stimulation, production testing, and equipping the well for production, all prior to the commencement of the actual production of oil or gas in paying quantities, or in the case of an injection or service well, prior to when the well is plugged and abandoned.

Condensate: A light hydrocarbon liquid obtained by condensation of hydrocarbon vapors. It consists of varying proportions of butane, propane, pentane, and heavier fractions, with little or no ethane or methane.

Cuttings: The fragments of rock dislodged by the bit and brought to the surface in the drilling mud.

Dehydrate: To remove water from a substance. Dehydration of crude oil is normally accomplished by emulsion treating with emulsion breakers. The water vapor in natural gas must be removed to meet pipeline requirements; a typical maximum allowable water vapor content is 7 lb per MMcf.

Desander: A centrifugal device used to remove fine particles of sand from drilling fluid to prevent abrasion of the pumps. A desander usually operates on the principle of a fast-moving stream of fluid being put into a whirling motion inside a cone-shaped vessel.

Desiccant: A substance able to remove water from another substance with which it is in contact. It may be liquid (as triethylene glycol) or solid (as silica gel).

Desilter: A centrifugal device, similar to a desander, used to remove very fine particles, or silt, from drilling fluid to keep the amount of solids in the fluid to the lowest possible level. The lower the solids content of the mud is, the faster the rate of penetration.

Drilling Fluid: The circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure. A water-based drilling fluid is the conventional drilling mud in which water is the continuous phase and the suspended medium for solids, whether or not oil is present. An oil-based drilling fluid has diesel, crude, or some other oil as its continuous phase with water as the dispersed phase. Drilling fluids are circulated down the drill pipe and back up the hole between the drill pipe and the walls of the hole, usually to a surface pit. Drilling fluids are used to lubricate the drill bit, to lift cuttings, to seal off porous zones, and to prevent blowouts. There are two basic drilling media: muds (liquid) and gases. Each medium comprises a number of general types. The type of drilling fluid may be further broken down into numerous specific formulations.

Drill Pipe: The heavy seamless tubing used to rotate the bit and circulate the drilling fluid. Joints of pipe 30 ft long are coupled together by means of tool joints.

Drill String: The column, or string, of drill pipe, not including the drill collars or kelly. Often, however, the term is loosely applied to include both the drill pipe and drill collars.

Enhanced Oil Recovery (EOR): A method or methods applied to depleted reservoirs to make them productive once again. After an oil well has reached depletion, a certain amount of oil remains in the reservoir, which enhanced recovery is targeted to produce. EOR can encompass secondary and tertiary production.

Formation: A bed or deposit composed throughout of substantially the same kinds of rock; a lithologic unit. Each different formation is given a name, frequently as a result of the study of the formation outcrop at the surface and sometimes based on fossils found in the formation.

Formation Water: The water originally in place in a formation.

Fracturing: A method of stimulating production by increasing the permeability of the producing formation. Under extremely high hydraulic pressure, a fluid is pumped downward through tubing or drill pipe and forced into the perforations in the casing. The fluid enters the formation and parts or fractures it. Sand grains, aluminum pellets, glass beads, or similar materials are carried in suspension by the fluid into the fractures. These are called propping agents. When the pressure is released at the surface, the fracturing fluid returns to the well, and the fractures partially close on the propping agents, leaving channels through which oil flows to the well.

Gas Plant: An installation in which natural gas is processed to prepare it for sale to consumers. A gas plant separates desirable hydrocarbon components from the impurities in natural gas.

Gathering Line: A pipeline, usually of small diameter, used in gathering crude oil from the oil field to a point on a main pipeline.

Glycol Dehydrator: A processing unit used to remove all or most of the water from gas. Usually a glycol unit includes a tower in which the wet gas is put into contact with glycol to remove the water. and a reboiler, which heats the wet glycol to remove the water from it so the glycol can be recycled.

Heater-treater: A vessel that heats an emulsion and removes water and gas from the oil to raise it to a quality acceptable for pipeline transmission. A heater-treater is a combination of a heater, free-water knockout, and oil and gas separator.

Hydraulic Fracturing: The forcing into a formation of liquids under high pressure to open passages for oil and gas to flow through and into the wellbore.

Hydrocarbons: Organic compounds of hydrogen and carbon, whose densities, boiling points, and freezing points increase as their molecular weights increase. Although composed of only two elements, hydrocarbons exist in a variety of compounds because of the strong affinity of the carbon atom for other atoms and for itself. The smallest molecules of hydrocarbons are gaseous; the largest are solid.

Hydrostatic Head: The pressure exerted by a body of water at rest. The hydrostatic head of fresh water is 0.433 psi per foot of height. The hydrostatic heads of other liquids may be determined by comparing their gravities with the gravity of water.

Oil and Gas Separator: An item of production equipment used to separate the liquid components of the well stream from the gaseous elements. Separators are vertical or horizontal and are cylindrical or spherical in shape. Separation is accomplished principally by gravity, the heavier liquids falling to the bottom and the gas rising to the top. A float valve or other liquid-level control regulates the level of oil in the bottom of the separator.

Perforate: To pierce the casing wall and cement to provide holes through which formation fluids may enter or to provide holes in the casing so that materials may be introduced into the annulus between the casing and the wall of the borehole. Perforating is accomplished by lowering into the well a perforating gun, or perforator, that fires electrically detonated bullets or shaped charges from the surface.

Permeability: A measure of the ease with which fluids can flow through a porous rock.

Pig: A scraping tool that is forced through a pipeline or flow line to clean out accumulations of wax, scale, and so forth, from the inside walls of a pipe. A cleaning pig. travels. with the flow of product in the line, cleaning the walls of the pipe with blades or brushes. A batching pig is a cylinder with neoprene or plastic cups on either end used to separate different products traveling in the same pipeline.

Porosity: The quality or state of possessing pores (as a rock formation). The ratio of the volume of interstices of a substance to the volume of its mass.

Produced Water: The water (brine) brought up from the hydrocarbon bearing strata during the extraction of oil and gas. It can include formation water, injection water, and any chemicals added downhole or during the oil/water separation process.

Propping Agent: A granular substance (as sand grains, walnut shells, or other material) carried in suspension by the fracturing fluid that serves to keep the cracks open when the fracturing fluid is withdrawn after a fracture treatment.

Sediment: The matter that settles to the bottom of a liquid; also called tank bottoms, basic sediment, and so forth.

Separator: A cylindrical or spherical vessel used to isolate the components in mixed streams of fluids.

Shale Shaker: A series of trays with sieves that vibrate to remove cuttings from the circulating fluid in rotary drilling operations. The size of the openings in the sieve is carefully selected to match the size of the solids in the drilling fluid and the anticipated size of cuttings. It is also called a shaker.

Stock Tank: A crude oil storage tank.

Surfactant: A substance that affects the properties of the surface of a liquid or solid by concentrating on the surface layer. The use of surfactants can ensure that the surface of one substance or object is in thorough contact with the surface of another substance.

Tank Battery: A group of production tanks located in the field that store crude oil.

Weighting Material: A material with a specific gravity greater than that of cement; used to increase the density of drilling fluids or cement slurries.

Wellbore: A borehole; the hole drilled by the bit. A wellbore may have casing in it or may be open (i.e., uncased); or a portion of it may be cased and a portion of it may be open.

Well Completion: The activities and methods necessary to prepare a well for the production of oil and gas; the method by which a flow line for hydrocarbons is established between the reservoir and the surface. The method of well completion used by the operator depends on the individual characteristics of the producing formation or formations. These techniques include open-hole completions, conventional perforated completions, sand-exclusion completions, tubing-less completions, multiple completions, and miniaturized completions.

Wellhead: The equipment used to maintain surface control of a well including the casinghead, tubing head, and Christmas tree.

Well Stimulation: Any of several operations used to increase the production of a well.

Workover: One or more of a variety of remedial operations performed on a producing oil well to try to increase production. Examples of workover operations are deepening, plugging back, pulling and resetting the liner, squeeze-cementing, and so on.

Workover Fluids: A special drilling mud used to keep a well under control when it is being worked over. A workover fluid is compounded carefully so it will not cause formation damage.

1. Introduction

The United States Environmental Protection Agency ("EPA" or "the Agency") was granted authority to establish a national framework for solid waste management under the Resource Conservation and Recovery Act of 1976 (RCRA; Public Law 94-580). The intent of this law is to conserve energy and natural resources, reduce the amount of waste generated, and ensure that waste is managed in a manner that protects both human health and the environment. Subtitle C of RCRA provides EPA primary authority to promulgate and enforce federal regulations that address management of hazardous wastes from the initial point of generation to the ultimate point of disposal (i.e., "cradle to grave"). Subtitle D of RCRA provides EPA authority to promulgate standards for non-hazardous waste disposal; however, states have the primary authority to implement and enforce these standards. The RCRA statute does not define which wastes are hazardous and what management practices are most appropriate. These determinations are made by EPA based on a review of the potential hazards posed by the individual waste streams.

1.1. Regulatory History

When EPA first proposed regulation under Subtitle C of RCRA in 1978, the Agency deferred the applicability of most of the hazardous waste treatment, storage, and disposal standards for six categories of "special wastes," which included drilling muds and oil production brines from oil and gas operations. This deferral was intended to last until the Agency could perform further investigation into the composition, characteristics and degree of hazard posed by these large-volume wastes (43 FR 58946). In response to the proposed rulemaking, both Houses of Congress introduced legislation and held hearings and debates to determine whether and how special wastes should be regulated. Because it appeared likely that Congress would act to exempt certain wastes related to utility and energy development, EPA temporarily excluded the special wastes from the final hazardous waste regulations, stating that "this exclusion will be revised, if necessary, to conform to the legislation which is ultimately enacted" (45 FR 33084).

On October 21, 1980, Congress amended RCRA with the 1980 Solid Waste Disposal Act Amendments, which included provisions that addressed special wastes (Public Law 96-482). Specifically, Section 3001(b)(2)(A) ("the Bentsen Amendment") temporarily exempted drilling fluid, produced water and other wastes associated with the exploration, development and production (E&P) of crude oil, natural gas and geothermal energy from regulation under Subtitle C until further study of the associated risks had been completed. This provision required EPA to determine whether regulation under Subtitle C was warranted, submit findings to Congress and publish a final regulatory determination. Furthermore, it stipulated that any future regulation of E&P wastes under Subtitle C would take effect only if authorized by an act of Congress.

The Agency transmitted a Report to Congress entitled *Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy* on December 28, 1987 in three volumes that separately covered oil and gas, geothermal, and all associated appendices (U.S. EPA, 1987a,b,c). EPA concluded in this report that stringent regulation from cradle to grave under RCRA Subtitle C was not warranted for these wastes because enforcement of existing state and federal programs would generally be adequate to control the wastes, the large waste volumes generated could severely strain capacity at existing Subtitle C facilities, and the inflexibility of the Subtitle C program would create a great permitting burden on regulatory agencies that could result in undue delays for exploration and production operations. Based on these findings, EPA issued a final determination in 1988 that maintained the exemption from RCRA Subtitle C for E&P wastes associated with primary field operations (53 FR 25447).

Exemption from RCRA Subtitle C does not mean that these wastes cannot cause harm to human health or the environment if improperly managed. Rather, EPA concluded that any risks associated with these wastes could be effectively controlled by improvements to existing state and federal regulatory programs. Therefore, the Agency has since pursued a multi-pronged strategy that includes further research, cooperative work with states to review and update programs, federal action outside RCRA Subtitle C, and voluntary programs to reduce waste generation.

1.2. Changes within the Industry

A combination of economic drivers and technological advancements have resulted in changes to the national energy landscape over the past three decades. The two most significant advancements have been the widespread adoption of hydraulic fracturing and directional drilling, which allowed expanded drilling for crude oil and natural gas in black shale and other "unconventional" formations. Hydraulic fracturing is the injection of fluids into the formation at pressures high enough to fracture nearby rock and provide conduits for the oil or gas to flow into the well. Directional drilling is the installation of wells at an angle (deviated or horizontal wells) that allows greater contact between the well and the formation to maximize the fractured area. Although both technologies have existed in some form for years, recent innovations allowed combined application to formations that were previously considered uneconomical to access. Production from unconventional formations represents a growing share of the national output, though a majority is still produced from "conventional" formations located across the country. **Figure 1-1** illustrates the different types of wells and hydrocarbon-bearing formations that are currently in production.

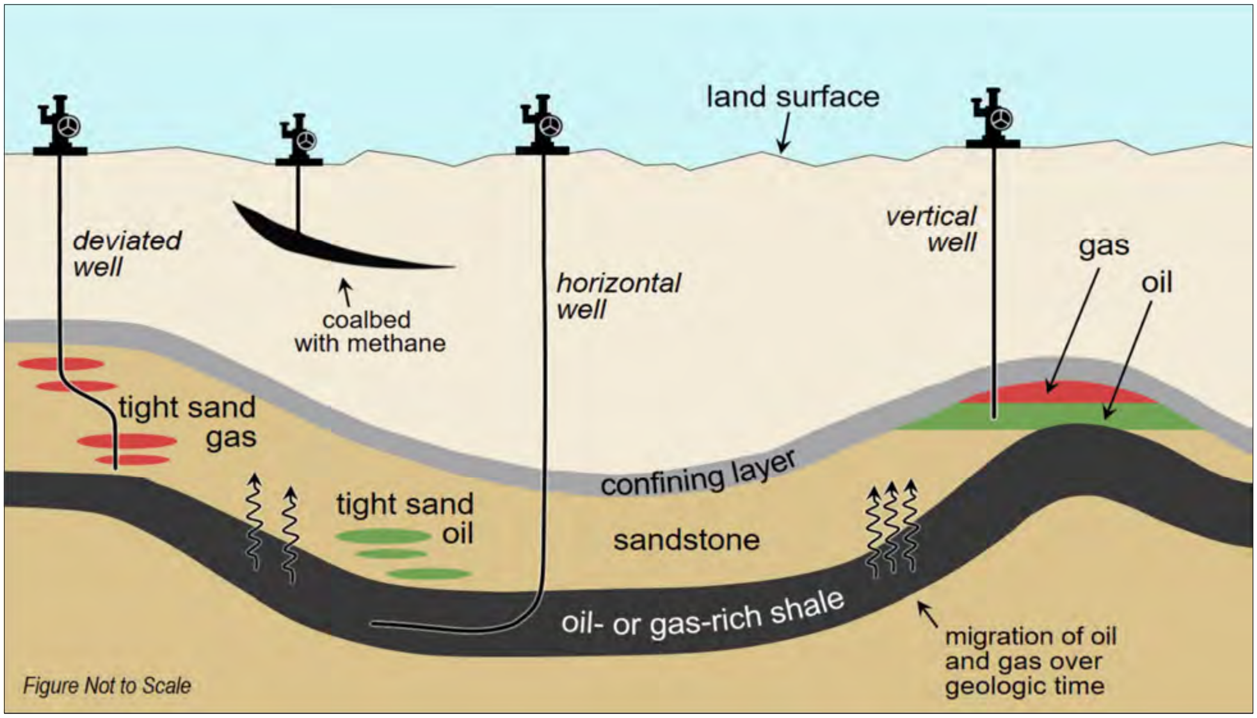

Figure 1-1: Examples of the Different Types of Oil and Gas Reservoirs and Production Wells.

Conventional hydrocarbon formations are composed of higher-permeability rocks (e.g., sandstone, limestone, dolomite) that initially produce economically-significant volumes of oil or gas without the need for hydraulic fracturing. Hydrocarbons typically do not originate in these formations. Instead, the oil and gas have been driven into these formations from deeper source rocks by a combination of temperature, pressure, and density gradients. Conventional formations are typically located beneath an impermeable ("confining") layer that limits further migration of the hydrocarbons toward the land surface. Vertical wells are the most common type of well drilled in these formations because the permeable rock allows hydrocarbons to flow toward a centralized well with minimal assistance. As a result, vertical wells represent the vast majority of wells that have been drilled to date and all the wells considered in the 1987 Report to Congress.

Unconventional hydrocarbon formations are composed of lower-permeability rocks (e.g., shale, coal beds) that must be hydraulically fractured to produce economically-significant volumes of oil or gas. These formations are often the source rock where the hydrocarbons formed. However, both oil and gas may also become trapped in other low-permeability ("tight") formations above the source rock. Drilling in unconventional formations typically requires directional drilling to maximize the impact of hydraulic fracturing. As a result, horizontal wells are a growing fraction of new wells drilled in the United States.

1.3. Document Purpose and Scope

On May 4, 2016, the Environmental Integrity Project, together with six other parties, filed a lawsuit with the United States District Court for the District of Columbia that alleged EPA had failed to perform non-discretionary duties under RCRA, specifically:

- Review, and if necessary revise, Subtitle D criteria for oil and gas wastes (40 CFR Part 257).
- Review, and if necessary revise, state plan guidelines for oil and gas wastes (40 CFR Part 256).

EPA entered into a consent decree on December 28, 2016 that established March 15, 2019 as the deadline for the Agency to either sign a notice of proposed rulemaking under the aforementioned statutes or to sign determinations that revisions are not necessary at this time. The deadline was later extended to April 23, 2019 in response to a temporary lapse in government appropriations that resulted in unavoidable and cascading delays as a result of the Agency shutdown.

The purpose of this document is to summarize the information currently available to EPA about the generation, management and ultimate disposition of wastes from E&P operations currently exempt from regulation under RCRA Subtitle C. These wastes are those associated with primary site operations integral to the location of hydrocarbon and geothermal reservoirs, extraction of resources, and removal of impurities necessary to transport the product offsite. This does not include wastes generated as part of offsite transportation, refinement and manufacturing operations. There are a number of wastes that fall under this exemption, but not every type is generated at each drilling site. EPA has taken steps to provide additional clarity on the scope of the E&P exemption through a 1993 *Federal Register Notice* (58 FR 15284) and an informational booklet (U.S. EPA, 2002).

EPA conducted a review of publicly available literature drawn from a wide array of government, industry and academic sources to understand what information has become available since the most recent update to the Agency's regulatory framework. This review focused on the structure of the industry, the volume and composition of wastes generated, actual waste management practices, applicable state regulations, and documented cases of environmental damage that resulted from any of these practices. The greatest changes within this industry have been in the production of crude oil and natural gas. Available data indicate that geothermal energy remains limited to a few states and has not undergone a similar surge in production. Accordingly, the majority of new information identified in the literature is focused on production of crude oil and natural gas. Therefore, the discussion in this document also focuses primarily on these associated wastes.

The information gathered for this document will be used to determine whether a reasonable probability of adverse effects to human health or the environment exists from the management of E&P wastes. Based on this review, EPA will identify any further steps necessary to prevent or substantially mitigate potential sources of harm, which may include updates to regulations or other practical and prudent non-regulatory actions.

2. Summary of Agency Actions

To help fulfill the obligations enumerated in the consent decree, EPA first reviewed existing sources of information relevant to the current state of E&P waste management and then conducted an extensive literature review to identify information that had since become available. This section details the actions previously undertaken by EPA in support of RCRA to improve existing regulatory programs and enhance understanding of both the industry and the associated wastes. EPA has also taken a number of additional actions related to E&P wastes under other Agency programs, these actions are outside the scope of this review.[1] Subsequent sections of this document discuss information that was assembled through the literature review, organized around specific factors that EPA considered relevant in its review.

2.1. 1992 Background for NEPA Reviewers

Pursuant to the National Environmental Policy Act (NEPA) and Section 309 of the Clean Air Act, EPA reviews and comments on major federal actions that may significantly affect environmental quality. EPA developed a background document on E&P site operations to assist EPA staff with development of comments on NEPA documents for the exploration and production of oil and gas on federal lands (U.S. EPA, 1992a). EPA recognized that this document may also be useful to operators that plan work on federal lands and federal land managers that prepare Environmental Impact Statements.

This document provides general descriptions of site operations, environmental impacts that may be associated with each operation, possible prevention/mitigation measures, and types of questions that should be raised as part of the Agency's review. It is not intended to be exhaustive and does not include discussion on impacts to floodplains, archaeological resources, and other traditional NEPA concerns that can be present at any type of development. Rather, it focuses on operations specific to oil and gas with the greatest potential to impact the environment, which include well site and road construction, drilling fluid and cuttings management, produced water disposal, product gathering systems (pipelines and storage tanks), and production operations. The document outlines general concerns about impacts to groundwater, surface water, air, ecosystems and sensitive receptors, though it acknowledges that every operation is unique and additional analyses could be necessary to fully understand the risks posed by a specific project.

2.2. 1992 Review of Operations in Alaskan North Slope

EPA led a study to evaluate the objectives, implementation and enforcement of the state regulatory program for E&P wastes on the North Slope of Alaska. This study included information from site visits to the North Slope by personnel under contract to EPA in 1988; a review of state implementation and enforcement actions; available information on facility history and waste management practices; and

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[1] A summary of the different actions taken across the Agency to better understand and address potential environmental impacts from E&P operations is available online at: https://www.epa.gov/uog.

comments received on a 1989 draft report from the Alaska Department of Environmental Conservation (AKDEC), the oil and gas industry, environmental groups, and other interested parties. The Agency completed a report documenting the results of the case study in 1992 (U.S. EPA, 1992b).

EPA found evidence of improved waste management practices on the North Slope and significant increased attention to environmental issues. However, EPA also observed significant tracts of dead vegetation during site visits surrounding various service company sites. Service companies perform a variety of operations on the North Slope, including supplying oil field chemicals, vehicle maintenance, fuel service and drum disposal. EPA also observed impacted vegetation adjacent to a number of well pads that appeared to be the result of various spills. EPA documented ongoing activities believed to be associated with observed damages, such as releases through reserve pit berms and dikes, mishandling of oily wastes, and poor housekeeping practices with regard to handling of chemicals and equipment.

To address the issues identified during this study, EPA made a series of recommendations. First, to dedicate additional resources for training, compliance monitoring and enforcement to improve compliance on the North Slope. Second, to strengthen enforcement of existing regulations, with a focus on service company operations. Finally, to improve coordination among state agencies to save resources by eliminating duplication of effort and simplifying compliance and enforcement activities. EPA also recognized that the state had already taken positive steps to improve the regulatory program for these wastes. The program had recently been updated, which may not have been fully captured in the Agency's report, and additional reviews had been scheduled. In addition, AKDEC had plans for additional staff positions, though that had not occurred at the time of this report.

2.3. 1996-1999 Oil Field Waste Pit Program

EPA Region 8 and the U.S. Department of Interior (U.S. DOI) Fish and Wildlife Service (FWS) Region 6 created a team to assess the management of E&P wastes. Co-regulators participating in the effort included state regulatory agencies, tribal agencies, and the U.S. DOI Bureau of Land Management and Bureau Indian Affairs. The primary objectives of this effort were to determine where oily waste in open pits posed a significant threat to migratory birds or other wildlife and to assess the potential threat posed by these facilities to surface water and groundwater resources. EPA compiled the results of this effort and provided recommendations to strengthen the effectiveness of state regulatory programs (U.S. EPA, 2003).

Between 1996 and 1999, sites were assessed in all six states in EPA Region 8 (i.e., Wyoming, Montana, Colorado, North Dakota, South Dakota, Utah). Initial assessments were conducted by visual inspection during flyovers. The criterion for identifying potential problem sites was exposed oil, either on the ground or on the surface of a pit. However, other observed conditions (e.g., discharges to surface water, abandoned drums) that may pose a risk to human health or the environment were also identified as warranting further investigation. In less than four years, 15% to 20% of the approximately 28,000 pits (based on information provided by co-regulators) in EPA Region 8 were observed during aerial surveys. Many of these sites were found to be well-managed. Most pits (between 80% and 90%) did not present an apparent threat to the environment and were not flagged for further attention. 516 sites, some with multiple pits, were identified as warranting ground inspection and 475 were ultimately visited.

When apparent problems were identified from the aerial assessments, the information was shared with co-regulators who in turn distributed it to the regulated community. Owners and operators of potential problem sites were informed that their sites would be inspected no less than thirty days after the initial contact giving the operators an opportunity to address existing problems. As a result, a large percentage of flagged sites had addressed the problems prior to ground inspections. Problems that persisted at the time of the ground inspection were subsequently resolved through either compliance assistance or enforcement actions (e.g., RCRA Section 7003). In total, 348 informal actions (e.g., notice of violation) and 80 formal enforcement actions were taken. Of the facilities visited, 61% of production facilities and 100% of centralized disposal facilities required some sort of follow-up to correct environmental conditions or non-compliance.

EPA made a series of recommendations to address the waste management issues identified during this effort. First, to improve communication channels and relationships among co-regulators and Agency programs by sharing information and improving the collective understanding of the various state and federal regulatory requirements. Second, to continue improvements to regulatory programs by incorporating minimum standards compiled by EPA, the Interstate Oil and Gas Compact Commission (IOGCC), the American Petroleum Institute (API) and other organizations. Finally, to strengthen compliance monitoring and enforcement, with a particular focus on commercial disposal facilities.

2.4. 2000 Associated Waste Reports

Data collection in support of the 1987 Report to Congress focused primarily on produced water and spent drilling fluid which accounted for over 98% of total volume of E&P wastes generated. Many of the remaining lower-volume wastes were co-managed in the same management units and so were anticipated to have a minimal impact on the composition of the commingled waste. However, EPA continued to compile and analyze available information on other E&P wastes from contacts within other federal agencies, literature reviews, and industry databases to address data gaps that remained for these lower-volume wastes. In 1992, EPA collected and analyzed samples of wastewater and solid waste from various E&P operations. These and other available data were discussed in three separate reports, collectively known as the Associated Waste Reports:

- Tank Bottoms and Oily Debris (U.S. EPA, 2000a)
- Dehydration and Sweetening Wastes (U.S. EPA, 2000b)
- Completion and Workover Fluids (U.S. EPA, 2000c)

These reports summarize information on how the wastes are generated, waste volume and composition, management practices, and damages that could result from mismanagement. Available information showed enormous variability in the volume, composition and management of each waste. Yet the small number of samples relative to the volume and diversity of these waste streams, as well as analytical issues, such as matrix interference, introduced uncertainty into the data. EPA was unable to determine whether the data provided a reasonable distribution of waste concentrations or what factors contributed most to high waste concentrations. These uncertainties prevented the Agency from drawing broad conclusions about the wastes. However, EPA was able to provide recommendations for waste minimization and pollution prevention techniques that could be adopted by the industry to reduce the quantity of waste generated.

2.5. 2010 Review of Damage Cases

The Natural Resources Defense Council (NRDC) submitted a petition to EPA on September 8, 2010 requesting that E&P wastes be regulated as hazardous under Subtitle C of RCRA. The petition argued that "the toxicity of exploration, development and production wastes, their release into the environment, threats to human health, the increasing amount of these types of wastes being generated, the inadequacy of existing state regulations, enforcement and oversight, and the feasibility and economic benefits of using disposal techniques that are less harmful to the environment all support regulation under Subtitle C." In support of the petition, NRDC provided information on alleged release incidents of E&P waste. A list of the citations contained in the petition is provided in **Appendix A: (Damage Cases)**. In response, EPA examined the documents listed in the petition, as well as the additional sources referenced in those documents, to better understand the nature and frequency of incidents alleged to have caused harm to human health or the environment.

EPA identified 260 separate incidents from the sources provided that involved management of E&P wastes in 18 states between 1980 to 2010. Of these, a total of 176 involved management in pits, 12 involved some form of land application (e.g., land farming), 68 involved other miscellaneous releases (e.g., air emissions, spills), and the remaining four had insufficient information available to reliably evaluate. The sources also had information on 1,936 reports of citizen complaints, spills and other releases in three states. EPA examined these additional incidents, but found that many were occurred some time ago and it was not possible to determine the cause or nature of the incident or the alleged damage. Therefore, EPA excluded these additional reports from the review.

The vast majority of incidents reviewed were the result of non-compliance with current state regulations. All but two the 176 incidents related to management in pits and one of the 12 incidents related to land application could be attributed to violations of state regulations. This indicated that improved enforcement of existing regulations could have prevented most of the identified incidents. Based on the review of data provided by NRDC, it remained unclear that imposition of new federal regulations would substantially reduce issues of non-compliance. Rather it suggested that increased inspections and tighter enforcement of existing state regulations would reduce the frequency of violations.

2.6. 2014 Review of State Regulations

Many states developed and updated legislation and regulations in response to the increased use of hydraulic fracturing at E&P sites. EPA undertook a review of state regulations to better understand exactly how state regulations had changed since the 1988 Regulatory Determination and any gaps in coverage that may exist (U.S. EPA, 2014a). This review included a direct reading of published state regulations and statutes for pits and tanks, as well as reports and databases compiled by State Review of Oil and Natural Gas Environmental Regulations (STRONGER) and the U.S. Department of Energy (DOE). In total, EPA reviewed regulations from 26 of the 33 states that account for nearly all natural gas production in the United States. To ensure that the Agency's understanding and representation of the state regulations were accurate, EPA followed up with staff from each state agency.

This review did not aim to rank or otherwise evaluate the quality of individual state programs. Instead, it identified trends and common elements among the states. EPA found that state regulations for pits and tanks commonly included requirements for liners, secondary containment, minimum setback distances, minimum freeboard, inspection, maintenance, closure and reclamation. In contrast, states often did not have requirements for groundwater monitoring, leachate collection, air monitoring or waste characterization. The absence of these particular requirements is notable because it is a divergence from typical state programs for other wastes (e.g., municipal solid waste), though it is known that additional requirements are often included in the facility permits to allow consideration of differences in local geology, land use, water resources and other factors. However, EPA was not able to conduct a similarly thorough review of individual permits as part of the analysis.

2.7. 2014 Compilation of Best Management Practices

The Agency conducted a literature review to develop a list of publicly available sources of best management practices (BMP, also known as "voluntary management practices") for E&P wastes in pits, tanks, and land application/disposal units (U.S. EPA, 2014b). The purpose of this effort was to expand awareness and encourage the continued improvement of existing BMPs. EPA reviewed a total of 85 publicly available documents and databases developed by industry, state and federal agencies, and non-governmental organizations that range from international to regional in scope. From this list of sources, EPA selected 14 examples of BMPs for more in-depth summary. It is important to note that this study did not aim to evaluate or advocate for any specific practice, rather it was an attempt to provide information on specific practices in common use throughout the industry.

Based on the review of existing documents, EPA concluded that there is a great deal of existing guidance on BMPs that is readily available to the public. Many of these sources include recommended technical criteria for pits and tanks that cover one or more of the following areas: permitting, construction, operations (e.g., maintenance, inspection, monitoring, testing, remediation), and closure. These criteria are designed to be flexible and allow practices to be matched and adapted to the needs of the specific project and local environment. There are also ongoing efforts by various stakeholder groups to continuously refine and expand upon existing guidance.

2.8. 1988-2019 Voluntary Initiatives

The Interstate Oil and Gas Compact Commission (IOGCC) was chartered by Congress in 1935 and represents the governors from 30 oil and gas producing states. In 1988, IOGCC proposed a peer review for state regulatory programs for E&P wastes. EPA provided grant funding to the IOGCC to develop and administer these reviews. The Agency also provided grant funding to citizen groups to encourage their participation in the state reviews. From 1990 through 1997, the IOGCC administered voluntary reviews of 17 individual state regulatory programs for the oil and gas industry through a multi-stakeholder process. When deficiencies were identified, the IOGCC team provided recommendations for improvements. However, in 1997, this review process was discontinued.

EPA continued to work with the stakeholders to revive the review process and, in 1999, STRONGER was established as an independent, non-profit educational organization to continue the administration of state reviews. The multi-stakeholder board of directors includes equal representation from the oil and gas industry, state and federal regulatory agencies, and environmental public advocacy groups. EPA provided grant funding and participated on all reviews as an official observer. All reviews are open to the general public. Altogether, this provides a series of checks and balances to the review process that ensures the finalized recommendations are appropriate and impartial.

The original guidelines used in the review of state programs were completed in 1990 based on minimum acceptable standards developed for six topic areas by subcommittees and a survey of existing regulatory programs in oil and gas producing states.[2] These guidelines have been updated multiple times since then to reflect emerging issues such as abandoned wells, radioactivity, hydraulic fracturing and recycled fluids. The updates also incorporated EPA guidance developed since 1990. Draft guidelines are distributed to states, environmental groups, industry associations, and posted on the STRONGER website for public comments. The comments received are incorporated and a final draft is prepared for board approval. The most recent update to the guidelines were adopted in 2017 (STRONGER, 2017). These guidelines extend beyond the scope of RCRA and include recommendations for other topics such as well construction, data management, and fee calculation.

To date, 22 state programs have been reviewed by IOGCC or STRONGER at least once. These states collectively account for over 94% of onshore oil and gas production in the United States. A total of 45 separate reviews have been conducted among these states that include 22 initial reviews, 15 follow-up reviews, and 8 single-topic reviews (i.e., hydraulic fracturing, air quality).[3] As of 2009, STRONGER estimated that over 75% of the recommendations (306 of 405) had been adequately incorporated into state programs (STRONGER, 2016). These recommendations have led to documented changes to state programs for pits, tanks, offsite disposal, centralized facilities, spill reporting, corrective action, remedial standards, and other areas. In addition, some states have taken steps to further characterize wastes, share information with the public, and increase staffing to support enforcement.

In addition to IOGCC and STRONGER, EPA has also funded initiatives for individual states. These include grants to Alaska to identify and promote pollution prevention opportunities for the oilfield service industry (AKDEC, 1994) and to Texas to develop a waste minimization and outreach program for operators in Texas (TXRRC, 2001). EPA continues to support efforts to reduce the amount of waste

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2) The six initial topic areas included: pits, land application, commercial facilities, state and federal relations, personnel and resources, organization and coordination, and statutory authority.

3) Reports for all STRONGER reviews are made available online at: http://www.strongerinc.org/state-reviews.

generated and ensure that waste is managed in a manner that protects both human health and the environment.

3. Industry Overview

The oil and gas industry is expansive and encompasses the exploration, extraction, refining, transport and marketing of oil and gas as a fuel source and feedstock for a range of commercial products. This document focuses on the upstream sector of the industry that engages in E&P for crude oil and natural gas from subsurface formations. This section summarizes the available information on the structure of this industrial sector, the operations performed in the course of normal business operations, and the types and quantities of waste that may be generated in the process.

3.1. Summary of Site Operations

The first step in E&P operations is a pre-siting assessment of local geology to determine the potential for oil and gas production. Areas that might contain oil or gas reserves are first identified using field surveys and seismic data before obtaining the mineral interests on the property from the landowner and approval to drill from the relevant state agencies. Exploratory wells may initially be installed onsite to gather more detailed geological data on rock and fluid properties, initial reservoir pressure, and reservoir productivity. If exploratory wells identify a formation that can produce salable quantities of crude oil or natural gas, then the development wells may be installed to extract the hydrocarbons.

Well exploration, development and production involves a wide array of operations to install the well, extract the hydrocarbons, remove of impurities from the crude oil and natural gas prior to distribution, and maintain the long-term integrity of the well. The following text provides a general summary of common operations that may be performed during the installation and productive life of a well, as well as the wastes that may be generated. This discussion is not intended to provide an exhaustive list of operations or waste types; this document groups wastes into broader waste streams based on similar composition and management practices.

3.1.1. Well Installation

A drilling pad is first prepared to support a drilling rig and any ancillary equipment, such as trucks associated with the operation and trailers to house personnel and equipment. The size of a pad typically ranges between one-half and one acre, depending on the nature of the operation and the number of wells that will be drilled. The lease or property boundaries and well location are staked out and the site is excavated to clear the area of trees and other vegetation. Then an access road ("lease road") is built and any pits and tanks needed to manage waste are installed.

Modern oil and gas wells are typically drilled with rotary drill rigs. These rigs rotate the drill pipe with an attached drill bit ("drill string") to create the borehole ("wellbore"). As drilling progresses, additional drill pipe segments are added in successive sections ("joints"). The threads on each joint are coated with a compound that protects the threads and prevents seizing when the joints are connected together. At predetermined intervals, drilling is halted and the drill string is removed from the wellbore to install a steel casing. The purpose of this casing is to prevent collapse of the surrounding rock into the wellbore, isolate high-pressure formations, prevent intrusion of formation fluids into the wellbore during construction, and avoid mixing of hydrocarbons and other contaminants with overlying aquifers during production.

The first interval of casing ("conductor casing") extends a relatively short depth, typically between fifty and several hundred feet, to prevent collapse of the initial wellbore and to provide support for deeper casing strings. After each interval is installed, cement may be pumped down the casing to seal the annular space. When drilling resumes, the drill bit is advanced to a point just below where the next casing string or surface casing will extend. The second interval of casing ("surface casing") is smaller in diameter and typically extends anywhere from 50 to 100 feet below the lowermost aquifer of potential use, as specified by state requirements. Subsequent intervals of casing ("intermediate casing") are installed as needed to reach the target formation and isolate unstable formations that may collapse or cause loss of fluid circulation. If this interval is located in a stable ("competent") formation, the operator might choose not to install intermediate casing and produce through an open hole. The final interval of casing ("production casing") typically runs the full depth of the well and isolates the production zone from other formations. **Figure 3-1** provides an example of standard well casing configurations.

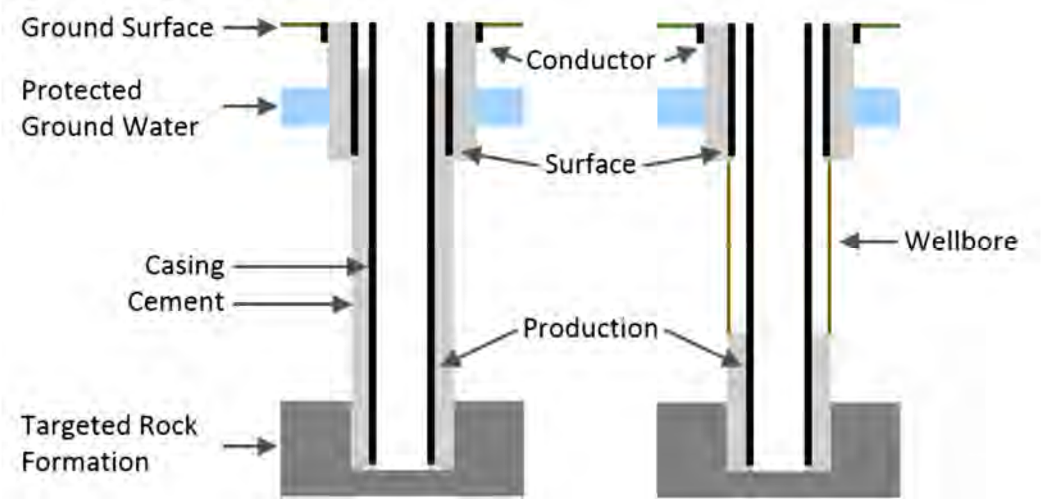

Figure 3-1: Diagram of Standard Well Casing Configurations.

Wells may be advanced directly beneath the well pad ("vertical well") or at an angle that can extend some distance beyond the footprint of the well pad ("deviated well"). The initial portion of a deviated well is typically vertical and drilled the same as any other vertical well. At the point the well begins to deviate ("kickoff point"), the curved section of the well is drilled using a hydraulic motor mounted directly above the bit and powered by the drilling fluid. This allows the drill bit to be rotated by the hydraulic motor without also rotating the drill pipe. Various sensors in the drill string provide information about the location and speed of the bit and the temperature and pressure of the formation, which allows precise control over the movements of the drill string. Deviated wells may be installed at a range of different angles, though wells in unconventional formations are often installed fully parallel with the hydrocarbon formation ("horizontal well") to allow greater contact between the well and the formation for hydraulic fracturing.

During well installation, an engineered fluid is circulated down the drill pipe and out of nozzles in the drill bit (“drilling fluid” or “drilling mud”). This fluid is used to cool and lubricate the drill bit, control pressure within the borehole, seal drilled formations to prevent fluid loss, and to transport drill cuttings to the surface. The type of drilling fluid used depends on the characteristics of the formations that will be drilled:

- Gas-based fluids (GBFs) can be entirely gas (carbon dioxide, nitrogen) or may be gas entrained in water with foaming agents (e.g., surfactants). GBFs are used to drill wells under low-pressure and low-temperature conditions in relatively shallow wells and formations like limestone and coalbeds.
- Water-based fluids (WBFs) typically consist of 80% water and 20% clay and other additives. The water can be either fresh or salt water. WBFs are used to drill deeper wells under moderate-to-high pressures and low-to-moderate temperatures.
- Oil-based fluids (OBFs) typically consist of around 55% petroleum distillate, 30% water, and 15% clay and other additives. OBFs are used to drill wells under extreme temperatures and pressures where water could evaporate or freeze (e.g., Arctic drilling) or where reactive formations could be encountered (e.g., hydratable shale, salt domes).
- Synthetic-based fluids (SBFs) are formulated similar to OBFs. SBFs are oil-like fluids formulated from vegetable esters derived by reacting an acid with an alcohol, olefins or alkenes (e.g., ethene), synthetic paraffins (paraffin-like material produced from natural gas), and alkyl benzenes (single ring aromatic hydrocarbons). SBFs are formulated to biodegrade more quickly in the environment and have lower bioaccumulation potential. These synthetic fluids tend to be more expensive and so are primarily used when drilling in environmentally sensitive areas, such as offshore and coastal areas, that require performance equivalent to an OBF.

Drilling fluid may simply be foam, fresh water or salt water at the start of drilling. However, as drilling progresses and formation pressures and temperatures increase, new fluids may be introduced that contain additives to increase the weight and enhance the performance of the fluid. Weighting agents are commonly added to increase the specific gravity (weight) of the fluid. Barium sulfate is often used as the weighting agent in WBFs, OBFs and SBFs but hematite (iron oxide) may also be used, particularly in OBFs. Another common additive is clay (typically bentonite) to further increase the specific gravity of the fluid and to help protect and seal wellbore formations.

Drilling fluids return to the ground surface through the annular space between the drill pipe and the wellbore. The used fluids are mixed with the fragments of soil, rock and other pulverized material that are dislodged by the drill bit (“drill cuttings”). Cuttings are mechanically separated from the drilling fluids to the extent practicable with equipment such as filter belts or centrifuges and sent to a reserve pit or tank. Recovered drilling fluids are treated and reused until the fluids become too contaminated to recycle, the geological conditions in the wellbore require new fluid formulation, or drilling has been completed. At that point, the spent drilling fluid is also sent to the reserve pit or tank. Drill cuttings and spent drilling fluid are the wastes generated in greatest volumes during well installation. A number of other wastes may be generated in smaller volumes that include spent spotting fluid, water used to wash the drill rig, and spills of various materials around the drill rig (e.g., cement) may be generated in smaller volumes over the course of drilling. These wastes are typically managed together with the drill cuttings and drilling fluid in onsite reserve pits or tanks prior to disposal.

3.1.2. Well Completion and Production

Once the well has been installed, any drilling fluid remaining in the well is replaced with a dense fluid free of any solids that could react with the formation water or otherwise plug the production zone. This fluid is often a heavy brine made with dissolved inorganics salts (e.g., chloride, bromide) that is used to control the pressure down-hole and to prevent formation fluids from entering the well while the well is completed. Once the completion fluid is in place, a perforating gun loaded with shaped charges is lowered into the production zone and remotely fired. The charges pierce the casing and cement, creating holes that will allow oil and gas to flow into the wellbore once the completion fluid is removed.

Well stimulation techniques may be used after well completion to widen and connect conduits in the formation and allow the oil and gas to flow more freely into the well. Acid may be injected at lower pressures and allowed to remain within the well for some time to dissolve any limestone, dolomite or calcite minerals present within the reservoir rock. Other fluids may be injected at higher pressure to create new fractures within the rock, also known as hydraulic fracturing. Common base fluids for fracturing are water or an energized mixture of water and entrained gas (e.g., nitrogen, carbon dioxide). Less common base fluids may be a mixture of water and petroleum distillate or entirely hydrocarbons and alcohols. In specific cases, acids may be used as the primary fracturing fluid to dissolve carbonate reservoirs. After the initial fracturing, gelling agents are added to increase the viscosity of the fluid and to facilitate transport of a proppant into the fractures so that the pressure in the formation does not reseal the fractures. Common proppants include various sizes of sand, ceramic beads and sintered bauxite. Next, a gel breaker is injected into the well to reduce the viscosity of the fracturing fluid and allow it to return to the surface without the proppant. These fluids may also contain a number of other additives intended to protect the integrity of the well and the formation during injection, such as friction reducers, scale and corrosion inhibitors, biocides and others. Further discussion of these other additives can be found in the *Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0* (U.S. EPA, 2015a).

The fluids produced from a well are typically some mixture of crude oil, natural gas and associated water. This mixture is immediately directed to one or more oil and gas separators that use baffles or other means to partition the different phases based on density. Natural gas rises to the top of the tank. Depending on the volume of gas generated and the available infrastructure, the natural gas may be flared off or collected for sale. Natural gas may require additional treatment to remove impurities prior to sale. Common treatments include passing the gas through specialized filters to remove either water vapor ("dehydration") or acidic gases, such as hydrogen sulfide and carbon dioxide ("sweetening"). These treatments may produce other salable products, such as elemental sulfur, compressed carbon dioxide, and natural gas liquids (e.g., propane, butane). The remaining natural gas, which is primarily methane, is sent to a transmission line for transport for sale.[4] The separated crude oil is skimmed off the top of the water and sent to a heater treater that accelerates the breakdown of any emulsified water by applying heat. The remaining crude oil is sent to tanks for storage until it can be transported offsite for sale or further refinement. **Figure 3-2** provides an example of typical operations to separate out oil and gas for transport.

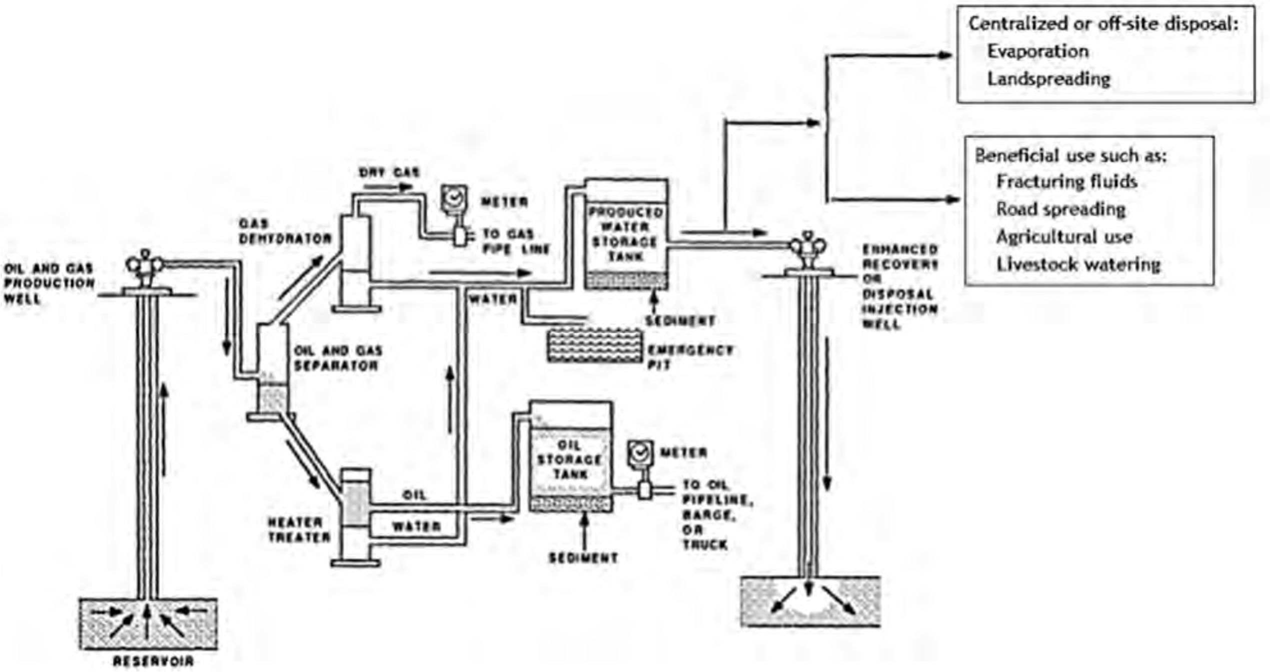

Figure 3-2: Typical Production Operation for Oil, Gas, and Water Separation.

The waste generated in the greatest volume during production by far is the wastewater that flows from the well. At first, the wastewater might be composed primarily of hydraulic fracturing fluids that have returned to the surface ("flowback"), but over time the injected fluids will mix with the water in the hydrocarbon-bearing formation ("formation water"). This mixing makes it difficult to determine what fraction of the wastewater originates from the formation at any given time. Therefore, the waste liquids generated from a well are collectively referred to as "produced water." At the ground surface, produced water is separated from any salable hydrocarbons and sent to pits or tanks for storage prior to disposal or recycling back into fracturing fluids.

Another waste routinely generated during production consists of solids that settle out and accumulate in flowlines, pits, tanks and other equipment along the production line. These solids are commonly referred to as sediment, sludge or vessel bottoms. Depending on where in the production line the sediment accumulates, it may contain a variable mixture of proppant, formation solids, chemical precipitate, paraffins, condensed liquids, heavy hydrocarbons and other substances that settle out of solution. These solids must be cleaned out of the pits and tanks periodically and are expected to be managed as a separate waste stream. Cleaning may be done manually or with the aid of mechanical

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[4] Because natural gas often requires processing to remove water vapor and other impurities prior to entering the sales line, gas plants are considered to be part of primary operations regardless of the location with respect to the wellhead.

devices ("pigs") used to scrape the insides of narrow pipes and flowlines. If the solids contain high levels of oily residue, the solids may be sent to a crude oil reclamation facility to salvage the oil. Occasionally, if the solids have a high fluid content, they may be disposed along with the produced water. Otherwise, the solids are likely to be sent as a separate waste stream for disposal.

A number of additional waste streams may be generated periodically during oil and gas production at far smaller volumes than produced water. Examples include filter socks used to remove solids from produced water, spent sorbents used to remove impurities from natural gas (e.g., glycols, amines, solid desiccants), and backwash used to the clean filters for reuse. Backwash and other wastewater may be managed in the same pits and tanks as produced water, but spent filters and sorbents are expected to be handled as a separate waste stream for disposal.

3.1.3. Well Maintenance

A variety of maintenance operations ("workover operations") may be required during the operational life of a well to maintain or enhance production. It may be necessary to first stop the flow of production fluids from the formation by pumping a high-density fluid similar to the completion fluids down the well to control formation pressure. If the well is damaged, it may be necessary to repair or replace downhole equipment. If the hydrocarbon formation becomes plugged with sand, paraffin or other fine grained materials, it may be possible to use a combination of hot liquids, acids and other physical or chemical treatments to remove the accumulations. If production cannot be restored, other options may include re-stimulating the well through hydraulic fracturing, plugging the wellbore with cement and re-completing the well in an upstream location, or re-drilling the well into a deeper production zone. Because many of these operations are similar to those conducted for well installation and completion, many of the wastes generated are also similar.

One distinct workover waste is pipe scale that forms when oversaturated minerals precipitate out of produced water and adhere to the inside of production tubing and gathering lines. Scale buildup can clog pipes and cause significant drops in production. Some types of scale can be readily removed through a combination of acid solution or mechanical scrapers. The dissolved or dislodged scale will then become incorporated into settled solids or other waste streams. However, some types of scale are highly recalcitrant and may require equipment to be removed from service in order to dislodge the scale. In some cases, the equipment may be disposed with the scale still intact. Given the difficulty of removal, this type of scale is expected to be managed and disposed as a separate waste stream.

3.2. Oil and Gas Production Rates

Both the U.S. DOE Energy Information Administration (EIA) and the Independent Petroleum Association of America (IPAA) compile statistics on crude oil and natural gas production in the United States. Available data show that onshore production occurs in 34 states, though a minority of states account for the majority of production. **Table 3-1** summarizes the states with the greatest number of active (i.e., producing) wells. These data were drawn primarily from *The Distribution of U.S. Oil and Natural Gas Wells by Production Rate* (U.S. DOE, 2018a). This dataset does not currently include any data for Idaho, Illinois or Indiana and so total well counts were drawn from relevant state agency websites. The number of gas wells in these three states were drawn from the EIA data series, *Number of Producing Gas Wells* (U.S. DOE, 2018b) and the number of oil wells was calculated by subtraction.

Table 3-1. Estimated Number of Active Wells in 2016 by State

Rank	State	Total Number of Wells	Number of Oil Wells	Number of Gas Wells	Percent of All Wells
1	Texas	309,970	174,654	135,316	29.5%
2	Oklahoma	83,977	36,002	47,975	8.0%
3	Pennsylvania	80,426	11,489	68,937	7.7%
4	Kansas	74,050	51,326	22,724	7.1%
5	New Mexico	58,338	17,837	40,501	5.6%
6	West Virginia	56,971	3,704	53,267	5.4%
7	Colorado	54,987	8,885	46,102	5.2%
8	California	52,848	48,865	3,983	5.0%
9	Ohio	45,154	13,124	32,030	4.3%
10	Louisiana	36,777	19,003	17,774	3.5%
11	Wyoming	33,783	10,090	23,693	3.2%
12	Illinois	32,100	32,064	36	3.1%
13	Kentucky	19,705	5,145	14,560	1.9%
14	North Dakota	14,396	13,942	454	1.4%
15	Michigan	13,595	3,689	9,906	1.3%
16	Utah	12,622	4,192	8,430	1.2%
17	Arkansas	11,671	1,875	9,796	1.1%
18	New York	10,873	3,120	7,753	1.0%
19	Montana	10,173	4,645	5,528	1.0%
20	Virginia	8,161	9	8,152	0.8%
	Top 20 States	**1,020,577**	**463,690**	**556,917**	**97.2%**
	All U.S. Wells	**1,049,560**	**481,781**	**567,779**	**100%**

Total Illinois Wells: https://www.dnr.illinois.gov/OilandGas/Pages/AboutOilAndGasInIllinois.aspx

The IPAA estimated there were a total of 1,072,973 active wells (578,167 oil and 494,806 natural gas) in 2016 (IPAA, 2017). These counts differ somewhat from EIA estimates, though the overall order of magnitude is the same between the two sources. The IPAA does not provide a similar breakout by state, which prevents more in-depth comparisons. Counts by well type are complicated by the fact that individual wells can produce a mixture of crude oil and natural gas. For record-keeping purposes, wells are often designated as either oil or gas based on which is produced in greater quantities.[5] Thus, well counts do not provide a reliable proxy for the total production of oil or gas in individual states. **Table 3-2** summarizes data on oil and gas production in the highest producing states from the EIA data.

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5) One barrel of oil is equivalent to approximately 6,000 ft^3 of natural gas.

Table 3-2. Estimated Crude Oil and Natural Gas Production in 2016 by State.

Rank	Crude Oil Production			Natural Gas Production		
	State	Volume (MMBL)	Percent of Total Volume	State	Volume (Bcf)	Percent of Total Volume
1	Texas	1,176	36.4%	Texas	8,126	24.8%
2	North Dakota	378	11.7%	Pennsylvania	5,313	17.0%
3	California	186	5.8%	Alaska	2,868	10.1%
4	Alaska	179	5.5%	Oklahoma	2,468	7.8%
5	Oklahoma	154	4.8%	Wyoming	1,848	6.7%
6	New Mexico	146	4.5%	Louisiana	1,708	5.6%
7	Colorado	116	3.6%	Colorado	1,702	5.5%
8	Wyoming	73	2.2%	Ohio	1,440	5.2%
9	Louisiana	56	1.7%	West Virginia	1,375	5.0%
10	Kansas	38	1.2%	New Mexico	1,285	4.1%
11	Utah	31	0.9%	Arkansas	823	2.2%
12	Montana	23	0.7%	North Dakota	609	2.1%
13	Ohio	22	0.7%	Utah	365	1.0%
14	Mississippi	20	0.6%	Kansas	243	0.7%
15	Illinois	9	0.3%	California	196	0.7%
16	Alabama	8	0.3%	Virginia	120	0.5%
17	West Virginia	7	0.2%	Michigan	101	0.4%
18	Pennsylvania	6	0.2%	Alabama	100	0.3%
19	Michigan	6	0.2%	Kentucky	92	0.3%
20	Arkansas	5	0.2%	Montana	52	0.2%
	Top 20 States	**2,640**	**82%**	**Top 20 States**	**30,834**	**95%**
	Total U.S.	**3,232**	**100%**	**Total U.S.**	**32,592**	**100%**

MMBL = Million Barrels
Bcf = Billion Cubic Feet
Crude Oil Production: https://www.eia.gov/dnav/pet/PET_CRD_CRPDN_ADC_MBBL_M.htm
Natural Gas Production: https://www.eia.gov/dnav/ng/ng_prod_sum_a_EPG0_FGW_mmcf_a.htm

The IPAA estimated national production to be 3,231 MMBL of crude oil and 32,800 Bcf of natural gas (IPAA, 2017), which align well with EIA estimates. It is clear from EIA data that production varies considerably among states and that a greater number of wells does not always translate to higher production. One reason is the age of the wells. Although wells can be re-stimulated by various means to recover output, production will inevitably decrease over time as the local reserves are depleted. Wells that no longer produce more than 10 BL of oil or 60,000 ft^3 of natural gas per day are classified as marginal wells (or “stripper wells”). The Interstate Oil and Gas Compact Commission (IOGCC) estimated that in 2016 a total of 396,023 oil wells and 381,334 gas wells had marginal production. These wells account for around two-thirds of active wells in the country and nearly all of the wells in some states. Altogether, marginal wells are estimated to produce between 284 and 404 MMBL of crude oil and 1,880 and 2,760 Bcf of natural gas, around 10% of nation-wide production (U.S. DOE, 2016a,b; IOGCC, 2017; IPAA, 2017). While the number of marginal oil wells and associated production have remained steady over the last two decades, the number of marginal gas wells and associated production have nearly doubled (IPAA, 2017). This change reflects broader trends in the oil and gas industry over this time period. **Table 3-3** provides a comparison of industry statistics from 2016 with those reported in the 1987 Report to Congress.

Table 3-3. Change in Industry Statistics, 1985 to 2016

Source	Source: U.S. EPA (1987a)		Source: IPAA (2017)	% Change
	EPA	IPAA	IPAA	IPAA
Total Active Wells	842,000	889,970	1,072,973	+20.6%
Wells Completed per Year	70,000	70,796	14,379	-79.7%
Petroleum Production (MMBL)	3,650	3,274	3,231	-1.3%
Natural Gas Production (Bcf)	16,100	19,600	32,600	+66.3%

MMBL = Million Barrels
Bcf = Billion Cubic Feet

This comparison shows that production of oil has remained stable over the past three decades, while production of natural gas increased substantially. The increase in natural gas production is attributed primarily to the adoption of directional drilling and hydraulic fracturing that allowed access to oil and gas trapped in black shale and other unconventional formations. In 2016, a total of 14,379 wells were completed. Over the same time period, the number of active horizontal wells increased by around 6,200 (IPAA, 2017; U.S. DOE, 2018a). **Figure 3-3** shows the location of the major tight oil and shale gas plays across the United States. It is notable that many states with these plays are also those with the greatest annual production volumes (e.g., Texas, Oklahoma, Pennsylvania).

A simple comparison of production statistics at two points in time does not provide a complete picture of how the industry changed in the intervening time. The production boom in the early 2000s resulted in a dramatic increase in the number of oil and gas wells drilled, though the annual number of wells never reached the same levels reported in 1985. Over the same period, oil and gas production increased substantially. The increased production has been maintained so far, even as the number of new wells decreased in recent years. **Figure 3-4** provides a year-by-year comparison of the number of wells completed each year and the annual production volume over the past two decades (IPAA, 2017; U.S. DOE, 2018c,d).

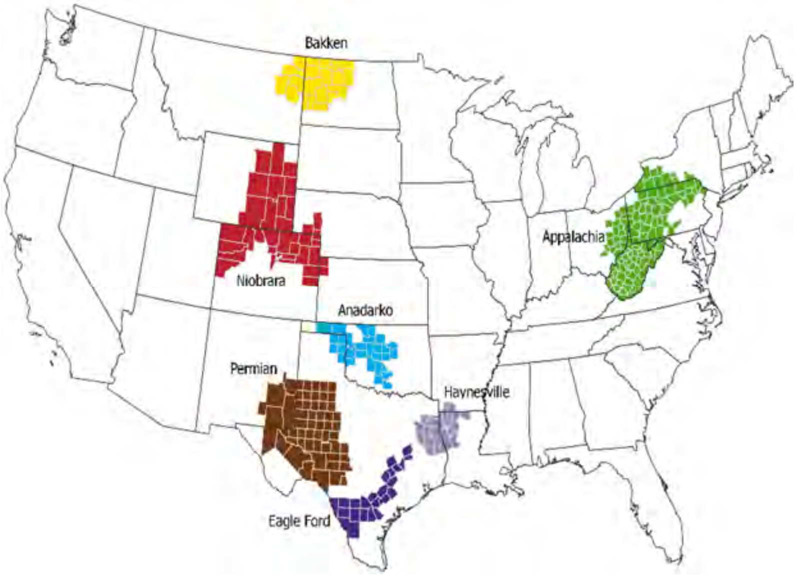

Figure 3-3: Major Shale Gas and Tight Oil Plays

Source: (U.S. DOE, 2018d)

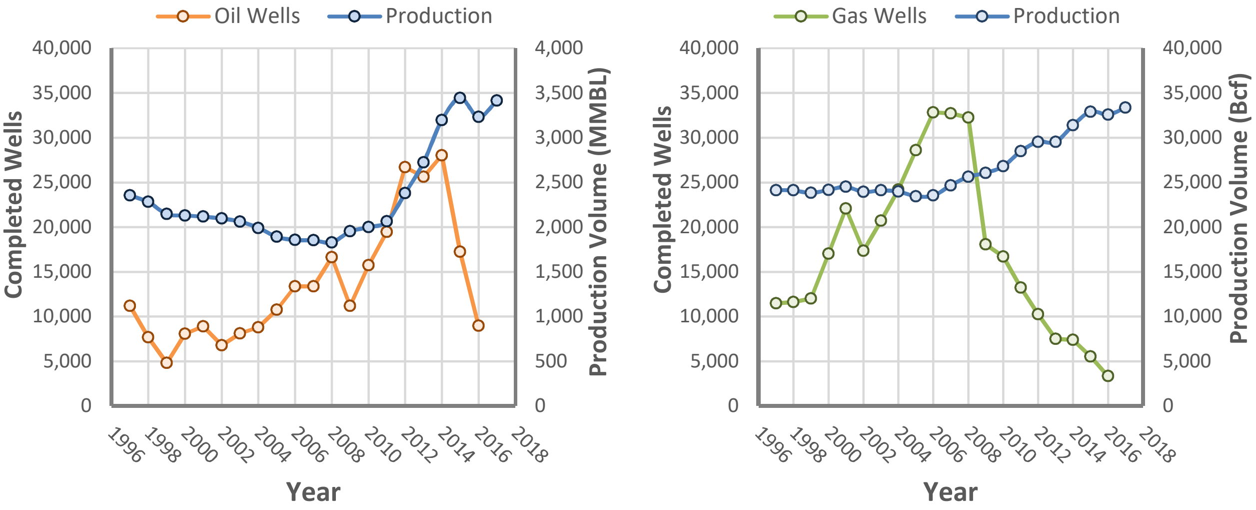

Figure 3-4: Comparison of Well Completion and Production Volume, 1997 to 2017.

The recent decline in the number of drilled wells reflects advances in the available technology and drilling techniques. Between 2000 and 2016, the fraction of wells in operation that are horizontal increased from 1% to 12% (U.S. DOE, 2018a). Horizontal wells provide greater contact between the well and the reservoir rock and so are capable of producing greater volumes of product. In 2017, only 1% of vertical wells were able to produce more than 100 BL/day of crude oil, but 30% of horizontal wells exceeded this production volume (U.S. DOE, 2018e). The growing number of horizontal wells have allowed sustained production growth even as the well count has fallen. Current forecasts predict that production from tight oil and shale gas formations will continue to grow into 2019, driven in part by recent discoveries in the Permian basin (U.S. DOE, 2018f; U.S. DOI, 2018).

3.3. Waste Generation Rates

The exploration and production of crude oil and natural gas generates substantial quantities of waste compared to many other industrial sectors. However, information on waste volumes is not routinely collected nationwide. Although some states collect and maintain data on the wastes generated within their respective boundaries, the methods and metrics used to collect these data are not uniform (U.S. GAO, 2012). In addition, some states exempt certain wastes from regulation and so data may not be available. This makes it difficult to compare and aggregate data on a wider scale.

Some recent efforts have been made to provide estimates for individual wastes. The U.S. DOE Argonne National Laboratory (ANL) estimated that 21,000 MMBL of produced water were generated in 2007 (U.S. DOE, 2009), while the Ground Water Protection Council (GWPC) estimated a total of 21,180 MMBL were generated in 2012 (GWPC, 2015). However, these estimates do not fully capture the increased production in unconventional formations or the more recent decline in the number of wells completed each year. Therefore, these estimates may no longer be fully representative.

The most recent national-scale estimates for many E&P wastes are from the American Petroleum Institute (API, 2000). API used data from a 1995 survey to calculate relationships between production metrics (e.g., volume of oil produced) and the volume of waste generated. These relationships were then used to scale waste volumes based on various production metrics in 2000. For the purposes of this discussion, EPA used the same relationships to update waste volumes based on more recent production metrics. **Table 3-4** summarizes the estimated waste generation in 2016.

Table 3-4. Estimated E&P Waste Generation in 2016

Waste Type	Density (Tons/BL)	Volume (MMBL)	Mass (MM tons)	Percent of Total
Drilling Fluids/Mud	0.21	93.4	19.6	0.4%
Drill Cuttings	0.23	33.5	7.5	0.2%
Stimulation/Workover Fluids	0.18	7.2	1.3	< 0.1%
Settled Solids	0.24	2.7	0.64	< 0.1%
Pipe Scale	Insufficient Data Available			
Produced Water	0.18	24,942	4,452	97.7%
Natural Gas Treatment Residuals	0.18	0.31	0.06	< 0.1%
Wastewater Treatment Residuals	0.31	249	77	1.7%
Hydrocarbon Bearing Soil and Debris	0.22	1.8	0.4	< 0.1%
Total		**25,330**	**4,559**	**100%**

MMBL – Million Barrels

Use of the same scaling factors assumes that the relationships between production and waste generation have remained constant over time. However, the volume of waste generated by a given well is related to the type of hydrocarbon produced, the geographic location of the well, and the method of production (U.S. GAO, 2012). Therefore, shifts in overall type, location and age of wells can all affect this relationship. API estimated that, between 1985 and 1995, the average volume of produced water generated for every barrel of oil increased by 1.4 barrels as a result of growing population of aging wells in conventional formations (API, 2000). Since that time, the existing fleet of wells has continued to age and newer wells have been drilled in unconventional formations. These new wells tend to be drilled a greater distance through the producing formation and generate greater quantities of produced water early in the life of the well. As a result, current estimates may underestimate waste volumes to some degree. Nevertheless, these estimates still provide a reasonable comparison of relative waste volumes. Produced water is the E&P waste generated in the largest volume by far and this is unlikely to change. However, this does not mean that the other wastes are not as environmentally significant.

3.4. Economic Structure

Under RCRA, EPA is generally prohibited by statute from considering cost as a basis for whether regulation is necessary. However, the Agency is also required by executive order to quantify both the expected costs to the industry and benefits to human health and the environment from significant regulatory actions. This information allows the Agency to transparently assess and communicate the potential impacts of different actions to the public. Therefore, EPA assembled available data on the economic structure of the oil and gas industry.

The North American Industry Classification System (NAICS) is the standard used by federal agencies to classify business establishments for the purpose of collecting, analyzing and publishing statistical data related to the economy. The NAICS numbering system employs a 2 to 6-digit code that designates individual industrial sectors with increasing specificity based on the number of digits. The entire upstream oil and gas subsector is captured by the 3-digit code NAICS 211: Oil and Gas Extraction. The industry can be further subdivided into two 6-digit NAICS national industries: NAICS 211120: Crude Petroleum Extraction and NAICS 211130: Natural Gas Extraction. The information in this section is profiled at the 3-digit NAICS industry segment level.

A number of organizations collect data on the economic conditions of the oil and gas industry and the contributions to the U.S. economy. For example, both the Bureau of Economic Analysis and the EIA collect data on the consumption and production of crude oil and natural gas and petroleum products, and the Federal Reserve Bank reports capacity utilization for the industry which measures how much capacity is being used of the total available capacity for production. A variety of peer-reviewed publications have analyzed the market structure, pricing, and concentration of the industry and there are a variety of sources used to assess the financial conditions of firms in the industry (i.e., SEC filings are available to assess the financial conditions of public companies). The following text provides a brief summary of available data on revenue and employment in the oil and gas industry.

3.4.1. Revenue

Revenue data provide insight into the economic conditions of the oil and gas industry over time. Economic Census data are widely used to assess economic impacts as a percentage of revenue; however, these data are only collected every five years. **Table 3-5** summarizes the available data on revenue in the Oil and Gas Extraction sector from the Economic Census for years 2007 and 2012. Data for the 2017 Economic Census are not slated for release until September 2019.

Table 3-5. NAICS 211: Oil and Gas Extraction – Revenues

Year	Number of Establishments	Value of sales, shipments, receipts, revenue, or other business (Million $)	Average sales, shipments, receipts, revenue, or other business per establishment (Million $)
2012	6,735	$310,960	$46.1
2007	6,260	$255,105	$40.7
Percent Change		**17.96%**	**11.74%**

Source: https://www.census.gov/programs-surveys/economic-census/data/tables.html

Between 2007 and 2012, the overall Oil and Gas Extraction sector experienced increases in revenue. EIA predicts natural gas and natural gas liquids have the highest projected production growth (U.S. DOE, 2019). The EIA predicts strong growth in U.S. natural gas production, but points towards heightened uncertainty regarding future oil supply and demand as a result of international market conditions, though EIA's natural gas price projections depend more on domestic factors that drive supply, including domestic resource and technology assumptions, than on international conditions (U.S. DOE, 2019).

3.4.2. Employment

The Economic Census collects data on the number of individuals that are employed at both the firm and establishment level. The U.S. Census Bureau (Census) considers an establishment to be a single physical location where one predominant activity occurs, while a firm can have multiple establishments defined by a unique Employer Identification number issued by the Internal Revenue Service. The Economic Census provides extensive statistics on U.S. businesses, but the data are only collected every five years, most recently in 2012. The Census also collects the *Statistics of U.S. Businesses* series annually, which provides more limited data. **Table 3-6** reports the number of firms, establishments and employees by employment size in the NAICS 211: Oil and Gas Extraction sector by using data from the *Statistics of U.S. Businesses*, which has historical data available back to year 1988.

Table 3-6. Oil and Gas Extraction - Employment in 2016

Employment Size	Number of Firms	Number of Establishments	Employment
0-4	3,913	3,919	6,562
5-9	818	830	5,306
10-19	427	446	5,562
20-99	396	481	14,203
100-499	98	246	14,858
500+	108	1,408	75,649
Total	**5,760**	**7,330**	**122,140**

Source: https://www.census.gov/data/tables/2016/econ/susb/2016-susb-annual.html

Combining the data on employment with the number of reported firms provides an estimate of the average employment per firm. In 2016, the Oil and Gas Extraction sector employed an average of 21 employees per firm. The Small Business Administration defines small firms as having 1,250 or fewer employees for both NAICS 211120: Crude Petroleum Extraction and NAICS 211130: Natural Gas Extraction. By this standard, the percentage of small firms and establishments in the industry is high. Over 99 percent of firms are considered small, while over 80 percent of establishments are considered small.

3.4.3. Resolution of Available Data

EPA is not aware of any publicly-available sources that provide economic data for this industrial sector at a finer resolution than the establishment or firm level. There is little information available about the number and type of wells, pits, tanks and other relevant operational units associated with each establishment or firm. Therefore, it is difficult to know how the costs of regulatory requirements for specific types of operational units, such as wells, pits, or tanks, would be distributed across the industry. Any evaluation of potential economic impacts would require extrapolation and estimation of cost and revenue based on some assumptions about the number and type of operating units present. This represents a major source of uncertainty in any analysis.

4. Waste Management

Wastes that are generated over the course of E&P operations must be managed prior to disposal or reuse. There are a variety of options for onsite or offsite management available. The purpose of this section is to describe the most common methods to store and dispose of waste that fall under the jurisdiction of RCRA. Although a large fraction of wastes are ultimately disposed through injection wells, either for disposal or enhanced recovery (GWPC, 2015), these specific practices are not addressed in this document.

EPA attempted to assemble specific information from state permits for the various waste management units (e.g., pits, landfills, land application facilities); however, a comprehensive review of these permits was not feasible at this time. The number of permits and associated documentation is enormous and often requires foreknowledge of individual wells or waste management units to access each one (e.g., well number, county). Therefore, this section instead aims to use available information to provide a general overview of different waste management practices for E&P waste and some of the major environmental design considerations for each.

4.1. Pits

Pits (alternately referred to as "impoundments," "ponds," "lagoons" or "sumps") are generally excavated areas of land where waste is placed for temporary storage or ultimate disposal. These pits are typically constructed below grade, though there may be berms or dikes around the perimeter that extend above the ground surface. The size of the pit is dictated primarily by the volume of waste that will be generated. Therefore, pits that service multiple wells will tend to be larger.

There is limited information available on the current number of pits in operation. Between 1996 and 2002, EPA estimated a total of 28,000 pits at E&P sites across Colorado, Montana, North Dakota, South Dakota, Utah and Wyoming (U.S. EPA, 2003). In 2019, Colorado reported a total of 3,426 active pits (CODNR, 2019), which is a substantial decrease from the 10,950 pits previously estimated in this state by EPA despite the increase in shale gas production over the past decade. It is unknown whether a similar decrease has occurred in other states. The literature suggests that multi-well pits are becoming more common and may include water recycling systems to provide water for drilling and completion of subsequent nearby projects (Carpenter, 2014). Regardless of location, pits have a number of design considerations based on the types of materials managed and applicable state regulations.

Pits may be constructed with compacted local soils or lined with a range of different materials, such as concrete, compacted clay or high-density polyethylene. Liners may be installed to prevent infiltration of stored fluids into the underlying soil. This prevents loss of materials (e.g., fresh water) or release of contaminants to the surrounding environment (e.g., produced water). **Figure 4-1** provides an example of two separate pits with a geomembrane liner. The larger pit contains drill cuttings, while the smaller pit contains drilling fluid that will be circulated into the well.

Figure 4-1: Pits with Visible Liners.
Source: Left: Bill Cunningham, U.S. DOI Geological Survey; Right: U.S. EPA

Most pits are open to the air, which may allow birds and other wildlife to come in direct contact with the waste. These pits may not attract birds during the drilling process due to human activity and noise. However, once the drilling rig and other equipment are removed from the well pad, animals may be attracted to the water and insects entrapped in the pit fluids (U.S. DOI, 2009). A number of states recommend or require netting or another type of barrier around pits to prevent access by wildlife and intruders. Fencing and netting may be constructed from a range of materials, such as chain link, barbed wire, and fabric. **Figure 4-2** provides examples two pits with both fencing and netting.

Figure 4-2: Pits with Fencing and Netting.
Source: Left, U.S. DOI Fish and Wildlife Service; Right, U.S. EPA

State regulations specify over 20 different types of pits based on various factors, such as the duration the pit will be in use (e.g., temporary, permanent), the stage of operations (e.g., drilling, production) or the materials that will be managed (e.g., fresh water, produced water). However, the terminology used by different states can overlap and conflict. Therefore, EPA focused on broad categories of pits for the purposes of this general discussion.

4.1.1. Reserve Pits

Reserve pits are used for the storage of the wastes (e.g., drill cuttings, spent drilling fluid) generated during well installation. The primary wastes that are managed in these pits include drill cuttings and spent drilling fluids. However, used completion fluids and other miscellaneous, smaller-volume wastes may also be placed in these pits. Reserve pits are temporary and only active until the well has been installed and the wastes have either been removed or prepared for disposal in place. Installation time varies considerably but is generally on the order of a few weeks to a few months. Most states require closure of reserve pits within 6 to 12 months of completion of drilling so the total length of time a reserve pit may be present on a site is expected to be between 6 and 15 months. As a result of the relatively short lifespan of these pits, it is anticipated that the majority of units currently in operation have been constructed in compliance with current state regulations. However, reserve pits that service multiple wells on a single pad may operate for longer periods of time.

It is unknown how many reserve pits are currently in operation. Under the assumption that there is one reserve pit associated with each well drilled, there could have been as many as 14,379 new reserve pits created in 2016 (IPAA, 2017). The actual number is likely to be lower, as some sites will use tanks or centralized pits. Pits are sized primarily based on the total length that will be drilled, which can vary considerably based on the formation and the type of well. Horizontal wells can generate anywhere between 30 and 70% more cuttings than vertical wells (Johnson and Graney, 2015). A study conducted by the U.S. DOI Fish and Wildlife Service reported that pits in two areas of Wyoming range in size from 10,200 to 24,000 ft^2 (U.S. DOI, 2009). A recent study in Texas estimated the average area of reserve pits designed for long residence times to allow solids to settle out was 75,000 ft^2 with a volume of 25 MBL (Redmon et al., 2012). SkyTruth reviewed aerial photography around permitted drilling locations to identify the number and size of pits across Pennsylvania. **Table 4-1** provides the estimated number of pits and associated areas identified by this effort. The same effort also tracked the presence of pits over time and found that nearly 80% of the pits identified were no longer present three years later. This indicates that many of the pits identified onsite are likely to be shorter-lived reserve pits.

Table 4-1. Summary of Pit Sizes in Pennsylvania

Year	Number of Pits	Average Area (ft^2)	Median Area (ft^2)
2005	11	1,998	1,132
2008	237	3,415	1,834
2010	581	11,211	6,568
2013	529	24,780	20,374

Source: https://www.skytruth.org/2014/10/pa-drilling-impoundments-2005-2013/

When well installation is completed, the free liquids in the reserve pit are generally removed to the extent practicable, either through pumping or evaporation. The remaining solids are a mixture of drill cuttings and residual solids left by the drilling fluids that may include additives, such as bentonite clay and barite. Any residual liquids that are intermingled with these solids may be stabilized with lime or fly ash prior to disposal. Pits may be closed in different ways depending on state requirements. In some states, the waste solids may be disposed in place by folding the liner over the dewatered drill cuttings and backfilling the pit with soil. In other states, the cuttings and any liner must be removed and disposed of at an offsite facility approved by the state to accept E&P wastes.

4.1.2. Production Pits

Production pits are used for the storage of wastes generated during well production. The primary waste managed in these pits is produced water. These pits will also gradually accumulate sludge at the bottom of the pit from settling of suspended solids and precipitation from produced water. Other smaller-volume wastes may also be placed in these pits. These pits can be present throughout the lifespan of a well, which may extend anywhere from 15 to 50 years. EPA identified one state that reported the number of production pits. The California State Water Board conducted an inventory of pits that contain produced water, as well as the numbers that are both lined by the state. **Table 4-2** provides a summary of reported active production pits as of January 2019.

Table 4-2. Number of Active Production Pits in California

Region	Total	Lined	Unlined
Central Coast	41	32	9
Los Angeles	76	76	0
Central Valley	561	31	530
Santa Ana	2	0	2
Total	**680**	**139**	**541**

Source: https://www.waterboards.ca.gov/water_issues/programs/groundwater/sb4/oil_field_produced/produced_water_ponds/

EPA identified little information about the typical size of production pits. However, pits associated with horizontal wells are expected to be much larger than other pits to accommodate the large volumes of produced water generated. EPA previously estimated that between 0.3 and 1 million gallons (7.1 to 23.8 thousand barrels) of water can be produced in the first 10 days after hydraulic fracturing, primarily from the flowback of injected water (U.S. EPA, 2016a). Due to the large volume of waste produced over a short period of time, such large pits may not always be economical to construct onsite. Centralized pits in the Permian Basin of Texas have been reported to be as large as 320,000 ft^2 (McEwan, 2012).

When production is complete, the liquids in the production pit are removed to the extent practicable. This may be accomplished through pumping, evaporation or discharge to ground or surface water. Liquids that are removed from the pits may be disposed or recycled for use at nearby wells. It has been estimated that hydraulic fracturing produced about 660,000 MBL of produced water for disposal in 2017 and of that, about 14% was treated and reused (Presley, 2018). Additional treatment may be applied to solid residuals (e.g., sludge) including thickening, stabilization, and dewatering processes prior to disposal. These solid residuals may be sent to a landfill, land spread, or incinerated (Morillon et al., 2002).

4.1.3. Other Pits

Figure 4-3: Flare Pit.

Source: U.S. DOI Fish and Wildlife Service

There are a number of other specific pits that may be present at E&P sites. Some of these pits may be used to hold specific wastes, such as well blowdown or gas processing condensate. Other pits may be used for specific events. For example, emergency pits are used to contain excessive or unanticipated amounts of fluids generated during an emergency situation in the drilling or operation of a well, such as a well blowout or a pipeline rupture. Flare pits are intended to collect any liquids that remain after hydrogen sulfide and other gases are burnt off. **Figure 4-4** shows an example of a flare pit. These pits are not intended for the prolonged storage of waste and are typically emptied as soon as possible after use. There is little information available on the number of these pits. However, because of the specific uses for these pits, the size tends to be much smaller than reserve or production pits.

4.2. Tanks

Tanks are prefabricated structures used both to separate waste from product and to store wastes prior to transport offsite. Tanks may be installed aboveground or below the surface. The size of individual tanks typically ranges between 100 to 1,000 BL, depending on the rate of production. The number of tanks needed at a site will vary based on the quality and quantity of crude oil, natural gas and produced water generated. If a well produces high-quality oil and little gas or water, a site may only require a single tank to store oil. However, a site with heavy oil and substantial gas or water production may need anywhere from two to ten tanks to separate and manage the various products and wastes. Multiple tanks at E&P sites are commonly grouped together in batteries that include the tanks, flow lines and the other equipment necessary to manage produced fluids. Colorado reported a total of 1,561 active tank batteries (CODNR, 2019). Under the assumption that the prevalence of tank batteries is similar among states and there is an average of three tanks per battery (i.e., separator, heater-treater, storage), EPA scaled the number reported for Colorado for each state based on the number of active wells and estimated there to be around 90,000 tanks across the country. However, this number may be higher in high-producing regions. Regardless of the number of tanks, there are a number of design considerations that depend on applicable state regulations and both the quantity and quality of the oil produced.

Tanks and the associated piping may be constructed from a variety of materials, such as steel, fiberglass or polyvinyl chloride. Each material has specific strengths and weaknesses based on the temperature, fluid corrosiveness, service pressure, duration of production, and operating costs at a given site. Steel can sustain high-pressure flow and is easily welded, but can be prone to corrosion when exposed to highly saline fluids (e.g., produced water). Although steel may be coated to protect against corrosion, these treatments may not be effective at extreme temperatures (Heintz, 2005). Fiberglass tanks are light and resistant to corrosion, but are less conductive and so may be more susceptible to damage from lighting strikes if not properly grounded (Wood, 2014). Polyvinyl chloride is a relatively inexpensive option, but is not well-suited for high-pressure flow.

Tanks may leak during operation as a result of damage (e.g., puncture), degradation (e.g., corrosion) or human error (e.g., overfilling). Therefore, secondary containment is often required to prevent releases from migrating from the initial point of release before the spill can be identified and addressed. A example design recommendation is for secondary containment to be large enough to hold 1.5 times as much fluid as is stored in the largest tank; however, alternate volumes may be specified by state regulations. Containment may be constructed from range of materials. **Figure 4-5** shows examples of tank design with secondary containment.

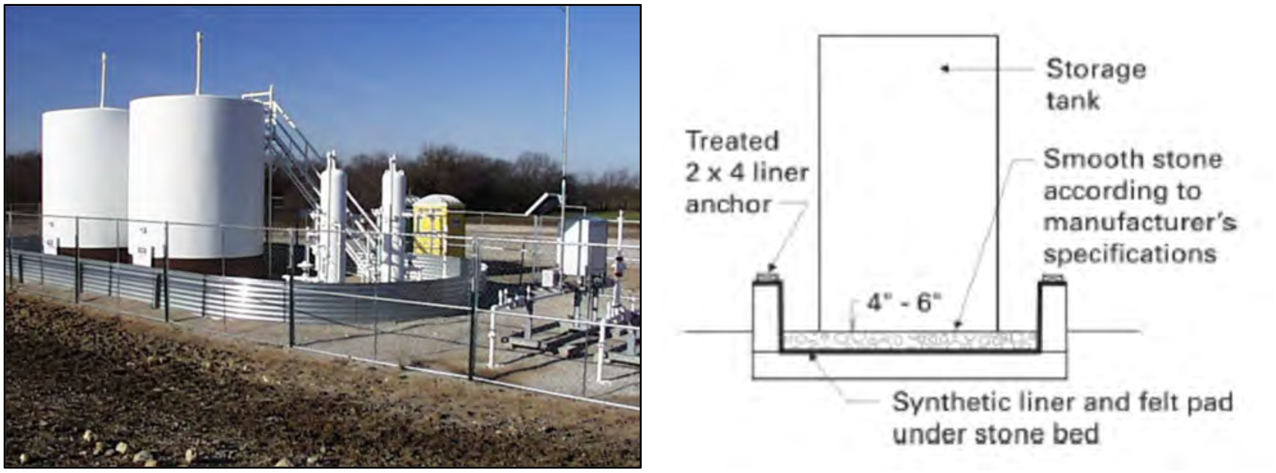

Figure 4-4: Tanks with Secondary Containment.
Sources: Left, U.S. EPA; Right, UWCE (2005)

4.2.1. Closed-Loop Drilling

Closed-loop drilling fluid systems are an alternative to reserve pits in which the flow path is not open to the atmosphere. In a closed-loop system, a series of tanks are used together with specialized equipment (e.g., screen shakers, hydrocyclones, centrifuges) to separate drilling fluid from drill cuttings and other solids. This process minimizes the amount of fluid retained on the waste solids and maximizes the amount of fluid recycled back into the drilling process. Minimizing the volume of waste solids through fluid removal results in less waste ultimately disposed (Redmon et al., 2012). Prior to disposal this dried waste may be stored in piles or dumpsters prior to transport offsite. Use of closed-loop drilling is often considered a best management practice (NMEMNRD 2000; TXRRC, 2001).

4.2.2. Production Tanks

When a well begins to produce salable quantities of oil or gas, additional tanks are required to separate the product from the waste. The most common types of production tanks are separator tanks (e.g., wash tanks, settling tanks, gun barrel tanks) that use density differences to separate crude oil, natural gas and produced water; heater-treater tanks that use heat from the sun or another source to rapidly break down emulsions of oil and water; and storage tanks that hold the separated materials until ready for transport for sale or disposal. The composition of a tank battery may change over the life of the well. Tanks may be added or removed to support changes in the volume of oil and produced water generated. As the nature of production changes, different specialized equipment will need to be brought in to meet different needs. For example, a well may initially have sufficient natural pressure to maintain flow. However, as the natural pressure falls, it may be necessary to add equipment, such as a hydraulic lift to maintain production. **Figure 4-6** shows an example of the types of production tanks that may be present at E&P sites.

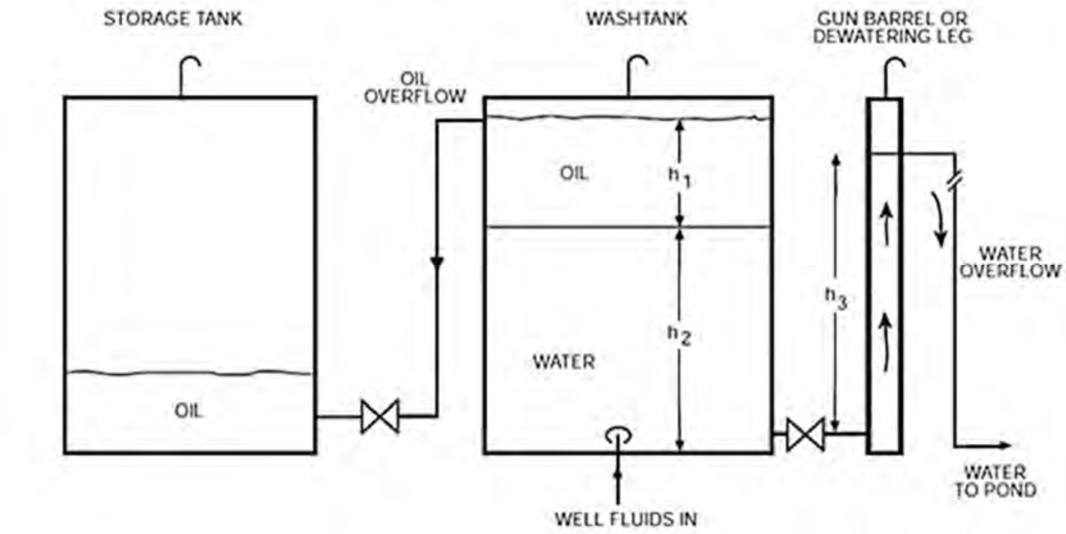

Figure 4-6: Diagram of Production Tanks.
Source: Courtesy of ESD Simulation Training, Inc.

Tanks are neither intended nor suited for the disposal of waste. Therefore, at the end of the useful life, all tanks should be cleaned out and transported offsite. This involves draining fluids from the tank and removing any solids (i.e., sludge) that have accumulated on the tank bottom. The tanks that are removed may be disposed, reused or recycled depending on the state of the tank.

4.2.3. Modular Large Volume Tanks

Modular large volume tanks (MLVTs) are freestanding aboveground tanks assembled in the field with sectional frame that supports a synthetic liner that provides primary containment for fluids. These types of tanks are more easily dismantled after use for transport to another location. However, because of the greater number of seams present in the tank structure, there may be greater risk of catastrophic failure if the tanks are not properly assembled and maintained. These tanks have been used to hold both fresh water for use in hydraulic fracturing operations and wastewater from E&P operations, though some states may place restrictions on the materials that may be stored in these tanks. **Figure 4-6** shows some examples of modular tanks.

Figure 4-5: Modular Large Volume Tanks.
Source: Tipton (2013)

4.3. Land Application

Land application is the general practice of disposing of waste on surficial soils. Some states use different terminology (e.g., land treatment, landfarming) to distinguish between application of different waste types or method of application (e.g., surface spread, tilled). The primary purpose of this practice is to promote decomposition of organic compounds. After application, the soil may be periodically tilled to amend the soil with nutrients or aerate the waste to promote decomposition. **Figure 4-8** shows some examples of how E&P wastes may be land applied to the soil.

Land application may occur onsite around the well pad or offsite. Offsite disposal may occur at state permitted facilities or on private land with the agreement of the landowner. It has been reported that farmers have been paid to allow application of E&P waste to lower-productivity rangeland or pasture. It is unknown what effects the application of E&P waste may have on the quality and productivity of the soil; this is an area of ongoing research (OCES, 2017).

Figure 4-6: Land Application of E&P Wastes.
Source: OCES (2017)

There are a number of design considerations for land application units based on the waste disposed and where it is applied. Onsite applications typically occur only once and are generally limited to cuttings drilled with water-based fluids. Offsite application may occur multiple times with a wider range of wastes. States may place restrictions on the types of waste applied based on measured level of organics (e.g., total petroleum hydrocarbons [TPH]), salts (e.g., chloride), and radioactivity (e.g., radium) or based on the types of waste considered likely to have high levels of these constituents (e.g., oil-based drilling fluid, horizontal cuttings). Restrictions may also be placed on where the waste is applied to limit the potential for offsite migration (e.g., permeable soil, steep slope, flood zones).

EPA did not identify any formal records of application onsite or offsite to private land. Offsite land application is addressed in the regulations of at least eleven other states, though the location and number are not publicly available (U.S. DOE, 2006). The size of land application facilities is often unknown. Facilities identified in Texas range between 12 acres divided into 4 separate cells and 517 acres divided into 17 cells. One permit in Kansas shows an area of 160 acres divided into 10 separate cells (KCC, 2012).

4.4. Other Offsite Disposal

There are a number of options for disposal of E&P waste at offsite facilities. Costs vary depending on the location of the disposal facility, the method used for disposing of the waste, the type of waste, and the extent of competition in the local or regional area. Although the costs of disposal are an important consideration, transportation costs, laboratory fees, and other associated costs will also influence the decision. Generally, operators will not be inclined to transport waste more than 50 to 75 miles unless no other alternatives are available (U.S. DOE, 2006).

The availability of offsite facilities dedicated to E&P wastes varies by state. A 2006 report conducted by the Argonne National Laboratory found that eight states with higher oil and gas production had a dedicated network of offsite disposal facilities overseen by the state regulatory agency (i.e., Arkansas, Colorado, Louisiana, New Mexico, Oklahoma, Texas, Utah, Wyoming). Seven states with less oil and gas production did not have the same degree of infrastructure (i.e., Alabama, Michigan, Mississippi, Nebraska, North Dakota, Pennsylvania, West Virginia). The remaining states had no industry-specific infrastructure (i.e., Alaska, Arizona, California, Florida, Illinois, Indiana, Kansas, Kentucky, Missouri, Montana, New York, Ohio, Tennessee, South Dakota, Virginia) (U.S. DOE, 2006). It is likely that states without dedicated facilities for E&P wastes rely on the existing infrastructure for disposal of other solid wastes (e.g., municipal solid waste landfills) to manage E&P wastes.

4.4.1. Landfills

Offsite landfills may be used for the disposal of certain E&P waste solids. These permitted landfills may accept waste from a range of sources (e.g., municipal solid waste landfills) or may be dedicated solely to E&P wastes. The wastes must meet the acceptance criteria for the landfill and so the composition of the waste may determine the type of landfill selected. States have reported rejecting drill cuttings for use as alternate daily cover as a result of high TPH and oily residue (ASTSWMO, 2015). The number of offsite landfills that accept E&P wastes is not known. However, based on a review of state regulations and websites, EPA is aware of both commercial and municipal solid waste landfills accepting certain E&P wastes. Recent reports indicate that there is a trend in states with high oil and gas production toward dedicated landfills (Karidis, 2017). In Texas, multiple new disposal facilities have recently been constructed that include composite liners, leak detection systems, and groundwater monitoring (Sandoval, 2018).

4.4.2. Other Treatment and Disposal Facilities

Other treatment and disposal facilities may be used for the management of E&P waste solids and liquids. This broad category of facilities is differentiated from landfills because the wastes sent to these facilities are not permanently disposed on the ground surface. These facilities may be owned and operated by one or more oil and gas operators ("centralized facilities") or by entities other than the oil and gas operator ("commercial facilities"). Some examples of treatment include crude oil reclamation and wastewater treatment. Treatment can result in the reclamation of a useful product that might be sold (e.g., crude oil), but can also generate new wastes that may be more concentrated than the original E&P waste and must be disposed appropriately (e.g., water treatment residuals). Examples of disposal include underground injection, percolation and evaporation. These facilities may use pits and tanks, similar to those found near the wellsite, to store waste prior to treatment or disposal. **Figure 4-9** provides examples of an evaporation pit with sprayers used for disposal of produced water (left) and a centralized pit used for storage of produced water prior to water treatment (right).

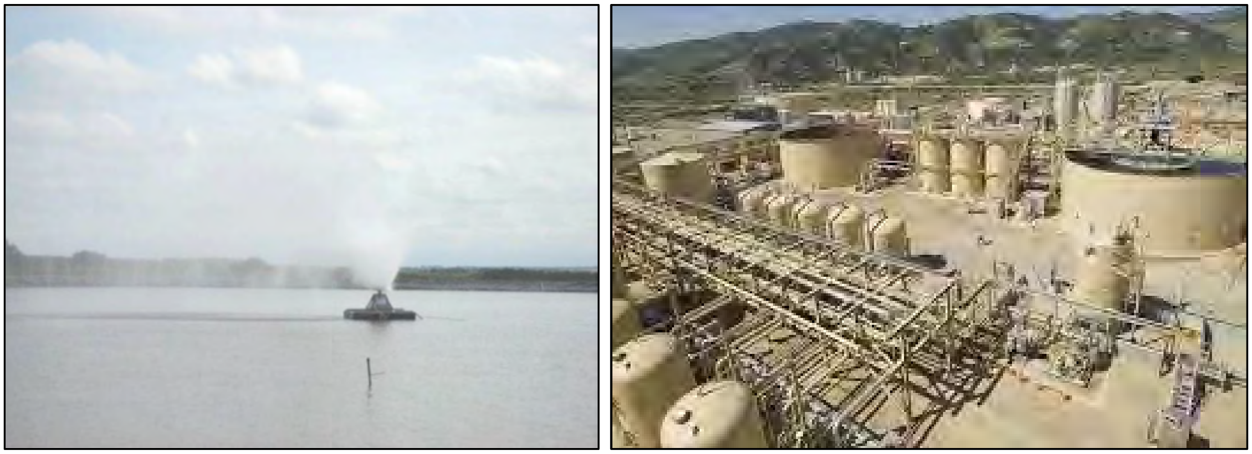

Figure 4-7: Treatment and Disposal Facilities.
Sources: Left, Tipton (2013); Right, U.S. DOI (2013)

Information on the total number of different treatment and disposal facilities that accept E&P wastes is limited. Between 1996 and 2002, EPA identified 36 centralized disposal facilities across Colorado, Montana, North Dakota, Utah and Wyoming (U.S. EPA, 2003). EPA more recently estimated that up to 74 centralized water treatment facilities may accept waste liquids from hydraulic fracturing (U.S. EPA, 2016a). The Texas RRC provides a current list of 107 permitted "commercial recycling and surface disposal facilities," more than half of which are located in the Permian Basin. Many of these facilities are dedicated to reclamation or recycling of waste, though 28 are also permitted for disposal of treatment residuals. Several of the permits reviewed from Texas note the that residual wastes may be disposed through onsite burial, deep well injection, or burial in RCRA Subtitle C facilities. These permits also provide specifications for the size of pits, along with detailed requirements for waste acceptance, constructing, waste testing, operating, groundwater monitoring, and closure. **Table 4-3** provides examples of the types and sizes of pits present at select facilities in the Permian Basin.

Table 4-3. Examples of Disposal Pit Sizes in the Permian Basin

Facility Name	Facility Size	Pit Type	Number	Pit Area (ft^2)	Capacity (MBL)
Howard County Treatment, Recovery and Disposal Facility	144 Acres	Receiving	3	99,500	94.3
		Collecting	1	130,000	76.1
		Disposal	5	798,000	5,100 to 6,700
Wishbone Facility	Not Provided	Receiving	2	4,000	4.3
		Disposal	10	Various Sizes	280 to 11,000
Midland SWD/Sludge and Disposal Facility	39.2 Acres	Collecting	3	6,000 to 88,200	1.6 to 23.7
		Disposal	4	1,500 to 448,200	900 to 2,900

Source: https://www.rrc.state.tx.us/oil-gas/applications-and-permits/environmental-permit-types-information/commercial-surface-waste-facilities/commercial-recyclingdisposal-permits-list/

4.5. Beneficial Use

Beneficial use is a broad term that describes the practice of utilizing non-hazardous materials in a productive fashion as an alternative to disposal. State programs generally have an administrative mechanism in place that allows a generator to submit a request for a specific beneficial use. The relevant state agency reviews the request to determine whether the proposed use is appropriate. Beneficial use determinations are often made on a case-by-case basis after consideration of factors, such as the benefit provided, the long-term performance of the use, and any potential risks to human health or the environment (U.S. EPA, 2013). In some states, the structure for these determinations is clearly defined and tools, such as application forms and detailed guidance, have been made available to assist the applicants. In other states, regulatory language is written broadly and the specific data collection and demonstration requirements are not specified upfront.

In 2013, the Association of State and Territorial Solid Waste Management Officials (ASTSWMO) conducted a survey of state management practices. A total of 11 states of the 28 that responded to the survey indicated they had approved various beneficial uses, such as drill cuttings (road base, concrete, grading), drilling fluid (concrete), sludge (road application), and produced water (dust suppressant, de-icing) (ASTSWMO, 2015). Other uses that have been reported for produced water in some western states include livestock watering, irrigation, and streamflow supplementation (U.S. DOI, 2011). Approval for these and other uses is often predicated on the use meeting certain criteria. States have reported rejecting proposed uses because of unsuitable composition, either physical (e.g., grain size) or chemical (e.g., oil and grease, chloride, radium, sulfate) (ASTSWMO, 2015). However, there is little publicly available information about the frequency at which different states have approved beneficial uses, the volumes that have been diverted to these uses, and where the uses occur.

5. Waste Characterization

EPA conducted a literature review on the composition and environmental behavior of wastes generated during well exploration and production operations. This information is needed to characterize the potential magnitude of exposures that may result if wastes are released into the environment. As part of this review, EPA assembled data for multiple types of wells (e.g., oil, coal bed methane, geothermal) into an E&P constituent database. The majority of identified data are for oil and gas wells in non-coal formations. These are the most numerous wells drilled across the country, both historically and currently. These wells were also the primary focus of *Onshore Oil and Gas Human Health and Environmental Risk Assessment* (U.S. EPA, 1987). Therefore, the review of data in this document focused on wastes from these wells. Further discussion of the approach to assemble and review the data are provided in **Appendix B (Constituent Database)**.

Each of the following subsections summarize the available data for an individual waste type. Where feasible, EPA calculated summary statistics for the concentration and activity of inorganic elements, organic compounds and radioisotopes ("constituent levels") in each waste type. When factors that might affect waste composition were identified, EPA separated out the data to facilitate comparison and discussion. In particular, EPA focused on potential differences between the wastes from horizontal and vertical wells as a proxy for conventional and unconventional formations to understand whether and to what extent hydraulic fracturing might affect waste composition. EPA did not compare wastes from individual formations because it would further subdivide the available data and make meaningful comparisons more difficult. The summary statistics and comparisons presented in this document are intended to provide the Agency's current understanding of constituent levels based on available data, which in some cases are limited in quantity and geographic coverage. Even if the statistics do not capture the full variability of each waste, the calculated values still provide useful information on the possible magnitude of constituent levels in each waste, the relative constituent levels among different wastes, and where data gaps still exist.

5.1. Spent Drilling Fluid

Drilling fluids (also referred to as "drilling muds") are the materials used during well installation to cool and lubricate the drill bit, control pressure within the borehole, seal drilled formations to prevent the loss of drilling fluid into the formations and the influx of water from the formation into the borehole (i.e., annulus), and to transport drill cuttings to the surface. These fluids are pumped downhole through a hollow drill string and exit through nozzles in the drill bit back to the surface through the space between the drill and the walls of the borehole. Once back at the surface, drilling fluid is mechanically separated from the drill cuttings with equipment such as filter belts or centrifuges and treated to the extent necessary for reuse. The fluids are considered spent once the composition is no longer suitable for reuse, when changing geological conditions in the well require a new fluid formulation, or when the wells are complete (U.S. EPA, 1987d). Spent drilling fluids are assumed to be managed primarily as an aqueous waste, though there are known instances where the fluids are evaporated or otherwise dewatered prior to disposal as a solid. However, few data were identified for the residual solids and so EPA did not separately discuss leachate from this waste.

5.1.1. Bulk Concentration

Drilling fluid is initially composed of a base fluid (e.g., water), solids (e.g., bentonite, cellulose) and other chemical additives. The majority of drilling fluids use water as a base (API, 2000). As a result, the majority of available data are for water-based fluids. However, oil- and synthetic-based fluids are still used to address specific drilling scenarios, such as clay formations that could expand in the presence of water. Additionally, compressed gases (e.g., air, nitrogen) have been used to drill in certain carbonate and coal formations. Thus, EPA incorporated the limited data available for other drilling fluids. However, due to the near absence of data on these other fluid types, it is not possible to draw any separate conclusions about the resulting wastes.

Although the composition of the fluids is precisely engineered prior to use, the fluids will mix with cuttings and formation water during drilling. This can introduce contaminants into the fluid that are then transported back to the surface. The scope of treatment is often limited to restoring the physical properties of the fluid necessary for reuse (U.S. DOI, 2011). As a result, recycling has the potential to result in further accumulation of contaminants in the fluid.

Inorganic Elements

EPA identified a total of four studies that measured inorganic elements in drilling fluid. Three of these studies drew samples from vertical wells in at least eight states (U.S. DOE, 1979; API, 1987; U.S. EPA, 1987d). EPA did not identify information that could be used to further weight the data to obtain a more representative national distribution, such as the volume of waste generated in each state. Therefore, data from each state were weighted equally. One other study drew samples from horizontal wells in Pennsylvania (Shih et al., 2015). **Table 5-1** presents the 50th and 90th percentile summary statistics of available data for inorganic elements in drilling fluid.

Table 5-1. Inorganic Elements in Drilling Fluid (mg/L)

Constituent	Vertical Wells			Horizontal Wells		
	n	50th	90th	n	50th	90th
Arsenic	5 / 8	0.01	0.02	10 / 12	0.03	0.18
Barium	8 / 8	1.3	4.9	32 / 32	23.8	1,810
Boron	8 / 8	0.85	6.1	32 / 32	2.5	15.1
Chloride	8 / 8	2,000	33,000	35 / 35	17,000	89,000
Chromium	4 / 8	0.05	0.16	13 / 21	0.25	1.3
Copper	4 / 8	0.01	0.03	12 / 20	0.17	0.53
Lead	2 / 8	0.07	1.0	12 / 13	0.05	0.30
Manganese	8 / 8	0.19	5.6	32 / 32	2.9	13
Molybdenum	6 / 8	0.13	0.20	11 / 13	0.11	0.41
Nickel	2 / 8	0.05	0.15	13 / 19	0.20	0.39
Sodium	8 / 8	2,100	16,000	33 / 33	11,400	33,900
Strontium	8 / 8	4.1	223	35 / 35	63	1,558
Zinc	5 / 8	0.07	0.20	18 / 25	0.09	1.7

n = Number of Samples Detected / Total

Concentrations from horizontal wells are generally higher than those from vertical wells. However, it is difficult to determine whether all of the observed differences are significant. The vertical dataset consists primarily of single samples from various states, which are unlikely to capture the full variability of any formation. The horizontal dataset shows there can be considerable variability within individual formations. At the same time, the horizontal dataset consists entirely of unfiltered samples. Additional constituent mass from solids suspended in solution could overestimate differences when compared with filtered vertical samples. Despite these uncertainties, the data still provide useful information that can be used to better understand the sources constituent mass and the potential differences between wastes from vertical and horizontal wells.

Barium exhibits the greatest proportional increase in concentration between the two datasets. If total suspended solids (TSS) are the source of high measured concentrations, then there must be a solid that is enriched in barium. Cuttings from the formation are likely to have similarly enriched concentrations of other common elements, such as iron and manganese. Another potential source of barium in drilling fluid is barite ($BaSO_4$). Barite is a common and high-density additive to drilling fluid. Industry-grade barite is typically greater than 90% $BaSO_4$ (U.S EPA, 1985). The low solubility of the barite mineral will keep most barium from dissolving into solution and so could contribute to disproportionately high barium concentrations. If barite is the source of high barium concentrations, there should be a relationship between TSS and barium. **Figure 4-1** presents a graph of the relationship between TSS and barium in the samples from Shih et al. (2015).

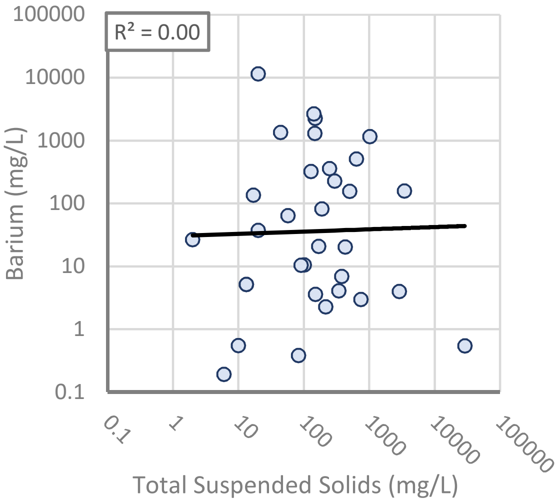

Figure 5-1: Relationship Between Barium and TSS in Spent Drilling Fluid

There is no relationship between barium and TSS; the highest barium concentrations correspond to some of the lowest TSS concentrations. Therefore, barite is not the primary source of barium in these samples. It is more likely that the suspended barite settled out of solution ("barite sag"). The other potential sources of dissolved barium are the water used as a base fluid and the formation water that mixes with drilling fluid in the borehole. The median barium concentration in formation water reported by Shih et al. (2015) is 1,010 mg/L. This is orders-of-magnitude higher than concentrations in either surface water and surficial groundwater, which rarely exceed 0.3 mg/L (ATSDR, 2007). Thus, formation water is the most likely source of barium in the drilling fluid from horizontal wells.

Another notable difference between vertical and horizontal wells is lead, which is the only constituent with higher concentrations measured in vertical wells. This may only be the result of small sample size, as the higher summary statistics are driven by a single sample. A similarly high sample is also present in the horizontal dataset, though it does not exert the same influence on the distribution. In both cases, the highest concentration is an order of magnitude greater than the remaining samples. There are a number of possible sources for lead. Naturally-occurring sulfide deposits can contain high concentrations of lead, zinc and other metals. Some of these deposits are known to be located alongside hydrocarbon-bearing formations (Kharaka et al., 1987; Leach et al., 2010). Another possible source is the materials used to construct the wells. One compound, commonly known as "pipe dope," is used to seal pipe joints and can contain more than 30% lead by weight (Kahn, 2011). This lead may leach into the drilling fluid as it circulates through the well (NRC, 1983). There is not enough information available to determine the source of the higher lead in these samples. However, this highlights the need to understand not only drilled formations, but also the drilling practices to fully understand potential waste composition.

Organic Compounds

EPA identified two studies that measured the organic compounds in drilling fluid. One study drew samples from vertical wells in seven states (API, 1987). EPA did not identify information that could be used to further weight the data to obtain a more representative national distribution, such as the volume of waste generated in each state. Therefore, the data from each state were weighted equally. One study drew samples from horizontal wells in one state (Shih et al., 2015). **Table 5-2** presents the 50th and 90th percentile summary statistics of the available data for organic compounds in spent drilling fluid.

Table 5-2. Organic Compounds in Drilling Fluid (mg/L)

Constituent	Vertical Well			Horizontal Well		
	n	50th	90th	n	50th	90th
Benzene	1 / 6	0.003	0.007	6 / 15	0.003	0.05
Toluene	3 / 7	0.005	0.01	7 / 15	0.008	0.20
Ethylbenzene	1 / 6	0.003	0.005	1 / 1	0.009	
Xylene	0 / 0	--		1 / 1	0.11	

n = Number of Samples Detected / Total

A majority of both vertical and horizontal data are non-detect. As a result, median concentrations often reflect a detection limit. Horizontal data have a higher detection frequency despite similar detection limits and have higher detected concentrations. This indicates that prolonged contact with formations with high-organic content may result in greater accumulation of organic compounds. However, further conclusions about the magnitude of any differences are limited by the amount of data available.

Radioisotopes

EPA identified two studies that measured radioactivity in spent drilling fluid (Shih et al., 2015; PADEP, 2016). These studies collected samples from horizontal wells in one state. Samples were only analyzed for radium isotopes because the lower solubility of other radionuclides were expected to result in dissolved activities far lower than radium (PADEP, 2016). **Table 5-3** presents the 50th and 90th percentile summary statistics of the available data for radium in drilling fluid.

Table 5-3. Radioisotopes in Spent Drilling Fluid (pCi/L)

Isotope	Horizontal Well		
	n	50th	90th
Radium 226	28 / 28	90.6	1,863
Radium 228	28 / 28	18.3	400

n = Number of Samples Detected / Total

The data show that both median and high-end activities of ^{226}Ra and ^{228}Ra are clearly elevated in spent drilling fluid from horizontal wells. Radium does not serve a function in the fluid and so is not intentionally added, though it might be a contaminant present in additives. EPA identified two studies that separately sampled the solid fraction of some drilling fluids (WVDEP, 2013; PADEP, 2016). The studies collected samples from horizontal wells in two states. These solids are expected to be a mixture of various additives along with some residual drill cuttings. In addition to radium, the samples were measured for uranium and thorium because of the greater potential for these radioisotopes to be present in the solid phase at comparable activities (PADEP, 2016). **Table 5-4** presents the 50th and 90th percentile summary statistics of available data for radioisotopes in the solids from drilling fluid.

Table 5-4. Radioisotopes in Residual Solids from Drilling Fluids (pCi/g)

Isotope	Horizontal		
	n	50th	90th
Uranium 235	2 / 9	0.06	0.10
Uranium 238	8 / 14	0.84	1.1
Radium 226	14 / 14	1.3	3.5
Radium 228	14 / 14	0.33	1.8

n = Number of Samples Detected / Total

Radium activities in the solids phase are substantially lower than the associated fluids from the same study, despite prolonged contact between the two media. Reported ^{226}Ra activity appears to be higher than the parent ^{238}U, which might indicate an outside source of radium in these samples. However, as noted by PADEP (2016), ^{226}Ra activities measured directly by gamma spectroscopy can be biased high when radium and uranium are both present at similar levels because current instruments cannot fully distinguish the energy signatures of ^{226}Ra and ^{235}U. The authors made no attempts to account for this interference in the reported data. If ^{226}Ra and ^{238}U are in approximate equilibrium (i.e., no major outside source or sink of radium), then there should be some relationship between ^{235}U activity and the magnitude of excess ^{226}Ra in each sample. **Figure 5-2** presents the relationship between ^{235}U and excess ^{226}Ra based on the raw gamma measurements.

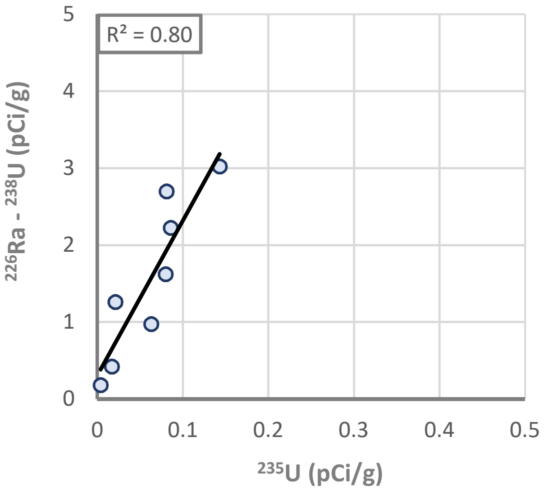

Figure 5-2: Relationship Between ^{235}U and Excess ^{226}Ra in Residual Solids from Drilling

The strong relationship indicates that a majority of excess ^{226}Ra activity can be attributed to interference from ^{235}U during measurement. Thus, ^{226}Ra in these samples is likely to be near equilibrium with ^{238}U. After adjustment for interference, ^{226}Ra activities all fall below the upper bound of 4.2 pCi/g measured in surface soil (U.S. DOE, 1981a). It is unclear why exposure to high-activity fluids does not result in enriched solids. It is possible that high dissolved solids in the fluids compete for binding sites on the surface of the solids and force the radium to remain in solution (Sturicho et al., 2001; IAEA, 2014). These results indicate that additives and other suspended solids are not the primary source of radium in spent drilling fluid. This is further corroborated by a comparison of total and dissolved activities in formation water samples reported by PADEP (2016), which found dissolved activities to be only 2% lower on average.

The potential sources of dissolved radium are the water used as a base fluid and the formation water that mixes with the drilling fluid within the borehole. The median activity in formation water reported by Shih et al. (2015) is 1,680 pCi/L $^{226+228}$Ra. This is several orders of magnitude greater than activities typically found in either surface water or surficial aquifers, which generally have a combined radium activity less than 5 pCi/L (ATSDR, 1990; Szabo et al., 2012). Therefore, formation water is the most likely source of activities reported in drilling fluid.

EPA identified one additional sample of solids from drilling fluid taken from Colorado; however, this sample was solidified prior to disposal in the landfill (CHDT, 2015). Although drilling fluids are typically disposed of as aqueous waste, high-solids fluids may be solidified prior to disposal on land. This sample is greatly enriched in radium, with a ^{226}Ra activity of 91 pCi/g and corresponding ^{238}U activity of only 0.2 pCi/g. The report provides no discussion on the materials used in solidification of the waste. Materials commonly used for other wastes include cement and fly ash. Like most materials drawn from the earth, these pozzolanic materials contain some radium. However, neither of these materials have been reported to have such disproportionately high radium activity (U.S. EPA, 1979; UNSCEAR, 2000). The more likely source of radium is drilling fluid, which has been shown to have disproportionately high radium activities that could easily support the activity measured in the solidified sample. If residual drilling fluid is used to hydrate a pozzolanic material, then the dissolved radium could be incorporated into the solidified mass. Alternately, if the drilling fluid were allowed to evaporate before solidification, this could also concentrate radium in the remaining solids. This suggests that waste management practices have the potential to result in higher activities than predicted based on measurement of solids alone. This represents a major source of uncertainty in the available data.

5.1.2. Summary – Spent Drilling Fluids

This review highlights the complexities of deep well drilling. Potential sources of constituent mass include additives to the drilling fluid, leaching from equipment, and mixing with the formation. In the borehole, drilling fluid is exposed to reducing conditions under elevated temperature and pressure. The fluid is then brought back to the surface where it is exposed to oxygen before being cycled through the borehole again. This process can be repeated multiple times before the fluid is spent and ultimately disposed. The impact of shifting environmental conditions on drilling fluid during use have not been well-explored in the literature. Therefore, any conclusions must be drawn from measurements of spent drilling fluids. The available data indicate that a major source of constituent mass in water-based drilling fluids is mixing of the drilling fluid with formation water in the borehole. Constituent levels (i.e., concentrations and activities) measured in formation water are sufficient to support levels measured in drilling fluid, though other sources previously mentioned also have the potential to contribute additional constituent mass. Available studies did not characterize produced water from the same wells, so it is not possible to determine the actual extent that mixing occurred in any sample.

The data available to characterize this waste are limited. Some studies only provide individual data points and so do not capture variability in any of the formations sampled, while others provide multiple samples for only a single formation. This makes it difficult to draw conclusions about the typical composition of this waste or the exact magnitude of any differences between vertical and horizontal wells. However, if the primary source of constituent mass is mixing with the formation as expected, then the relative composition of drilling fluids should mirror that of the formation water. The extent of mixing will depend on the distance drilled and the number of times the fluid is cycled through the borehole. Horizontal wells tend to be drilled greater distances through the formation than vertical wells. Thus, if constituent levels are higher in formation water from these wells, the same should be true of the drilling fluid.

Available data indicate that the majority of dissolved constituent mass remains in solution during waste management. There was no apparent enrichment of residual solids from the spent fluids. However, one sample of solidified waste had disproportionately high radium activity that suggests contributions from another source. It is possible that constituent mass from the fluids is retained on residual solids through solidification, evaporation or another process. If so, this could result in much higher constituent levels than predicted based on solids data. This represents a major source of uncertainty in the current data.

5.2. Drilling Solids

Drilling solids are a mixture of the wastes managed in reserve pits and tanks. Drill cuttings, which are the rock and minerals that are ground up within the borehole and brought to the surface during well installation, are typically the largest component of drilling solids. Cuttings are separated from the drilling fluid at the ground surface, but may subsequently be mixed with spent drilling fluid and other lower-volume wastes prior to disposal. The quantity and composition of the waste depends on the conditions at the drilling site. Without information about the drilling and waste management practices at a site, it is difficult to attribute measured constituent mass to a particular source. Thus, this discussion focuses on drill cuttings, but considers mixed drilling solids where data are available.

The composition of a single formation can vary considerably and deeper wells, like those necessary to access hydrocarbon-bearing formations, inevitably traverse a number of distinct formations. As a result, it can be difficult to define representative concentrations for cuttings. In recent years, the widespread adoption of directional drilling has resulted in a substantial increase in the total volume of drill cuttings generated. Depending on the diameter of the borehole, the depth to target formation and the lateral distance drilled, the additional horizontal cuttings have been estimated to represent anywhere between 30 and 70% of the total volume generated (Johnson and Graney, 2015). The black shale in these cuttings has been studied extensively in the literature. Therefore, this discussion focuses on the composition of black shale, but considers cuttings from above the hydrocarbon formation where data are available.

5.2.1. Bulk Composition

Black shale is a type of sedimentary rock characterized by higher organic carbon that typically ranges between 1% and 30% of the rock mass (Meyers and Mitterer, 1986). Extractable hydrocarbons in these rocks originate from the decomposition of high-molecular weight organic matter known as kerogen that decompose slowly at a specific range of temperatures and pressures found in some deep geological formations. During decomposition, a variety of simple and complex organic compounds can form alongside the economically-significant hydrocarbon deposits.

The inorganic fraction of black shale is composed of silicates and other minerals that form through deposition and diagenesis (Ketris and Yudovich, 2009). EPA identified several studies that evaluated the major mineral composition of black shales from California (Brumsack, 2005), Kentucky and Ohio (Perkins et al., 2008), Mississippi (Rimmer, 2004), and Pennsylvania (Balashov et al., 2015; Phan et al., 2015; Stuckman et al., 2015). Silicon dioxide (SiO_2) present in minerals such as albite, illite and quartz is the largest component of most samples, with content typically around 50% of the total mass. Other major components are aluminum, barium, calcium and iron oxides, which each account for up to 20% of the mass in individual samples. International studies that analyzed samples from China, Egypt, India, Namibia, Peru and Poland all reported similar ranges (El-Anwar, 2016; Piszcz-Karaś et al. 2016).

Inorganic Elements

EPA identified three primary studies that measured inorganics in black shale formations. Ketris and Yudovich (2009) assembled data on black shale from around the globe. Reported values reflect samples grouped into separate distributions based on lithology (e.g., carbonate) and weighted based on the frequency that each lithology was expected to occur. Chemak and Schreiber (2014) assembled data on gas-producing black shale in the United States. Reported values reflect equally-weighted data from the Antrim, Bakken, Eagle Ford, Marcellus, New Albany, Utica and/or Woodford formations. U.S. DOI (2017) also assembled data on black shale from around the globe. Reported values reflect summary statistics calculated from the raw data by EPA.[6] The different approaches used to aggregate data introduce some uncertainty and prevent further aggregation of the data from the different studies. Therefore, the focus of this comparison is to identify major trends in the data and not to provide a

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[6] EPA used data analyzed with either non-destructive methods or digestion methods with hydrogen fluoride to ensure reported values provide a best estimate of total mass. For most constituents, this was the majority of available data. The data were not further weighted based on lithology or other metrics. Non-detect samples were omitted because the high detection limits relative to the detected concentrations often overwhelmed summary statistics.

definitive distribution for any element. The inter-quartile range was used for the comparisons because it diminishes the effects of outliers that could skew higher percentiles and because these were the only summary statistics provided by Ketris and Yudovich (2009). **Table 5-5** provides a comparison of these different data sources for elements reported in two or more sources.

Table 5-5. Inorganic Elements in Black Shale (mg/kg)

Constituent	Global Black Shale[1]				Global Black Shale[2]				U.S. Gas-Producing Black Shale[3]			
	n	25th	50th	75th	n	25th	50th	75th	n	25th	50th	75th
Antimony	1,930	2.0	5.0	11	20,537	0.43	1.0	2.6	--	--	--	--
Arsenic	4,190	10	30	80	19,321	7.0	20	53	39	21	37	87
Barium	15,100	270	500	800	61,125	200	440	730	186	92	181	324
Beryllium	7,810	1.0	2.0	3.0	37,829	1.9	2.5	7.0	--	--	--	--
Cadmium	2,260	2.0	5.0	12	17,520	0.55	1.5	12	--	--	--	--
Chromium	21,900	50	96	160	56,921	30	70	100	199	54	84	119
Cobalt	21,000	10	19	30	51,878	5.2	10	18	169	5.0	14	21
Copper	25,740	35	70	150	45,659	20	50	100	--	--	--	--
Lead	20,520	10	21	40	49,534	15	27	46	--	--	--	--
Lithium	4,520	15	31	50	28,340	26	55	110	--	--	--	--
Manganese	19,600	200	400	800	50,150	110	252	500	--	--	--	--
Mercury	1,420	0.20	0.27	0.60	207	0.06	0.60	4.5	--	--	--	--
Molybdenum	18,480	6.0	20	60	35,685	7.0	15	40	303	27	74	116
Nickel	23,160	40	70	140	61,500	20	41	92	236	37	88	149
Selenium	1,650	3.0	8.7	30	8,589	1.4	3.1	8.0	--	--	--	--
Silver	9,000	0.40	1.0	2.4	19,619	0.45	1.0	3.0	--	--	--	--
Strontium	16,650	100	190	300	53,288	109	200	500	--	--	--	--
Thallium	2,710	0.50	2.0	10	4,512	0.60	0.96	4.3	--	--	--	--
Uranium	8,400	4.0	8.5	25	15,511	1.5	3.8	15	314	15	39	204
Vanadium	25,200	100	205	400	62,924	70	137	210	312	194	329	506
Zinc	13,300	60	130	300	47,115	51	105	200	187	64	108	340

1) **Source:** Ketris and Yudovich (2009)
2) **Source:** U.S. DOI (2017)
3) **Source:** Chermak and Schreiber (2014)
n = Number of Total Samples

The two global datasets are intended to reflect the same set of materials. Thus, any differences result from variability among the formations sampled and the methods used to weight the data. Differences are most pronounced for elements with the fewest data points (e.g., antimony, mercury, selenium). Yet the considerable overlap between the distributions of many elements provides some confidence that many of these elements have been adequately characterized.

Based on available data, many constituents in black shale are substantially higher than typical surface soils reported in *Geochemical and Mineralogical Data for Soils of the Conterminous United States* (U.S. DOI, 2013b), often by an order of magnitude or more. The metalliferous nature of black shale is well-documented in the literature. Various studies have reported elevated levels of antimony, arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, silver, thallium, thorium, uranium, vanadium and/or zinc (e.g., U.S. DOI, 1970, 1983; Ketris and Yudovich, 2009). These high concentrations cannot be attributed to unique properties of any individual basin (Tourtelot, 1979; Scott, 2017). Instead, high levels result from the complex interplay of multiple factors, which include the rate that organic matter deposited on the seafloor, the depth of the water column, both the extent and duration of anoxic conditions, and local water chemistry. Under the anoxic conditions present during the deposition of organic matter, redox-sensitive elements are sequestered from the water onto organic matter or reduced sulfur (Arthur and Sageman, 1994; Chemak and Schreiber, 2014; Scott et al., 2017).

Many elements in gas-producing shale are similar to global shale, but a few are noticeably higher. One key difference between these datasets is the amount of total organic carbon (TOC) present. Median TOC in gas-producing samples is 9.7%, while the median in samples from U.S. DOI (2017) is 1.7%. Constituents with an affinity for organic matter would be expected to concentrate in gas-producing shales. This is true for uranium, the element with the greatest apparent increase relative to global shales. The relationship between uranium and TOC can be so strong that gamma radiation has been used in the field as a proxy for TOC during well surveys (Lüning and Kolonic, 2003) and black shale formations were previously considered as potential sources of uranium ore (U.S. DOI, 1961). Other elements measured in gas-producing shale known to associate with organic matter include chromium, molybdenum, nickel, vanadium and zinc (Meyer and Robb, 1996; Wilde et al., 2004; Ross and Bustin, 2009; Scott et al., 2017). Moderate but consistent increases are seen in the data for molybdenum and vanadium, but the remaining constituents are not readily distinguishable from global shale. The absence of apparent differences might be attributed to other sources of these elements, particularly reduced sulfur. Arsenic, chromium cobalt, nickel and zinc are also known to associate with sulfidic minerals, such as pyrite (Meyer and Robb, 1996; Ross and Bustin, 2009; El-Anwar, 2016). The amount of free hydrogen sulfide in the water column is not directly linked to the amount of organic carbon that accumulates in a formation. Because higher concentrations of sulfur-bound elements may occur in regions of both high and low organic carbon, similar concentrations are possible in all formations. Thus, it is reasonable that all of the constituents associated with reduced sulfur are similar among different sample sets.

The constituent with an apparent decrease in gas-producing shale is barium. Under anoxic conditions, barium can remobilize and, as it diffuses upward and encounters waters with sulfate, reprecipitate as barite (Henkel et al., 2012). This upward migration of barium can lead to greater stratification within the black shale. As a result, barium enrichment can occur above black shale deposits to a greater degree than other elements (Dean et al., 1984; Schijf, 2007; Henkel et al., 2012; Engle and Rowan, 2014). Thus, barium is not necessarily depleted from the formation, but may be located in more concentrated lenses within and above the shale. This spatial variability may contribute to observed differences, as samples collected from horizontal cuttings or exposed rock outcrops have greater potential to miss more isolated barite deposits.

Overall, the similarities between datasets indicate that global black shale data can provide a useful estimate of potential concentrations for many elements in gas-producing black shale, though elements with a strong affinity for organic matter may occur at even higher concentrations. The concentrations in black shale may not be the same as the drilling solids that are ultimately disposed at the ground surface. During drilling and subsequent storage, black shale will be blended with surrounding rock facies, which may dilute the higher inorganic concentrations found in the black shale. It is known that many of the samples reflected in **Table 5-5** were collected from drill cuttings (as opposed to targeted outcrop samples) and so this blending is already reflected to some degree. The cuttings may also be mixed with spent drilling fluid and other wastes that can alter the overall composition of the waste. To better understand the extent to which these solids may differ from the initial cuttings, EPA reviewed available data on drilling solids.

EPA identified a total of four studies that measured inorganic elements in drilling solids collected from pits and tanks. Three drew samples from vertical wells in eleven states (Freeman and Deuel, 1984; API, 1987; U.S. EPA, 1987d). EPA did not identify information that could be used to further weight the data to obtain a more representative national distribution, such as the volume of waste generated in each state. Therefore, the data from each state were weighted equally. One study drew samples from horizontal wells, both above and within the hydrocarbon formation, in one state (PADEP, 2016). The horizontal well samples had been stabilized in preparation for land disposal. **Table 5-6** presents the 50th and 90th percentile summary statistics of available data for inorganic elements in drilling solids.

Table 5-6. Inorganic Elements in Drilling Solids (mg/kg)

Constituent	Vertical			Horizontal (Above)			Horizontal (Within)		
	n	50th	90th	n	50th	90th	n	50th	90th
Antimony	2 / 11	2.5	4.3	14 / 38	1.8	26	14 / 18	18	28
Arsenic	11/11	2.1	7.8	38 / 38	11	17	18 / 18	26	38
Barium	11/11	2,650	6,000	38 / 38	3,215	16,620	18 / 18	82,050	220,600
Cadmium	3 / 11	0.25	2.7	38 / 38	2.1	16	18 / 18	37	70
Chromium	11/11	7.3	24	38 / 38	25	196	18 / 18	112	231
Cobalt	11/11	3.6	7	38 / 38	25	36	18 / 18	24	40
Copper	11/11	8.2	17	38 / 38	38	55	18 / 18	84	128
Lead	11/11	14	120	38 / 38	25	36	18 / 18	112	363
Manganese	11/11	125	190	38 / 38	554	619	18 / 18	235	413
Mercury	3 / 11	0.03	0.08	38 / 38	1.0	2.1	18 / 18	2.5	6.1
Molybdenum	6 / 11	1.2	2.9	38 / 38	4.0	11	18 / 18	50	112
Nickel	11/11	6.3	14	38 / 38	61	90	18 / 18	119	261
Silver	2 / 11	0.15	1.3	38 / 38	2.9	20	18 / 18	38	56
Strontium	11/11	68	260	38 / 38	283	1,124	18 / 18	1,423	6,184
Uranium	0 / 0	--	--	38 / 38	3.7	6.6	18 / 18	19	49
Vanadium	11/11	8	11	38 / 38	121	209	18 / 18	12	173
Zinc	11/11	41	132	38 / 38	107	135	18 / 18	172	280

n = Number of Samples Detected / Total

Concentrations from vertical wells are generally lower than those from both sets of horizontal wells. Some differences may arise because the vertical dataset consists primarily of single samples from various states, which are unlikely to capture the full variability of any formation. The horizontal datasets show there can be considerable variability within individual formations, but not enough to explain the order of magnitude difference observed between the vertical and horizontal data. The more likely cause is the different analytical methods used to measure constituent concentrations. Vertical samples were prepared for analysis with acid digestion (HNO_3 + HCl),[7] while horizontal samples were analyzed directly with non-destructive methods. Non-destructive methods measure the entire constituent mass within the sample matrix, while digestion methods measure the constituent mass that can be liberated from the matrix with a combination of heat and acid (Gaudino et al., 2007). Some fraction of a recalcitrant waste may not dissolve during digestion. This can result in an underestimation of elements incorporated in the mineral lattice. These uncertainties limit the conclusions that can be drawn about differences between vertical and horizontal wells. Yet, similar trends are seen in both datasets.

In all three sets of data, the median concentrations of barium are substantially higher than the black shale reported in **Table 5-5**. The magnitude and frequency of higher concentrations indicates that a majority of the barium does not originate from drill cuttings. The other large-volume waste typically stored together with cuttings is drilling fluid. With modern equipment, fluid retention on cuttings is typically below 15% by mass (U.S. EPA, 2000d). The dissolved concentrations of barium measured in fluids are generally less than 1,800 mg/kg of water (**Table 5-1**).[8] In addition, the range of concentrations of barium and strontium measured in drilling fluid are similar, while those in pit solids are orders-of-magnitude different. Thus, retention of drilling fluid alone does not account for disproportionately high barium. The high ionic strength of the fluid also makes it unlikely that the high barium results from selective sorption onto the surface of cuttings. Therefore, the most likely source of barium is mixing of cuttings with barite that settles out of the drilling fluid.

Industry-grade barite is typically > 90% $BaSO_4$ (U.S EPA, 1985). The amount of barite used depends on the fluid density required to counteract increasing pressure within the formation and has been reported to range anywhere from 15 to 62% of the total mass of the fluid (NRC, 1983). Only a small fraction of barite is expected to adhere to cuttings during separation of fluids and cuttings at the surface, but greater accumulation is possible if spent fluids are stored together with cuttings. At higher drilling fluid densities, it would only require about 0.5 ft^3 of drilling fluid mixed with each 1 ft^3 of shale cuttings to achieve the 90th percentile barium concentration measured in the horizontal drilling solids.[9] At a minimum, drilling fluid must be used in equal volumes to the cuttings removed in order to fill the void in the borehole, though greater volumes are often be necessary. Thus, based solely on mass balance, barite in spent drilling fluids could account for high barium concentrations in the final waste. This accounts for the higher concentrations in horizontal solids relative to vertical solids, as higher water densities may be required to drill under the greater pressure in these formations.

Although barite is predominantly barium sulfate, it can also contain inorganic contaminants present alongside barite deposits. Previous analyses of barite have shown the additive can contain elevated concentrations of arsenic, chromium, cadmium, copper, mercury, lead and zinc (NRC, 1983; Candler et al., 1992; Neff, 2007). EPA previously concluded that veined deposits of barite tend to have higher

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7) A mixture of nitric acid (HNO3) and hydrochloric acid (HCl) is commonly used to digest a range of materials, such as organic matter, carbonates, phosphates and iron oxides. An example of a more aggressive acid is hydrofluoric acid (HF), which can be used to digest silicates that comprise a large fraction of some drill cuttings.

8) Assumed fluid density of 1.0 kg/L representative of fresh water to provide a high-end concentration per unit mass.

9) Assumed fluid density of 2.1 kg/L and a shale density of 2.7 kg/L.

concentrations of these inorganic elements than bedded deposits (U.S. EPA, 1996).[10] Veined deposits are often found together with sulfide, rare-earth, gold and silver minerals (U.S. DOI, 1958). Many of the contaminants reported in barite are elements that tend to associate with reduced sulfur, which are the likely source of these other inorganics. The Agency previously identified concerns with the potential toxicity of these inorganics to wildlife and, in 1996, finalized limits on the concentrations of cadmium and mercury allowed in stock barite that can be discharged to open waters as part of the *Oil and Gas Extraction Point Source Category, Offshore Subcategory; Effluent Limitations Guidelines and New Source Performance Standards* (40 FR 10664). However, higher-concentration barite might still be used in onshore drilling, as these wastes are not discharged directly to surface water. To better understand the extent to which barite may affect the composition of drilling solids, EPA compared concentrations in black shale (**Table 5-4**) and pit solids (**Table 5-6**). EPA found that the median concentrations of antimony, cadmium, mercury, silver and strontium in horizontal drilling solids are all considerably higher than the median values from the different black shale datasets. This indicates that the addition of barite to drill cuttings might substantially increase concentrations of some inorganic elements.

Organic Compounds

EPA identified a total of four studies that measured organic compounds in drilling waste. Two drew samples of drilling solids from vertical wells in eleven states (API, 1987; U.S. EPA, 1987d). EPA did not identify any information that could be used to further weight the data to obtain a more representative national distribution, such as the volume of waste generated in each state. Therefore, the data from each state were weighted equally. The remaining two studies drew samples of drill cuttings from horizontal wells, both above and within the hydrocarbon formation, in two states (WVDEP, 2015; Eitrheim et al., 2016). **Table 5-7** presents the 50th and 90th percentile summary statistics of the available data for organic compounds in drilling solids/cuttings.

Table 5-7. Organic Compounds in Drilling Solids (mg/kg)

Compound	Vertical Solids			Horizontal Cuttings (Above)			Horizontal Cuttings (Within)		
	n	50th	90th	n	50th	90th	n	50th	90th
Benzene	11 / 11	0.03	0.59	2 / 3	20	96	3 / 5	773	1,870
Ethylbenzene	11 / 11	0.35	2.8	1 / 1	58		2 / 3	28	32
Toluene	11 / 11	1.1	3.1	1 / 1	37		3 / 3	58	62
Xylene	0 / 0	--	--	1 / 1	390		3 / 3	390	438

N = Number of Samples Detected / Total

Concentrations in samples from horizontal wells both above and within the formation are substantially higher than those from vertical wells. Horizontal wells tend to be drilled within formations with higher organic content, which could account for the greater concentrations. However, there is additional uncertainty introduced into this comparison by the fact that vertical samples reflect drilling solids and the horizontal samples reflect drill cuttings. Concentrations in vertical samples may be diluted though mixing with other wastes; however, the majority of the waste is still anticipated to be cuttings and so dilution would not account for the orders-of-magnitude difference. The few samples of cuttings from

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[10] Veined deposits are those that fill cavities or fractures within a pre-existing rock formation. Bedded deposits are those that form as a distinct depositional layer within a stratified formation.

above the horizontal formation have concentrations similar to or lower than from within the formation. It is possible that these cuttings capture black shale that overlays the economically-significant target formation. As a result of the sources of uncertainty, few conclusions can be drawn without additional data.

Radioisotopes

EPA identified only one study that measured radioisotopes in drilling solids from one state (PADEP, 2016). Samples were collected from both above and within a horizontal formation. Each sample had been stabilized in anticipation of land disposal, though the study did not specify how stabilization was achieved. **Table 5-8** presents the 50th and 90th percentile of the available data for radioisotopes in drilling solids. To confirm the measured activities, some samples were directly measured with gamma spectrometry and indirectly calculated based on measurement with X-ray fluorescence (XRF) and natural isotope ratios. Where appropriate, both sets of measurements are presented for comparison.

Table 5-8. Radioisotopes in Stabilized Drilling Solids (pCi/g)

Isotope	Analytical Method	Horizontal (Above)			Horizontal (Within)		
		n	50th	90th	n	50th	90th
Uranium 235	γ-ray (^{235}U)	8 / 38	0.08	0.15	12 / 18	0.18	0.39
Uranium 238	γ-ray (^{234}Th)	20 / 38	0.80	1.6	12 / 18	1.2	3.4
	XRF	37 / 37	1.3	2.2	18 / 18	6.3	17
Radium 226	γ-ray (^{226}Ra)	38 / 38	2.1	3.8	17 / 18	3.8	9.9
Thorium 232*	XRF	37 / 37	1.8	2.0	18 / 18	1.4	1.8
Radium 228	γ-ray (^{228}Ac)	38 / 38	1.1	1.3	17 / 18	0.68	0.84

* PADEP (2016) reported ^{228}Ra and ^{232}Th activities that are nearly identical because values were based on ingrowth of the same short-lived progeny (^{228}Ac). Therefore, the ^{232}Th data are not useful for comparison and is not presented.
n = Number of Samples Detected / Total

The ^{238}U activities in samples calculated from XRF are often higher than those measured with gamma spectrometry. This might indicate that the activities of this isotope measured by gamma spectrometry are biased low. The low energy of ^{234}Th (63.3 keV) has been reported to result in higher counting error compared to other radioisotopes (U.S. DOE, 1981b). Yet some measured ^{226}Ra activities are greater than both measured and calculated ^{238}U activities. As noted by PADEP (2016), ^{226}Ra activities measured directly by gamma spectroscopy can be biased high when radium and uranium are both present at similar levels because current technology cannot fully distinguish the energy signatures of ^{226}Ra and ^{235}U. However, if ^{226}Ra and ^{238}U are in approximate equilibrium (i.e., no major outside source or sink of radium), then there should be a relationship between ^{235}U activity and the magnitude of excess ^{226}Ra measured in each sample. Even if activities measured with gamma spectroscopy are biased low, all of the samples were measured with the same equipment and so should reflect a similar bias. **Figure 5-3** presents graphs of vertical and horizontal samples based on the raw gamma measurements and presented on the same scale for comparison.

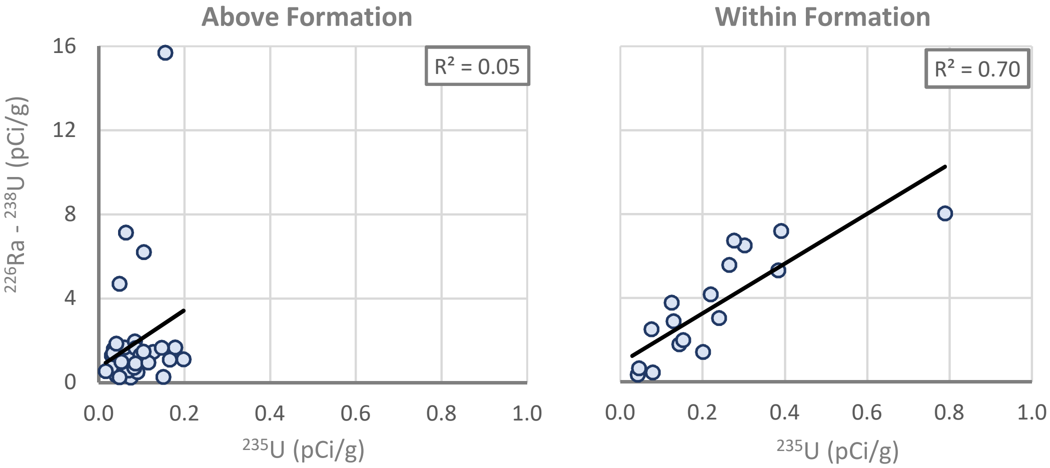

Figure 5-3: Relationship Between ^{235}U and Excess ^{226}Ra in Stabilized Drill Cuttings

There is a strong relationship between ^{235}U activity and excess ^{226}Ra in samples collected from within the formation, which is similar to the relationship observed for solids from drilling fluid (**Figure 5-2**). This indicates that the higher measured ^{226}Ra activity can be attributed to interference from ^{235}U. Thus, radium and uranium are expected to be in approximate equilibrium in these samples. This aligns with data from Eitrheim et al. (2016), which found ^{226}Ra activity in two samples of drill cuttings from within a shale formation to be similar to, but slightly lower than, ^{238}U activity.[11] Based on these data, it does not appear that stabilization substantially changed the radioisotope composition of drill cuttings. The drilling fluid from this formation is known to contain elevated radium, but these fluids may not have been retained on the stabilized waste. No information is available on how solidification/stabilization was achieved in these or other samples and so this represents a major source of uncertainty.

No such relationship is apparent for samples collected from above the shale formation. There are several outliers of high radium, though removal of these samples only worsens the correlation. The excess radium activity in remaining samples remains flat as ^{235}U increases, which might indicate that radium is depleted in these samples. In contrast, one sample of drill cuttings collected by Eitrheim et al. (2016) from above a shale formation contained ^{226}Ra activity similar to, but somewhat lower than, the ^{238}U activity. There is no single, clear explanation for the variable enrichment and depletion in these drilling solids. Depletion may result from mixing of the cuttings with highly saline drilling fluid. Unlike black shale, these rocks did not form in the presence of saline water, so it is possible that exposure to high salinity may disrupt equilibrium and cause the release of radium to solution. Higher radium activities may result from precipitation of barite out of solution as a result of quickly shifting water chemistry. Samples with elevated radium all exhibit increased barium concentrations in proportion to activity, while the remaining samples exhibit a flat relationship with barium. However, no information is available on how solidification/stabilization was achieved in these or other samples and so this represents a major source of uncertainty.

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11) Eitrheim et al. (2016) measured ^{226}Ra activity through the radon ingrowth method and so correction for interference from ^{235}U was not necessary.

5.2.2. Leachate

EPA identified three studies that measured both inorganic elements and organic compounds in leachate from drilling solids from wells drilled with water-based fluids (API, 1987; U.S. EPA, 1987; LADNR, 1999). No data were identified for radioisotopes. Because of the limited amount of data available for the different types of constituents, EPA did not break the discussion into separate sections. All available samples were collected from vertical wells located in at least thirteen states. The majority of available data are evenly distributed among the different states, but LADNR (1999) reported selected elements for a greater number of samples from Louisiana. The same study also reported samples from wells drilled with oil-based fluids. EPA combined the data without any weighting to compare wastes generated with water- and oil-based fluids. **Table 5-9** presents the 50th and 90th percentile of the available data for both inorganic elements and organic compounds in leachate from drilling solids for all constituents that were detected in at least half of samples.

Table 5-9. Constituent Levels in TCLP Leachate from Drilling Solids (mg/L)

Constituent	Vertical (Water-Based)			Vertical (Oil-Based)		
	n	50th	90th	n	50th	90th
Inorganic Elements						
Aluminum	14 / 26	0.25	1.4	0 / 0	--	--
Barium	44 / 56	1.9	5.0	124 / 142	2.2	6.5
Boron	17 / 24	0.9	2.2	0 / 0	--	--
Cobalt	19 / 24	0.02	0.05	0 / 0	--	--
Iron	22 / 26	2.4	26	0 / 0	--	--
Lead	40 / 54	0.11	0.88	91 / 142	0.14	0.83
Manganese	26 / 26	2.8	5.5	0 / 0	--	--
Nickel	16 / 26	0.05	0.09	0 / 0	--	--
Strontium	24 / 24	3.3	15	0 / 0	--	--
Zinc	20 / 26	0.78	6.2	0 / 0	--	--
Organic Compounds						
Toluene	22 / 30	0.03	0.83	0 / 0	--	--

n = Number of Samples Detected / Total

The available data provide only a few samples for most states and so are unlikely to capture the full variability of individual formations. For example, none of the studies report the equilibrium pH of the leachate. Alkaline wastes can counteract the fixed amount of acid used in the TCLP test increase the pH of solution, which can greatly alter the solubility of some constituents. This makes it difficult to determine what environmental conditions that these samples reflect. Despite the uncertainties, available data allow a comparison of samples drilled with water and oil-based fluids because the majority of samples are drawn from the same region. This comparison shows that both the median and high-end concentrations of barium and lead are similar in magnitude. Limiting the comparison to only samples from Louisiana does not alter this finding. Thus, there is no indication from available data that the type of drilling fluid used substantially alters the leaching behavior of inorganics from the waste. No comparisons could be conducted for any other constituents, including any organic compounds, as a result of a large number of samples with high detection limits.

5.2.3. Volatile Emissions

The presence of volatile organic compounds (e.g., benzene) and radioisotopes (e.g., radon) indicate there is potential for releases to the surrounding air. However, EPA did not identify any studies that measured volatile emissions of either type of constituent from drilling solids. Therefore, no conclusions could be drawn about the magnitude or frequency of these releases.

5.2.4. Summary – Drilling Solids

There are a number of factors that determine the composition of black shale, which may include the specific environmental conditions present at the time of formation (e.g., extent and duration of anoxia, local water composition), the degree of subsequent evolution (e.g., thermal maturity of hydrocarbons, extent of evaporation), and outside disturbances (e.g., uplift, intrusion from adjacent aquifers). All of these factors result in a high degree of variability among and within source rock. Despite the numerous sources of variability, there is substantial overlap in the concentrations of some elements among the three datasets. This provides some confidence that the range of potential concentrations in black shale has been adequately captured. However, the data also show the potential for higher concentrations of elements with a strong affinity for organic carbon (e.g., molybdenum, uranium) in the subset of gas-producing black shale. Drill cuttings are typically the largest volume waste in drilling solids and so these data may provide a reasonable order-of-magnitude estimate of constituent levels in the associated solids when direct measurements are not available.

The available data indicate that management of cuttings generated from both within and above the formation may increase the total constituent mass in the waste. Comingling of drilling fluids with cuttings at the ground surface can result in deposition of barite and other solids onto cuttings, which can in turn increase concentrations of barium and other inorganics. There is currently no evidence that adsorption of dissolved constituent mass from the drilling fluids onto the cuttings is a major source of constituent mass. However, if drilling fluid is incorporated into the solidified/stabilized waste, it may result in much higher constituent levels than predicted based on drilling solids alone. Limited data are available on the extent to which this might occur in the field, which represents a major source of uncertainty with the current data.

There are also limited data on the magnitude of releases from drill cuttings or drilling solids through leachate and volatilization. Available studies do not provide key information, such as the equilibrium pH of the measured samples. Because TCLP uses a fixed amount of buffer, wastes with high alkalinity may shift the final pH of the leachate closer to neutral. The solubility of some constituents can change dramatically over a small pH range and so this represents a major source of uncertainty. Thus, while available data provide useful information about the solubility of some constituents, it is difficult to draw conclusions about actual releases when the waste is disposed.

5.3. Produced Water

Produced water is any water drawn from the well as a byproduct of development and production. This includes both the formation water and flowback of any water injected into the well to enhance recovery. The volume of water generated can vary both by formation and individual well. Vertical wells, which tend to be sited in more permeable formations, can be relatively dry at first. However, as the pressure within the formation falls as a result of hydrocarbon withdrawal, formation water is more likely to come to the surface together with the oil or gas. It has been reported that these fields can produce more than five times the volume of water in later years (U.S. GAO, 2012). Later in the life of the well, additional water may be injected into nearby wells to increase pressure within the formation and displace remaining oil and gas ("waterflooding"). The injected water migrates through the formation and is then drawn back up through the production well. Horizontal wells, which tend to be sited in less-permeable formations, require water to be injected into the production well to liberate the oil or gas trapped within the rocks prior to the start of production ("hydraulic fracturing"). The injected water will return to the ground surface over a period of weeks to months. During this time, the continued mixing of injected and formation waters results in produced water that transitions from entirely injected water to entirely formation water. Additional water may be injected into a well periodically over the lifetime of the well to further stimulate production.

Records of the chemical composition of formation waters are available as far back as the early twentieth century (U.S. DOI, 1911). Initial interest in the composition of produced water was focused on the potential commercial applications for the salt content and the potential to recover precious metals (Rowan et al., 2015). As a result, early analyses were often limited to total dissolved solids (TDS) and certain economically-significant metals. High salinity is a defining feature of produced water from hydrocarbon formations. TDS in formation waters have been measured as high as 500,000 mg/L, over ten times more saline than seawater. Sodium and chloride alone can account for greater than 90% of the dissolved solids in the water (Schijf, 2007; U.S. DOI, 2017). Saline waters occur because the formations have been subjected to elevated temperature and pressure, which cause the evaporation and expulsion of water and further concentration of the remaining constituent mass. If a constituent becomes so concentrated that it exceeds saturation in the remaining water, it may precipitate out in solid deposits. It is possible that greater consolidation and evaporation in the dense formations that require horizontal wells results in higher constituent levels from the concentration of mass into smaller volumes of water. Therefore, EPA focused this review on potential differences in the wastes from vertical and horizontal wells to determine whether and to what degree differences exist. Produced water is assumed to be managed primarily as an aqueous waste and so EPA did not separately discuss leachate from this waste.

5.3.1. Bulk Composition

Variable amounts of data are available for each formation, which makes it difficult to aggregate the data in a representative way. To address this issue and to provide a more direct comparison with previous evaluations, EPA mirrored the approach used in the 1987 Technical Support Document (U.S. EPA, 1987d). EPA first grouped each state into zones based on similar geological formations, production activities, and climates. **Figure 5-4** presents the production zones used in this evaluation.

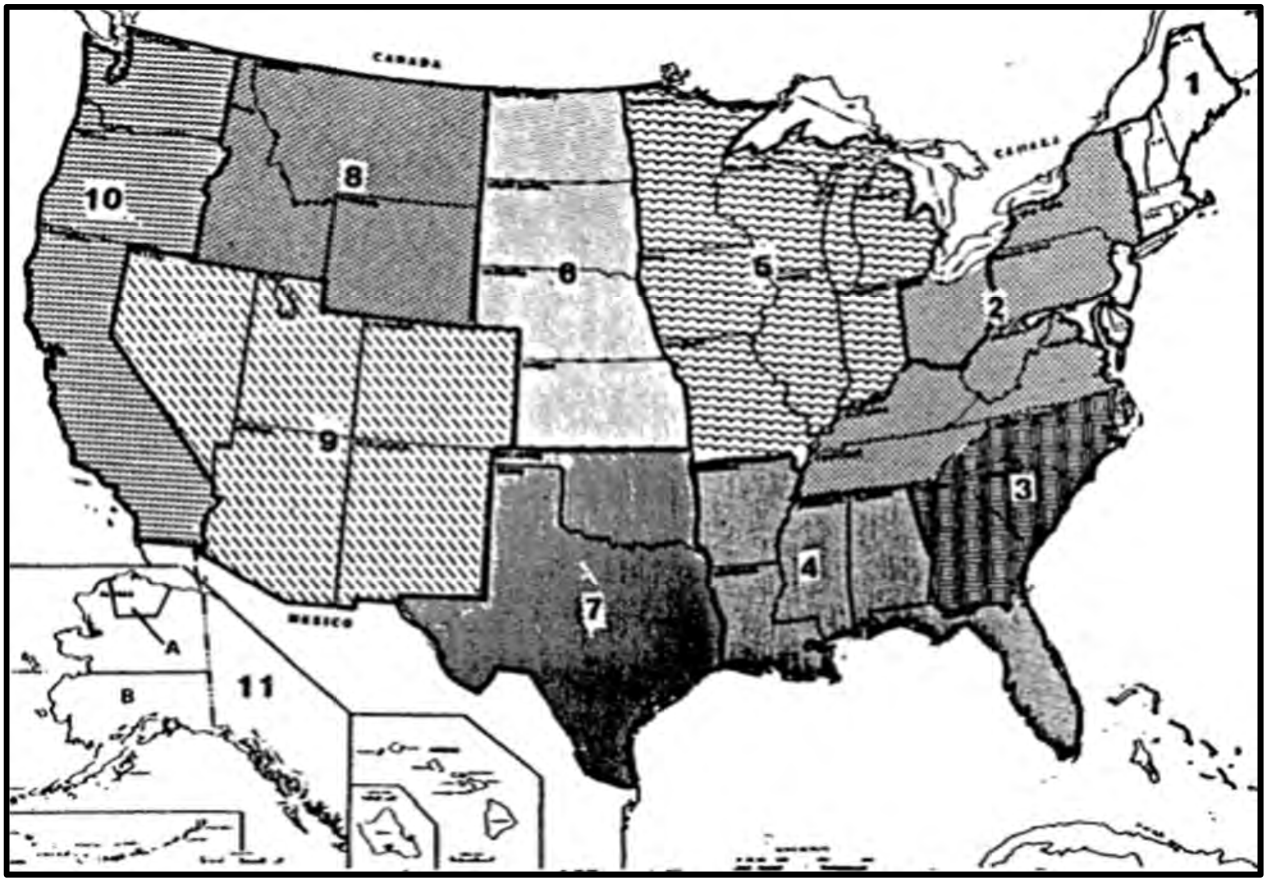

Figure 5-4: Oil and Gas Production Zones in the United States (U.S. EPA, 1987d)

The full dataset was sampled probabilistically with data from each region weighted based on the relative volumes of gross natural gas and crude oil produced in 2016 by each state from conventional and unconventional formations (U.S. DOE, 2018c,d). All data from a given region was weighted equally in each distribution. Some uncertainty is introduced by the fact that oil and gas production is not always correlated with produced water generation. EPA identified several sources of data on produced water volumes (API, 2000; U.S. DOE, 2009; GWPC, 2015). However, these data are often extrapolated from older reports and do not capture recent increases in production from the spread of directional drilling. In addition, although the amount of produced water generated in some high-producing states may be lower on a per-well basis, the greater number of wells still results in higher overall generation in these states. Therefore, weighting based on oil and gas production is considered reasonable for the purposes of this evaluation.

Inorganic Elements

EPA identified a number of studies that measured concentrations of inorganic elements in produced water from both vertical and horizontal wells. A summary of data collection efforts is provided in **Appendix B (Constituent Database)**. The summary statistics discussed in this section are based only on the data for formation water. It is clear from the literature that formation water is the primary source of inorganic constituent mass and, although flowback water will contain many of the same elements, concentrations in formation water are typically higher (MSC, 2009; Ziemkiewicz and He, 2015).

Flowback water can also be highly variable over time as a result of continued mixing with formation water. Thus, formation water provides the most reliable comparison of concentrations. **Table 5-10** presents the 50th and 90th percentile of the available data for inorganic elements in produced water from vertical and horizontal wells. The amount of data available varies by constituent. To best capture national variability, EPA limited the constituents presented below to those with data across multiple regions of the country. EPA further refined this list by removing constituents that were measured infrequently in high oil and gas-producing regions, which would skew summary statistics towards those few samples. A far greater number of samples are available for vertical wells. This is because a greater number of vertical wells have been drilled over time, which provided more opportunities to collect samples.

Table 5-10. Inorganic Elements in Produced Water (mg/L)

Constituent	Vertical			Horizontal		
	n	50th	90th	n	50th	90th
Major Ions (mg/L)						
Bicarbonate	36,060 / 36,060	380	1,731	50 / 52	289	1,281
Bromide	4,048 / 4,057	76	655	186 / 186	915	2,470
Calcium	39,512 / 39,512	1,760	13,846	267 / 267	4,430	20,100
Chloride	39,766 / 39,766	27,500	132,000	291 / 291	71,200	132,000
Magnesium	38,724 / 38,724	365	2,616	259 / 259	580	2,183
Potassium	15,844 / 15,844	141	1,270	205 / 206	326	1,030
Sodium	39,138 / 39,138	15,375	62,678	291 / 291	34,700	52,322
Sulfate	34,665 / 34,702	310	2,789	103 / 161	128	706
Trace Inorganics (mg/L)						
Aluminum	154 / 185	0.25	7.4	21 / 42	0.21	10
Arsenic	51 / 65	0.01	0.20	--	--	--
Barium	1,579 / 1,593	4.8	171	220 / 256	13	6,470
Boron	1,369 / 1,370	39	115	192 / 195	21	46
Cadmium	58 / 75	0.01	0.02	--	--	--
Cobalt	52 / 67	0.005	0.02	--	--	--
Copper	226 / 254	0.015	1.0	--	--	--
Fluoride	429 / 438	1.5	7.0	--	--	--
Iron	2,212 / 2,244	5.5	63	249 / 250	63	185
Lead	147 / 195	0.05	0.5	--	--	--
Lithium	1,652 / 1,652	5.1	50	--	--	--
Manganese	1,322 / 1,338	0.78	8.6	214 / 223	2.5	14
Nickel	58 / 73	0.03	0.05	--	--	--
Strontium	2,732 / 2,733	60	1,240	252 / 252	737	3,840
Zinc	212 / 217	0.40	3.3	63 / 69	0.22	2.0

n = Number of Samples Detected / Total

There is substantial overlap in the range of inorganic concentrations measured in produced water from vertical and horizontal wells. Although concentrations in horizontal wells tend to be higher overall, both well types can have similar high-end concentrations. It is possible the overlap of high-end concentrations reflects saturation of certain elements in formation water. Chloride and sodium have been reported to precipitate out as halite (NaCl) at the high concentrations reported in formation water (PDCNR, 2010; Rowan et al., 2015). In contrast, bromide salts are more soluble than chloride salts and so are less likely to precipitate at the comparatively low concentrations measured in formation water. The data show that horizontal wells have higher median and high-end concentrations of bromide than vertical wells. Another major difference between vertical and horizontal well concentrations is sulfate, which tends to be found at lower concentrations in horizontal wells. This might be the result of stronger reducing conditions in these formations. Reducing conditions can directly affect the solubility of redox-sensitive elements, such as iron, and indirectly affect the solubility of elements that are limited by the presence of sulfate, such as barium. A better understanding of such relationships may provide a means to gauge the representativeness of available data and fill remaining data gaps.

If constituent relationships are based on geochemistry, rather than the unique properties of individual formations or well types, then the relationship should not be isolated to a single formation or well type. Therefore, EPA initially drew data from all well types (e.g., oil, coal bed methane, geothermal) to identify potential relationships. The most common relationship reported in the literature is between TDS and alkaline earth metals (e.g., barium, strontium). Because of the constant valence (+2), these elements do not sorb as strongly to silicate surfaces as monovalent ions. Therefore, as the overall ionic strength of groundwater increases, competition for binding sites could force barium and strontium into solution (IAEA, 1990, 2014; Sturicho et al., 2001). EPA compared available data for halides and alkaline earth metals to identify potential relationships.

Chloride was selected as a proxy for TDS in this comparison because it is one of the most commonly reported analytes in produced water, is often the single largest contributors to TDS, and it eliminates double counting of barium and strontium included in the TDS measurement. While chloride may not directly compete with barium and strontium for binding sites, it provides a useful proxy for a range of cations that can. There is potential for chloride precipitation to weaken any relationship at the highest concentrations, though any relationships should still be apparent at lower concentrations. Although other ions, such as bromine, are less likely to precipitate, the relative lack of data for these ions can limit the conclusions that can be drawn from the comparisons. **Figure 5-5** presents the best-fit relationships between chloride and both barium (n = 3,540) and strontium (n = 4,927). All relationships are graphed on a log scale. The red lines reflect the best-fit curves, while the black lines represent the corresponding standard deviation.

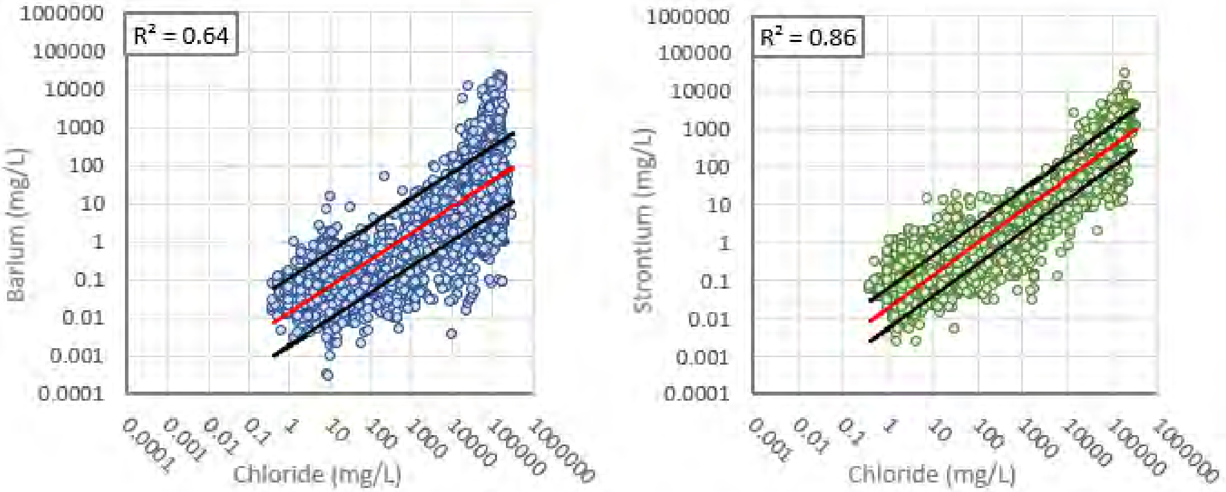

Figure 5-5: Relationships of Chloride with Barium and Strontium.

There is an apparent relationship between salinity and concentrations of both barium and strontium, though it is stronger for strontium. These relationships exist despite compounding sources of variability and uncertainty associated with data from different formations, well types, sample dates and analytical methods. EPA considered whether the strength of the relationships could be unduly influenced by extreme values. However, the available data are spread evenly over the reported interval and removal of individual studies, well types and statistical outliers did not diminish the overall relationship. Based on these findings, EPA reviewed the remaining dataset for other constituents that exhibit a relationship with salinity. Of the constituents with sufficient data for comparison, only lithium showed a similarly strong relationship ($R^2 = 0.78$). Lithium is a monovalent cation of the same elemental group as potassium and sodium. The presence of high concentrations of other alkali metals may result in competition that forces more lithium into solution, similar to barium and strontium.

Although salinity may influence the solubility of these constituents, it is clearly not the only factor. The standard deviation around each best-fit curve spans at least an order of magnitude. Other factors such as pH and dissolved oxygen might account for some of the remaining variability, though the relative importance of these other factors may change, depending on whether salinity dominates the water chemistry. EPA reviewed the literature to identify any other relationships that might exist and that could be evaluated with available data. The only relationships identified for barium and strontium were with bicarbonate and sulfate (Engle and Rowan, 2014). The authors noted that barium concentrations tend to be higher in sulfate-poor areas, while strontium concentrations tend be higher in bicarbonate-poor areas. An inverse relationship is present because bicarbonate and sulfate react with barium and strontium to form insoluble minerals that precipitate out of solution.

EPA conducted a direct comparison of barium and strontium as a function of bicarbonate and sulfate, but found no apparent relationships. To understand the reason for the lack of a direct relationship, EPA considered the fact that salinity is also an important factor in barium and strontium solubility. It is possible the abundance of other ions in saline groundwater may limit the rate of chemical reactions, resulting in greater retention of barium and strontium in solution. Therefore, EPA conducted an alternate comparison with both bicarbonate and sulfate expressed as a percentage of TDS. **Figure 5-6** presents the best-fit relationships between bicarbonate and barium (n = 1,120) strontium (n = 1,659) and between sulfate and barium (n = 2,595) and strontium (n = 3,689). All relationships are graphed on a log scale. The red lines reflect the best-fit curves, while the black lines represent the corresponding standard deviation.

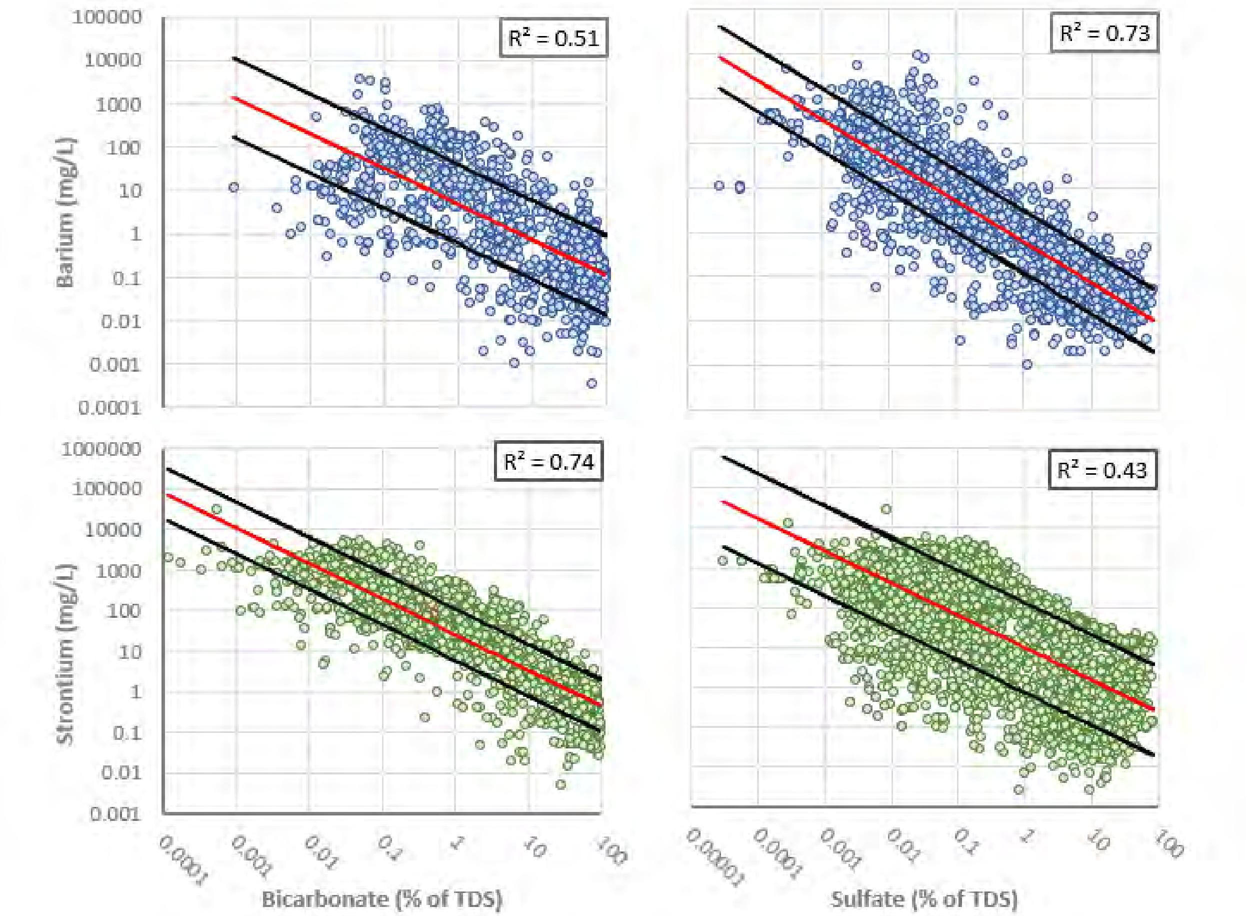

Figure 5-6: Relationship of Bicarbonate and Sulfate with Barium and Strontium.

As expected, bicarbonate and sulfate (as a percent of TDS) have an inverse relationship with barium and strontium. The strongest of these relationships are between barium and sulfate, which precipitate as barite ($BaSO_4$), and between strontium and bicarbonate, which precipitate as strontianite ($SrCO_3$). However, the same general trends are present for every combination. Differences in the strength of the relationships are likely because formation of barite and strontianite is more thermodynamically favorable and so exert greater control on dissolved concentrations. Barite has a lower solubility limit than celestite ($SrSO_4$), which can result in faster precipitation of barium in high-sulfate waters (Zhang et al., 2014). EPA reviewed the remaining dataset for any other constituents that exhibit a relationship with either bicarbonate or sulfate. Of the constituents with sufficient data for comparison, none were found to have a similarly strong relationship.

To better understand the combined impacts of bicarbonate, chloride and sulfate on barium and strontium, EPA conducted a multivariate regression analysis. For barium, the combination of chloride and sulfate was statistically significant and resulted in an $R^2 = 0.81$, which is a better fit than chloride ($R^2 = 0.64$) or sulfate ($R^2 = 0.74$) alone. For strontium, the combination of chloride, bicarbonate and sulfate was statistically significant and resulted in an $R^2 = 0.86$, which is a better fit than bicarbonate ($R^2 = 0.73$) alone, but is comparable to chloride ($R^2 = 0.86$). EPA used the equation generated from this analysis to probabilistically predict barium concentrations based on chloride and sulfate. Because far more data are available for these major ions, this approach can provide a comparison for measured barium data to gauge the representativeness of the available data. For each paired sample of chloride and sulfate, a barium concentration was calculated based on the best-fit equation and then allowed to vary based on the standard deviation. This process was repeated 100,000 times to ensure convergence of the results. The resulting dataset was sampled probabilistically with data from each region weighted based on the relative volumes of natural gas and crude oil produced in each state (U.S. DOE, 2018c,d). All data from a given region was weighted equally in the distribution. **Table 5-11** presents a comparison of barium from vertical wells based on empirical and modeled data. The comparison is limited to vertical wells because there are far fewer samples with paired chloride and sulfate compared to barium for horizontal wells, which introduces uncertainty into the comparison.

Table 5-11. Comparison of Measured and Modeled Barium Concentrations (mg/L)

Constituent	Measured			Modeled		
	n	50th	90th	n	50th	90th
Vertical	1,593	4.8	171	34,702	3.0	20

n = Number of Samples Measured/Modeled

There is general agreement between the median values of modeled and measured concentrations, though there is a substantial difference between high-end values. This may indicate that the measured data overestimate barium concentrations on a national-scale. Samples measured for both barium and sulfate tend to have lower sulfate concentrations than the larger dataset that allow more barium to remain in solution. It could also indicate that modeled concentrations underestimate concentrations to some degree. Precipitation of halide and other minerals within the formation places an artificial ceiling on modeled barium concentrations. Therefore, EPA concludes that the measured and modeled data can provide reasonable bounds on the potential barium concentrations in produced water. Future data collection and analysis can further refine this relationship and improve predictions.

Organic Compounds

EPA identified several studies that analyzed organics in produced water from vertical and horizontal wells. A summary of data collection efforts is provided in **Appendix B (Constituent Database)**. The full dataset for organic compounds was sampled probabilistically with data from each region weighted based on the relative volumes of natural gas and crude oil produced in each state (U.S. DOE, 2018c,d), the same as previously described for inorganic elements. All data from a given region were weighted equally in each distribution. The only compound with sufficient data to calculate summary statistics is benzene. The only well type with sufficient data are vertical wells. **Table 5-12** presents the 50th and 90th percentile of the available data for benzene in produced water from vertical wells.

Table 5-12. Organic Compounds in Produced Water (mg/L)

Constituent	Vertical		
	n	50th	90th
Benzene	27 / 32	0.23	4.9

n = Number of Samples Detected / Total

Although the most data are available for benzene, there are many other organic compounds that have been identified in produced water. As many as 1,400 to 2,500 compounds have been tentatively reported based on chromatogram energy peaks, though less than half this amount have been identified with confidence (Hoelzer et al., 2016; Khan et al. 2016). Many of these may be isomers, acids, substitutions and other variations of previously identified compounds. EPA identified eleven studies that analyzed for organics in produced water.[12] However, some of these studies only report whether a compound was detected and not the associated concentrations. These studies analyzed samples drawn from several unnamed conventional formations, as well as the Marcellus, Eagle Ford and Barnett shales.

The 1987 Technical Support Document (U.S. EPA, 1987d) analyzed a total of 444 organic compounds in produced water from vertical wells that included a range of volatile (n = 55), semi-volatile (n = 176), dioxin and dioxin-like compounds (n = 136) and pesticides (n = 77). Many of the compounds were below detection limits in all samples. The types of compounds detected most frequently include aliphatic hydrocarbons (i.e., C12 – 30), ketones (i.e., methyl isobutyl ketone, isophorone), alcohols (i.e., terpineol), phthalates [i.e., bis(2-ethylhexyl) phthalate], simple aromatic hydrocarbons (i.e., benzene, ethylbenzene, phenol and methylated substitutions, toluene), polycyclic aromatic hydrocarbons [i.e., 2-(methylthio)benzothiazole, dibenzothiophene, naphthalene and methylated substitutions] and other volatile organics (i.e., carbon disulfide). The compounds measured at the highest concentrations tended to be aliphatic and simple aromatic hydrocarbons, which are common components of crude oil. A concurrent study conducted by the American Petroleum Institute identified similar concentrations of many constituents (API, 1987).

Many of the same compounds reported in U.S. EPA (1987d) were also detected in more recent samples from vertical wells (MSC, 2009; Maguire-Boyle and Barron; 2014; Orem et al., 2014; Ziemkiewicz and He, 2015; Khan et al., 2016). These studies reported several additional compounds measured for, but not detected, in the 1987 studies. Examples include phthalates (e.g., di-n-octyl-phthalate), simple aromatic hydrocarbons (e.g., benzyl alcohol), polycyclic aromatic hydrocarbons (e.g., fluorene, phenanthrene, pyrene, pyridine) and other volatile compounds (e.g., bromoform, chloroform). Concentrations of these additional constituents were generally low and may be the result of improved detection limits. It is also possible that some of these compounds were added to injected water as a solvent, biocide, lubricant, tracer or other purpose. The attribution of compounds is complicated by uneven reporting of usage and the fact that some compounds added to injected water are the same as those that occur naturally in the formation. For example, naphthalene was reported in 19% of FracFocus 1.0 disclosures (U.S. EPA, 2016a). The practice of recycling produced water as the base fluid for hydraulic fracturing can also introduce naturally-occurring organics into the fluid. Furthermore,

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[12] API, 1987; U.S. EPA, 1987; Hayes, 2009; Maguire-Boyle and Barron; 2014; Orem et al., 2014; Abualfraj et al., 2014; Ziemkiewicz and He, 2015; Hoelzer et al., 2016; Khan et al., 2016, U.S. EPA, 2016c; USGS, 2016

the high temperature, pressure and salinity found in many hydrocarbon formations has the potential to transform the compounds through processes such as methylation and halogenation (Hoelzer et al., 2016).

MSC (2009), Orem et al. (2014) and Ziemkiewicz and He (2015) reported concentrations of organic compounds in the water at different stages of production. Compounds detected in water used as a base for hydraulic fracturing fluid include acetone, bromoform, naphthalene, trimethylbenzene and xylene. This indicates that the base is recycled produced water and so it is not clear if the detected compounds originate from the formation or additives. Compounds that were detected in the prepared fracturing fluid and that decreased over the first 20 days of production include bis(2-chloroethyl)ether, carbon disulfide and methylnaphthalene. The lack of contribution from the formation indicates that these compounds originate primarily from additives. Although 20 days is a relatively short timeframe relative to the lifespan of a well, it is also typically when the largest volumes of produced water are generated (U.S. EPA, 2016a). Therefore, the presence of these organic compounds may still be environmentally significant.

The organic compounds reported in produced water vary widely in solubility and hydrophobicity. Although potential health effect endpoints have been identified for some compounds, toxicity values have not yet been developed for many, particularly the various derivatives and degradation products (U.S. EPA, 2016a). Therefore, it is difficult to quantify the magnitude of potential risks associated with releases of these compounds to the environment.

Radioisotopes

EPA identified several sources that analyzed for radioisotopes in produced water from both vertical and horizontal wells. A summary of the data collection efforts is provided in **Appendix B (Constituent Database)**. The full dataset for radioisotopes was sampled probabilistically with data from each region weighted based on the relative volumes of natural gas and crude oil produced in each state (U.S. DOE, 2018c,d), the same as previously described for inorganic elements. All data from a given region were weighted equally in each distribution. The only isotope with sufficient data for summary statistics was ^{226}Ra. **Table 5-13** presents the 50th and 90th percentile of the available data for ^{226}Ra in produced water from vertical and horizontal wells. EPA also considered how reported sample errors could affect summary statistics, but the addition of error measurements to reported activities had negligible impact on the calculated summary statistics. Therefore, EPA only summarized reported activities in this table.

Table 5-13. Radioisotopes in Produced Water (pCi/L)

Constituent	Vertical			Horizontal		
	n	50th	90th	n	50th	90th
Radium-226	127 / 127	145	1,060	69 / 69	2,300	4,470

n = Number of Samples Detected / Total

This comparison indicates that both high-end and median activities of ^{226}Ra are higher in horizontal wells. These differences mirror those observed for barium and strontium. Radium is also an alkaline earth metal and so similar behavior is expected. Multiple studies have reported relationships between salinity and radium, but noted that the slope of the relationship can vary among formations (ILGS, 1983; Chermak and Schreiber, 2014). This aligns with previous findings that salinity is not the sole factor that influences barium and strontium solubility. EPA considered both chloride and bromide in the comparison due to similar amounts of paired data available. **Figure 5-7** presents the relationships for ^{226}Ra with chloride (n = 459) and bromide (n = 242). All relationships are graphed on a log scale. The red lines reflect the best-fit curves, while the black lines represent the corresponding standard deviation.

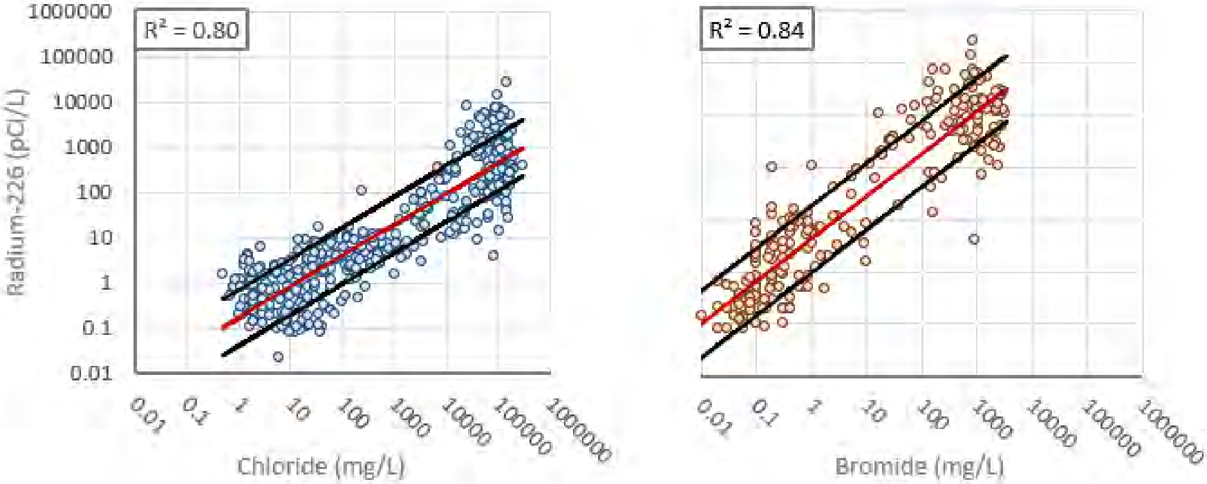

Figure 5-7: Relationship of Chloride and Bromide with Radium-226.

There is a clear relationship between salinity and radium activity. Both chloride and bromide provide a good fit. Although bromide provides a slightly better fit, this may be influenced by fewer data points clustered closer to the highest and lowest values. EPA also compared radium activity with bicarbonate and sulfate (as a percent of TDS), but did not identify any similarly strong relationships. This may be because the range of radium concentrations reported in literature all fall below the solubility limit of radium minerals, such as radium sulfate (Sturchio et al., 2001; SKB, 2008). The highest reported activity of 27,000 pCi/L corresponds to a dissolved concentration of only 0.027 µg/L. Instead, radium loss is driven primarily by co-precipitation with barium and strontium, which are part of the same group of alkaline earth metals (Zhang et al., 2014). It is possible that a relationship with bicarbonate and/or sulfate does exist; weak inverse trends can be seen in plotted data. Yet such an indirect relationship would be more complex than those identified for barium or strontium and may require other types of data or different handling of existing data to identify.

The majority of available studies sampled only for ^{226}Ra because the longer half-life of this isotope makes it more persistent in the environment. Omission of ^{228}Ra can substantially underestimate total radium activity in samples, which can result in an underestimation of risk and may skew relationships present in the data. Therefore, EPA explored both whether it is possible to predict ^{228}Ra activity based on measured ^{226}Ra activity and how inclusion of both isotopes may affect the relationship with salinity. The available literature is inconsistent on whether a relationship exists between radium isotopes. Some studies report a strong correlation between the two isotopes (Fisher, 1998), while others found a more moderate relationship (U.S. DOE, 2004) or none at all (ILGS, 1983). **Figure 5-8** presents the relationship between ^{226}Ra and ^{228}Ra (n = 120) and between chloride and $^{226+228}$Ra (n = 120). All relationships are graphed on a log scale. The red line represents the best-fit curve, while the black lines represent the corresponding standard deviation.

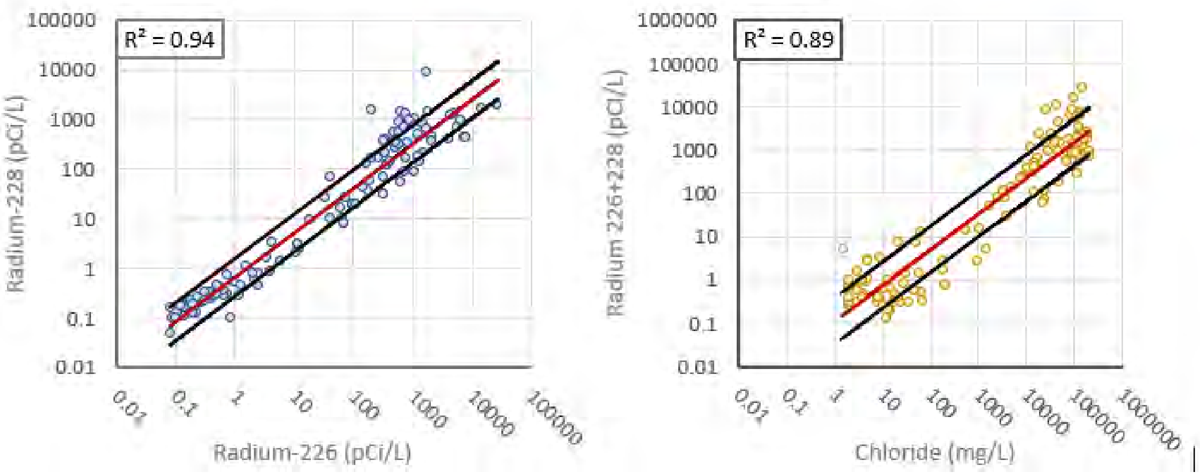

Figure 5-8: Relationships of Radium-226 and Radium-228.

This left graph shows a strong relationship between the activities of different radium isotopes. This is reasonable, given that all isotopes of radium will behave the same chemically. Anything that increases the solubility of ^{226}Ra should have a similar effect for ^{228}Ra. However, as ^{226}Ra activity increases, ^{228}Ra tends to decrease as a fraction of the total radium. Some studies have reported that the ratio of radium in produced water mirrors that of the parent rock (Sturicho et al., 2001). The decreasing radium ratio may reflect the greater potential for uranium to accumulate in the high-organic rock in hydrocarbon-bearing formations. The best-fit equation indicates that the average ^{228}Ra/^{226}Ra ratio will range between 0.3 and 0.4, based on the 50th and 90th percentile of measured ^{226}Ra activity. This compares well with previous estimates around 0.3 (U.S. EPA, 1993; Bernhardt et al., 1996). Inclusion of both isotopes shown in the right graph results in a noticeable shift in the best-fit line toward higher activities (e.g., 230 vs 98 pCi/L at 10,000 mg/L Cl). The addition of radium isotopes also results in a better fit though, again, this may be influenced by fewer data points clustered closer to the highest and lowest values.

To better understand the impact of chloride and bromide on dissolved ^{226}Ra activity, EPA conducted a multivariate regression analysis. This analysis was only conducted for ^{226}Ra because it is the only isotope with sufficient measured data to allow a comparison. EPA used the equation generated from the regression analyses to probabilistically predict ^{226}Ra activity based on measured chloride and bromide concentrations. For each sample of chloride or bromide, a radium activity was calculated based on the best-fit equation and then allowed to vary based on the standard deviation. This process was repeated a total of 100,000 times to ensure convergence of the results. The resulting dataset was then sampled probabilistically with data from each region weighted based on the relative volumes of natural gas and crude oil produced in each state (U.S. DOE, 2018c,d). Data from a given region were weighted equally in each distribution. **Table 5-14** presents a comparison of activities from empirical and modeled data.

Table 5-14. Comparison of Measured and Modeled Radium-226 Activities (pCi/L)

Constituent	Sampled			Modeled (Cl)			Modeled (Br)		
	n	50th	90th	n	50th	90th	n	50th	90th
Vertical	127	145	1,060	39,766	187	565	4,057	145	867
Horizontal	69	2,300	4,470	291	341	587	186	1,095	2,397

n = Number of Samples Measured/Modeled

There is overlap among the three datasets, though chloride and bromide both predict lower activities than reported in the literature. This could be because many studies tend to focus on individual wells or formations already known to have elevated radioactivity, which can skew the dataset higher. Predictions with chloride result in the lowest activities, similar to barium. Precipitation of halide and other minerals within the formation could place an artificial ceiling on modeled radium activities. Despite these uncertainties, the predicted activities generally agree with the overall magnitude of activities reported in the literature. Therefore, EPA concludes that the combination of measured and modeled data can provide reasonable bounds on estimates of potential radioactivity in produced water. Future data collection and analysis can further refine these relationships and improve predictions.

5.3.2. Volatile Emissions

The presence of volatile organic compounds (e.g., benzene) and radioisotopes (e.g., radon) indicate there is potential for releases to the surrounding air. However, EPA did not identify any sources that analyzed for volatile emissions of organic or inorganic constituents from produced water. Therefore, no conclusions can be drawn about the magnitude or frequency of these releases.

5.3.3. Summary – Produced Water

Based on the available data, EPA concludes that similar concentrations of some inorganics and radionuclides are possible in produced water generated from vertical and horizontal wells. As a result, the magnitude of releases to the environment or deposition to downgradient wastes (e.g., scale and production sludge) can be similar. The extent to which constituent concentrations in produced water are related to the permeability of the formation is not clear at this time because the available literature often does not provide this information about the sampled formations. However, the relationships identified from the literature indicate local geochemistry is more important than the specific well type in determining the magnitude of dissolved concentrations in the produced water.

The relationships identified from the literature cannot be used to predict the exact concentration in the produced water from any individual well. There are too many remaining sources of variability that result in a range of potential concentrations that extend an order-of-magnitude or more. However, these relationships may provide probabilistic distributions that can be used to predict likely concentrations in an area. Further investigation can refine known relationships and may also identify additional ones.

It is clear that there are also numerous organic compounds that may be present in produced water. However, insufficient data are available to compare these organic concentrations from vertical and horizontal wells. The most commonly detected organic compounds are commonly associated with hydrocarbons (e.g., benzene, toluene), but these compounds do not always originate from the formation. Source attribution is complicated by inconsistent reporting on additive usage in hydraulic fracturing fluids, chemical transformation within the subsurface, and the increasing practice of recycling produced water back into hydraulic fracturing fluid. Even when the structures of the organic compounds present are known, there may not yet be data on the potential mobility and toxicity. Without these data, the potential risks associated with releases to the environment cannot be quantitatively evaluated.

5.4. Pipe Scale

Pipe scale is the hard precipitate that accumulates on the walls of pipes and other equipment. There are multiple types of scale that can form, which depend on the minerals that are at or near saturation in the produced water. The scale that forms can occur as a single compound or as an amalgamation of similar compounds. The most common types of scale are carbonates (e.g., $CaCO_3$), halides (e.g., NaCl), silicates (e.g., Fe_2SiO_4), sulfates (e.g., $SrSO_4$) and sulfides (eg., PbS). Sulfate scale is the dominant type associated with oil and gas wells. There are two main causes of sulfate scale. The first is mixing of incompatible waters. When water injected into the well to enhance recovery has high sulfate levels relative to the formation water, then scale may precipitate instantaneously and in high volume. In extreme cases, this type of scale formation has completely clogged wells in under a day (Crabtree et al., 1998). The other cause is changes in mineral solubility as a result of the decreasing pressure and temperature of water as it is brought to the surface. Generally, minerals are about half as soluble at 77 °F (25 °C) than at 203 °F (95 °C), and about half as soluble at atmospheric pressure than at 7,000 psi (48 MPa), regardless of the initial concentration (Oddo and Thomson, 1994; Crabtree et al., 1998). This type of accumulation of scale can be gradual and might not be detected until the equipment is taken out of commission (Collins, 1975; Kan and Tomson, 2010).

Sulfate scale that forms on equipment surfaces is highly resistant to removal through either mechanical or chemical means. Scale inhibitors can be mixed in the injected water to reduce or eliminate scale formation either by increasing the solubility of the compound or by disrupting the ability of the scale to affix or grow on equipment surfaces (Crabtree et al., 1998). These additives can eliminate scale formation when the water is slightly oversaturated, but it may not be possible to entirely prevent scale formation when water is highly oversaturated (Kan and Tomson, 2010). Some of the scale may instead precipitate out as independent minerals or onto suspended solids before settling out of solution further down the production stream. The remainder of this section focuses on scale that forms as relatively homogenous deposits on equipment surfaces. Scale deposited in sludge further along the production stream is discussed in a subsequent section of this document.

5.4.1. Bulk Content

Common types of sulfate scale associated with oil and gas wells are anhydrite ($CaSO_4$), barite ($BaSO_4$) and celestite ($SrSO_4$). The amount of each that precipitates depends on the relative concentrations and solubility of these minerals in the produced water. Due to the extremely low solubility of barite, it is often the dominant mineral (Crabtree et al., 1998; Zhang et al., 2014). Scale samples collected from

Texas had an average composition of 31% Fe, 14% Ba, 2% Sr and 1% Ca (TXBEG, 1995).[13] Scale samples from Brazil had an average composition of 40% BaO, 9% SrO and only 3% FeO (Godoy and Petinatti da Cruz, 2003).[14]

Radium does not form an independent mineral phase because dissolved concentrations are orders-of-magnitude below saturation, even at the highest measured activities (Sturchio et al., 2001; SKB, 2008). However, radium will readily co-precipitate with barite by substituting for barium in the crystal lattice (Zhang et al., 2014). As a result, radium can precipitate regardless of the amount dissolved in water. A review of the literature indicates that radium is the primary constituent of concern associated with this waste stream. **Table 5-15** presents a summary of radium content in pipe scale from different states. EPA identified thirteen studies that provide data from nine states. EPA did not identify any data of the volume of scale generated in these or other states. As a result of this and differences in both sample size and reported activities among the studies, EPA did not attempt to further aggregate the data.

Table 5-15. Radioisotopes in Scale (pCi/g)

State	Well Type	Ra226			Ra228		
		n	50th	90th	n	50th	90th
California	Vertical	22 / 22	9.3	512	22 / 22	15	501
Kentucky	Vertical	13 / 13	1,711	2,164	10 / 10	45	55
Louisiana	Vertical	9 / 9	360	1,226	1 / 1	120	
Michigan	Vertical	11 / 12	539	1,466	11 / 12	60	111
New York	Vertical	7 / 7	1.0	5.2	4 / 6	0.60	2.5
North Dakota	Horizontal	38 / 40	148	1,434	38 / 40	76	599
Oklahoma	Vertical	8 / 8	1,715	1,851	1 / 8	0.05	4.0
Pennsylvania	Vertical	2 / 2	2.0	2.6	2 / 2	1.2	1.3
Texas	Vertical	37 / 37	895	2,436	37 / 37	1,295	3,880

n = Number of Samples Detected / Total

Both high-end and median scale activity are elevated in multiple states. Most studies reported instances of combined radium activities far greater than the upper bound of 4.2 pCi/g measured in surface soil (U.S. DOE, 1981a). Thus, there is clear potential for high activities in this waste. However, it is not possible to define a representative distribution of potential activities with available data because of the approach used to select sample locations. Some studies conducted an initial survey of operating equipment with hand-held instruments to guide sample collection toward areas of elevated activity. This preferential sampling of hotspots is likely to overestimate the prevalence of higher activities. A survey overseen by API concluded that between 10 and 30% of oil and gas wells in the United States produce radium-enriched scale in pipes and other equipment (API, 1989; Rood et al. 1998). However, the basis for that estimate is measurements taken around the external surface of the equipment. As a result, this estimate does not account for downhole accumulations that may occur over time. Furthermore, measurements on the external surface of equipment may underestimate the magnitude of radioactivity present due to shielding of gamma radiation. Based on the work of Bernhardt et al.

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[13] If all Ba and Sr are present as sulfates, these minerals would account for 25% and 4% of the total mass, respectively.

[14] If all Ba and Sr are present as sulfates, these minerals would account for 60% and 15% of the total mass, respectively.

(1996), a steel pipe with internal activity as high as 60 pCi/g ^{226}Ra could result in external measurements comparable to background.[15] However, greater exposures are possible when the scale is disturbed during management and disposal.

Although relatively low activities were reported for New York and Pennsylvania, the same studies measured produced water activities above 1,000 pCi/L ^{226}Ra. Therefore, there is ample radium available to precipitate if conditions are favorable. The measured concentrations of barium and sulfate are similar to those in states with higher scale activity and overlap with solubility limits modeled under standard environmental conditions (Langmuir and Melchior, 1985; SKB, 2008). This indicates that radium may precipitate gradually over time. It is possible that the small number of samples reported by these studies missed areas of higher activity. Recent studies have reported favorable conditions for scale formation from the horizontal wells in these states (Blauch et al., 2009; Engle and Rowan, 2014).

Many of the studies reported activities for both ^{228}Ra and ^{226}Ra in scale. The isotope ratio of ^{228}Ra/^{226}Ra in freshly deposited scale should mirror that of the produced water because different isotopes of the same element exhibit the same chemical behavior. However, the isotope ratio of scale will decrease over time. The shorter half-life of ^{228}Ra (i.e., 5.7 years) compared to ^{226}Ra (i.e., 1,600 years) results in the depletion of ^{228}Ra in older samples (Fisher and Hammond, 1994). Few studies reported the age of scale samples. In cases of gradual accumulation, it is often unknown how long scale is present in a pipe before it is removed from service and how long after that the samples have been stored in pipe yards or drums awaiting disposal. One study that measured ^{214}Pb and ^{214}Bi found these radioisotopes to be in approximate equilibrium with ^{226}Ra, but found ^{210}Pb was a factor of four lower (Landsberger et al., 2016). If decay of ^{226}Ra were the only source of ^{210}Pb (i.e., no independent precipitation), the age of this scale would be at least 10 years old. Another study estimated the age of scale found in a pipe yard to be nearly 30 years old (Zielinski et al., 2000). This is another source of uncertainty when defining representative activities at the time of disposal.

5.4.2. Leachate

EPA identified few studies that evaluated the leaching behavior of scale from oil and gas wells. Studies of similar scale from uranium mine tailings reported barite to be insoluble under typical environmental conditions, but more soluble under reducing conditions (Fedorak et al., 1986; Huck and Anderson, 1982; Huck et al., 1989; McCready et al., 1980). Chemical reduction of sulfate is often a slow process, but biologically-mediated reduction can occur at a much faster pace when conditions are favorable. Bacteria capable of reducing sulfates occur naturally in the soil, though the high concentrations of inorganic elements and organic compounds in produced water might inhibit bacterial growth (Phillips et al., 2001; U.S. DOE, 2004). As a result, the two available studies of oilfield scale focused on samples that had been incubated with soil or bacterial cultures to enhance releases. Phillips et al. (2001) incubated a scale sample of 1,300 pCi/g ^{226}Ra with and without bacteria isolated from production pit for ten months. The presence of sulfate-reducing bacteria increased the dissolved activity from 0.54 to

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[15] 60 pCi/g results in an estimated exposure rate around 7 microroentgens (μR)/hr. API (1989) reported median background exposure rates across the United States ranging from 5 to 9 μR/hr. MIDNR/DPH (1991) reported background rates in Michigan between 3 and 7 μR/hr, while U.S. DOI (1997b) reported rates in Kentucky between 7 and 8 μR/hr.

14.9 pCi/L ^{226}Ra. DOE (2004) incubated scale samples with soil collected from the sample area for two weeks. However, this study reported the leachate activity as a percentage of the original bulk activity. Without additional information on both the bulk activity of the sample and the liquid-to-solid ratio of the leaching test, these data cannot be converted to a comparable dissolved activity. Discussion solely in percentages can also give the misleading impression that the leachate activity is low. For example, the activity reported by Phillips et al. (2001) was equal to only 0.04% of the total mass.

Neither of the studies reported the final pH of the leachate. Therefore, there is uncertainty about the environmental conditions these samples reflect. This uncertainty may be minor, as geochemical modeling indicates that leaching from scale is independent of pH outside of extremely acidic ($pH < 2$) or basic ($pH > 12$) conditions (Huck et al., 1989). Yet shifts in pH could also inhibit the growth of bacteria that drive barite reduction. In addition, there are no data available on how leaching from the scale might change over time. Because the bacteria break down a fundamental component of the scale matrix as a source of energy, it may be reasonable to assume a substantial fraction of the radium could eventually be released.

Another source of uncertainty in the available data are that neither study measured releases of both ^{226}Ra and ^{228}Ra from scale. Therefore, both studies underestimate the magnitude of radium leached to some degree. Phillips et al. (2001) reported the activity of both isotopes in the scale sample, but only the leached ^{226}Ra activity. Under the assumption that the two isotopes are equally distributed in the scale matrix and thus have a similar potential to leach, total activity in the presence of sulfate-reducing bacteria would fall closer to 27.2 pCi/L $^{226+228}$Ra.

5.4.3. Air Emissions

Radon is the only member of the uranium and thorium decay chains that exists as a gas at room temperature. Two isotopes of radon, ^{222}Rn and ^{220}Rn, are created by the direct decay of ^{226}Ra and ^{228}Ra, respectively. The majority of studies do not analyze for ^{220}Rn because the much shorter half-life (i.e., 55 seconds) limits potential exposures, particularly when the gas must first migrate through soil or other porous media. Even for the longer lived ^{222}Rn (i.e., 3.8 days), some fraction of the gas will not escape into the atmosphere. Therefore, releases are frequently reported in terms of the relative amount of radon that does escape (i.e., emanation fraction). There is no correlation between the activity of this waste and the emanation fraction. Releases are controlled by the physical structure of the waste, rather than the overall activity, so these measurements can be used together with the activity in other samples to estimate potential emission rates.

EPA identified two studies that analyzed samples collected from Kentucky, Louisiana, Michigan, Oklahoma and Texas (Wilson and Scott, 1992; U.S. DOE, 1999b). Because the emanation fraction is not a function of activity, EPA combined data from the different states. The data are instead broken out based on the integrity of the scale samples. Some studies have reported substantial differences between the larger samples of intact scale still attached to the pipe and the smaller disturbed samples collected from the ground and drums. **Table 5-16** presents the 50th and 90th percentile of the available data for radon emanation from intact and disturbed pipe scale.

Table 5-16. Radon Emanation Fraction from Scale

Isotope	Emanation Fraction		
	n	50th	90th
Intact Scale	31 / 31	0.039	0.095
Disturbed Scale	18 / 18	0.135	0.239

n = Number of Samples Detected / Total

As reported in the literature, available data show that samples of disturbed scale tend to have higher emanation fractions. Because emanation is limited by the rate at which radon can migrate out of the scale, it is reasonable that scale with a higher surface area to volume ratio would also have higher relative emanation (U.S. DOE, 1999b; White and Rood, 2000; Phillips et al., 2001). The density of intact barite deposits on equipment is estimated to be around 2.6 g/cm^3, which is comparable to that of many rocks (U.S. DOE, 1996). The emanation fraction of this intact scale is comparable to undisturbed soil (Rood et al., 1998). In contrast, disturbed scale has emanation fractions comparable to uranium mine tailings (White and Rood, 2000). There is little overlap in the data for these two types of samples. Therefore, use of lower emanation fractions to estimate releases from scale that is separated from the pipe or otherwise disturbed during disposal is likely to underestimate potential exposures.

5.4.4. Summary – Pipe Scale

Available data show that pipe scale can form on oil and gas equipment in any region of the country. Radium activities in measured and modeled produced water from both vertical and horizontal wells are high enough to cause the activities measured in pipe scale. However, high dissolved radium activity alone does not guarantee that high-activity scale will form. Radium typically precipitates along with sulfate or carbonate minerals, so the rate and extent of precipitation depends on the chemistry of the formation. When scale forms on equipment surfaces, it may accumulate slowly and not be apparent until after the equipment has been taken out of service. Use of scale inhibitors can reduce the total volume that adheres on the equipment surfaces over time, but inhibitors may not completely prevent scale formation. If inhibitors only delay deposition, then greater radium accumulation may occur in downgradient wastes, such as production sludge.

Pipe scale is anticipated to be managed independently from other wastes because of the considerable effort required to physically or chemically dislodge the scale from equipment surfaces. However, the Agency identified little documentation on where pipe scale is currently disposed. The radium activities reported in the literature would pose additional management challenges, as the activities are frequently higher than the limits allowed in many landfills. It is important to note that the available data may be biased toward higher activities because some studies used hand-held instruments to guide sample collection toward areas of elevated activity. As a result, a greater fraction of the scale generated may have lower activities than predicted by the current dataset. However, remaining scale may also have elevated activities that are shielded from surface measurement by the metallic equipment. This represents a major source of uncertainty in the current data.

5.5. Production Sludge

Production sludge (hereafter referred to simply as "sludge") is a mixture of the solid and fluid residues (e.g., heavy hydrocarbons, formation solids, chemical precipitate) that collect in equipment and other vessels along the production stream. Sludge is typically found as a loose material and may also be referred to as sediment, bottoms or settlings. One study reported that the highest rate of sludge accumulation occurs in storage tanks (API, 1989), which may result from longer residence times. Yet, even there, accumulation can be a gradual process. Deposition rates have been reported between 1 and 4 cm/yr per well (U.S. EPA, 1993; Zielinski and Budahn 2007). Depending on the dimensions of an individual pit or tank, disposal of the accumulated sludge might not occur until years after the start of production.

5.5.1. Bulk Content

The composition of sludge is partly dependent on the characteristics of the produced water, though silica and barium compounds are often the primary minerals present (U.S. EPA, 2000a). Samples collected around the coast of Louisiana had an average solids composition of 50% SiO_2 and 20% $BaSO_4$ (Fisher and Hammond, 1994). Samples collected from Brazil had an average solid composition of 35% SiO_2 and 12% BaO (Godoy and Petinatti da Cruz, 2003).[16] Both studies also reported more minor contributions from aluminum, calcium and iron oxides. The barite in sludge is similar to that found in scale, but there are currently no practical means to separate this mineral from the remaining sludge due to the small size and brittleness of the precipitate (Fisher and Hammond, 1994; U.S. DOE, 2004). Therefore, the barite is considered to be a fundamental component of the sludge, rather than a mixture of separate wastes.

Inorganic Elements

EPA identified seven studies that measured inorganic elements in sludge. EPA separated the available data into two sets for comparison based on the analytical methods used in the studies. This is because of substantial differences identified between samples of drilling solids that had been analyzed with acid digestion methods and non-destructive methods. Four studies used digestion methods on samples from at least four states (API, 1987; U.S. EPA, 1987, 2000; Zielinski and Budhan, 2007). Three studies used non-destructive methods on samples collected primarily from one state, with additional samples from two others (Fisher and Hammond, 1994; Landsberger et al, 2012; Zhang et al., 2015). The majority of these data were drawn from vertical wells. The limited data available for horizontal wells fell within the range reported for vertical wells and so EPA combined the data from both types of wells for this comparison. **Table 5-17** presents the 50th and 90th percentile of the available data for inorganic elements in sludge detected in at least half of one of the datasets.

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16) If all of the measured BaO is present as BaSO4 then this would account for closer to 18% of the total mass, similar to samples collected from around the Gulf of Mexico.

Table 5-17. Inorganic Elements in Sludge (mg/kg)

Constituent	Acid Digestion			Non-Destructive		
	n	50th	90th	n	50th	90th
Antimony	0 / 0	--	--	15 / 17	27	54
Aluminum	9 / 9	1,500	16,221	2 / 2	46,500	50,100
Arsenic	6 / 7	3.3	4.3	17 / 17	64	436
Boron	8 / 8	34	143	0 / 0	--	--
Barium	9 / 9	1,340	8,735	21 / 21	101,000	231,000
Chromium	59 / 59	18	27	0 / 0	--	--
Cobalt	3 / 5	2.8	19	17 / 17	35	77
Copper	60 / 60	18	43	17 / 17	292	720
Iron	9 / 9	5,700	37,807	2 / 2	59,250	66,650
Lead	5 / 6	69	151	17 / 17	872	7,620
Manganese	9 / 9	72	578	0 / 0	--	--
Molybdenum	2 / 5	0.25	9.9	10 / 17	5.0	51
Nickel	49 / 59	16	30	17 / 17	32	127
Selenium	1 / 7	1.0	2.4	13 / 17	10	42
Strontium	11 / 11	200	256	18 / 18	3,425	29,570
Vanadium	12 / 12	8.9	26	0 / 0	--	--
Zinc	67 / 67	59	159	19 / 19	1,170	11,560

n = Number of Samples Detected / Total

Total concentrations are higher than acid-extractable concentrations for all constituents, regardless of where the samples were collected. Differences of an order of magnitude or more are too large to only be explained by regional variability. The more likely cause is that non-destructive analytical methods measure the full constituent mass within the sample matrix, while digestion methods measure the constituent mass that can be liberated from the matrix with a combination of heat and acid (Gaudino et al., 2007). If a fraction of the sludge is recalcitrant, it will not dissolve during acid digestion. This can result in an underestimation of the total concentration present in the waste. If the recalcitrant fraction will not be released from the sludge, it may not be appropriate to consider this additional mass in exposure estimates. However, studies have shown that reducing conditions can mobilize constituent mass from otherwise recalcitrant minerals, such as barite (Phillips et al. 2001; U.S. DOE, 2004). Therefore, it may still be appropriate to consider the total mass if the sludge is managed in a biologically-active, reducing environment. This is a major source of uncertainty in the current data.

Organic Compounds

EPA identified two studies that measured organic compounds in sludge (API, 1987; U.S. EPA, 1987). Samples were collected from vertical wells in at least three states. The uncertainties associated with measurement of inorganic elements are not anticipated to be as great a concern for organic compounds. Residual oil is typically present as a separate layer from other precipitate and so the mineral phase is less likely to interfere with laboratory analysis or to limit potential exposures. Therefore, given the relatively small number of samples available, EPA combined all available data into a single distribution. **Table 4-18** presents the 50th and 90th percentile of the available data for organic compounds in sludge.

Table 5-18. Organic Compounds in Sludge (mg/kg)

Constituent	Percentile		
	n	50th	90th
Benzene	7 / 8	63	218
Toluene	8 / 8	15	609
Ethylbenzene	9 / 10	21	307
Xylene	2 / 2	317	571

n = Number of Samples Detected / Total

All of the data were collected around 1987, so there is some uncertainty whether these data reflect the sludge that is currently generated. In the absence of more recent sludge data, EPA considered data for produced water because it is one primary source of the organic compounds in sludge. Samples collected in the last decade have a similar range of benzene, toluene, ethylbenzene and xylene (BTEX) concentrations as those from the 1980's. This indicates that current sludge has a similar potential to retain dissolved and emulsified organics from produced water. In addition, the equipment used to separate oil and water still relies on differences between the density of oil and water. This indicates that current sludge also has a similar potential to retain heavier hydrocarbons that settle out of the water. Based on these considerations, EPA concludes that available data can still provide useful information about the magnitude of potential concentrations. These data show that substantial enrichment of organic compounds in sludge is possible. However, the small number of total samples make it difficult to draw conclusions about the overall distribution of concentrations and how frequently higher concentrations will occur.

Radioisotopes

EPA identified thirteen studies that measured radioisotopes in sludge. The majority of these studies collected samples from vertical wells in eight states (MIDNR/MDPH, 1991; PADEP, 1992; CADHS/DC, 1996; Pardue and Guo, 1998; NYDEC, 1999; U.S. DOE, 1999a,b; U.S. EPA, 2000a; Zielinski and Budahn, 2007; Landsberger et al., 2012). Two studies collected samples from vertical wells in two states (U.S. DOE, 2014; Zhang et al., 2015). Radium is the most commonly measured radionuclide in sludge because it is the most highly concentrated in produced water and frequently co-precipitates with barium. As a result, this isotope is likely to be sequestered in the recalcitrant fraction of the sludge. However, the uncertainties associated with measurement of inorganic elements are not anticipated to be as great a concern for radioisotopes. Gamma radiation can easily pass through solid materials and so the mineral phase is less likely to interfere with laboratory analysis or to limit potential exposures. A number of radioisotopes may also be present in sludge from different sources, but the most data were available for radium because of the potential for high activities through barite precipitation. Given the variable amount of data available for each state and the substantial differences among the reported activities, EPA separated the data out by state. **Table 5-19** presents the 50th and 90th percentile of the available data for radium in sludge.

Table 5-19. Radioisotopes in Sludge (pCi/g)

State	Well Type	Radium 226			Radium 228		
		n	50th	90th	n	50th	90th
California	Vertical	5 / 5	2.3	10	5 / 5	3.7	11
Louisiana	Vertical	24 / 24	667	101,244	10 / 10	560	37,392
Michigan	Vertical	3 / 3	436	4,654	3 / 3	220	1,470
New York	Vertical	9 / 9	2.0	6.7	8 / 9	2.1	4.3
North Dakota	Horizontal	57 / 57	25	98	57 / 57	11	25
Oklahoma	Vertical	9 / 9	53	1,072	7 / 9	4.6	28
Pennsylvania	Vertical	25 / 25	0.7	1.1	25 / 25	0.7	1.5
	Horizontal	2 / 2	281	408	0 / 0	--	--
Texas	Vertical	29 / 29	124	760	29 / 29	44	187

n = Number of Samples Detected / Total

Measured scale activity is variable among the states. Yet most studies report instances of ^{226}Ra activities far greater than the upper bound of 4.2 pCi/g ^{226}Ra measured in surface soil (U.S. DOE, 1981a). Thus, there is clear potential for elevated activities in this waste. However, it is not possible to define a representative distribution of potential activities with available data because of the approach used to select sample locations. Some studies conducted initial surveys of the pits and tanks with hand-held instruments to guide sample collection toward areas of elevated activity, which may overestimate the prevalence of higher activities. For example, some samples from Louisiana reported by Fisher and Hammond (1994) have activities nearly two orders of magnitude higher than those measured in other states. Such high activities are theoretically possible and have been reported in pipe scale, but are unlikely to be as common as data from this study might suggest. Other studies may underestimate potential activities due to the small number of samples reported. For example, samples from California reported by CADHS/DC (1996) have lower activities than most other states. However, the same study identified much higher activities in both produced water and scale, which makes it likely that higher activities can also occur in sludge.

5.5.2. Leachate

The leachate data reported in the literature analyzed by TCLP (SW846 Method 1311). This single-point leaching test is intended to mimic acidic conditions that result from the decomposition of organic matter in a landfill. This scenario can result in high leachate concentrations both because the solubility of many constituents is highest at acidic pH and because strong acids can decompose mineral complexes that would otherwise hold the constituent mass in place (U.S. EPA, 2014c). As a result, these data have the potential to overestimate releases if wastes are managed under less extreme conditions. However, because this leachate test uses a fixed amount of buffer, wastes with high alkalinity may shift the final pH of the leachate closer to neutral. None of the available studies reported the final pH of the leachate. This is a major source of uncertainty for the available data because the solubility of some constituents can change dramatically over a small pH range. Thus, while available data provide useful information about the potential magnitude of releases, it is difficult to draw conclusions about potential releases.

Inorganic Elements

EPA identified four studies that measured inorganic elements in the leachate from sludge. These studies reported samples collected from at least five states, though the amount of data from each state is variable (API, 1987; U.S. EPA, 1987; 2000a; LADNR, 1999). LADNR (1999) and U.S. EPA (2000a) reported a considerable amount more data for one constituent (barium) than other studies collected from Louisiana and Pennsylvania, respectively. EPA did not identify information that could be used to further weight the data to obtain a more representative national distribution, such as the volume of waste generated in each state. Therefore, the data from each study was weighted equally. **Table 5-20** presents the 50th and 90th percentile of the available data for inorganic elements in leachate from sludge detected in at least half of samples.

Table 5-20. Inorganic Elements in TCLP Leachate from Sludge (mg/L)

Constituent	Vertical Well		
	n	50th	90th
Aluminum	7 / 8	0.40	6.1
Barium	320 / 376	1.4	7.7
Boron	10 / 11	1.1	3.6
Cobalt	3 / 4	0.02	0.04
Iron	11 / 11	25	120
Manganese	11 / 11	1.9	4.1
Nickel	4 / 6	0.05	0.47
Strontium	5 / 5	6.5	7.7
Vanadium	3 / 5	0.003	0.04

n – Detection Frequency

The elements detected with the greatest frequency tend to be those that are highly soluble (e.g., boron) or known to be deposited from produced water (e.g., barium, strontium). Most of these elements are the same as those commonly detected in the leachate from drilling solids. Although the remaining elements are non-detect in the majority of samples, this does not provide any indication that concentrations are low because many samples have high detection limits. Removal of these non-detect values would only bias the overall distribution higher. This results in uncertainty and makes it difficult to draw further conclusions about the overall distributions.

Organic Compounds

EPA identified four studies that measured inorganic elements in the leachate from sludge. These studies reported samples collected from at least five states, though the amount of data from each state is variable (API, 1987; U.S. EPA, 1987; 2000a; LADNR, 1999). LADNR (1999) and U.S. EPA (2000a) reported a considerable amount more data than other studies collected from Louisiana and Pennsylvania, respectively. EPA did not identify information that could be used to further weight the data to obtain a more representative national distribution, such as the volume of waste generated in each state. Therefore, the data from each study was weighted equally. **Table 5-21** presents the 50th and 90th percentile of the available data for organic compounds in leachate from sludge detected in at least half of samples.

Table 5-21. Organic Compounds in TCLP Leachate from Sludge (mg/L)

Constituent[1]	Vertical Wells		
	N	50th	90th
Benzene	254 / 390	0.18	14
Toluene	32 / 56	0.01	5.0
Xylene	39 / 51	0.04	1.8

n = Number of Samples Detected / Total

These data show substantial enrichment of organic compounds in sludge leachate is possible. This is reasonable given the elevated concentrations in the bulk sludge. However, because available samples are drawn primarily from two states, it is difficult to draw conclusions about the overall distribution of concentrations and how frequently higher concentrations will occur.

Radioisotopes

EPA identified several studies that measured radioisotopes in the leachate from sludge. However, most of the studies only discussed results graphically or qualitatively, preventing a reliable comparison of the data (Pardue and Guo, 1998; Phillips et al., 2001; U.S. DOE, 2004). One study reported data on ^{226}Ra leached from the sludge of two pits in Pennsylvania that stored produced water from horizontal wells (Zhang et al., 2015). This study reported leachate activities ranging between 98 and 378 pCi/L. One pit was sampled twice, with collection times set three years apart. The leachate from the two sampled sludges decreased somewhat from 378 to 268 pCi/L over three years, while the bulk activity of the sludge increased from 8.8 to 872 pCi/g. Over the same time, the barium content of the sludge increased substantially. This indicates that a majority of radium accumulated in the sludge is sequestered in barite. Zhang et al. (2015) suggests that the leachable radium is associated with carbonate minerals that form from reactions with atmospheric carbon dioxide. DOE (2004) reached a similar conclusion, noting that a greater fraction of radium was solubilized with nitric acid (HNO_3) from sludge than pure barite scale.

5.5.3. Air Emissions

Volatile organics and radon are the constituents most likely to be released from sludge into the surrounding air. EPA did not identify any studies that analyzed for volatile organics, but did identify one study that measured radon emanation. This study collected samples from Oklahoma (U.S. DOE, 1999b). **Table 5-22** presents the 50th and 90th percentile of the available data for radon emanation from sludge. As previously discussed for scale, values are commonly expressed as an emanation factor, which represent the unitless fraction of the radon released that is able to migrate out of the material and into the surrounding air. Emanation factors may be used together with the activity of radium present to estimate an overall emission rate.

Table 5-22. Radon Emanation from Sludge

Isotope	Emanation Fraction		
	n	50th	90th
Rn-222	8 / 8	0.110	0.181

n = Number of Samples Detected / Total

The limited number and geographic isolation of available samples may skew the overall distribution, though the direction and magnitude of any bias is unknown. The measurements from sludge all fall within the range reported for pipe scale, but are most similar to samples of disturbed scale. This is expected because the physical properties of sludge more closely resemble disturbed scale. Individual particles of barite and other minerals found in sludge are generally smaller and more brittle than intact scale that plates out on the surfaces of well tubing and other equipment (Rood et al., 1998). The higher ratio of surface area to volume of sludge provides more direct contact with the surrounding air, which increases the rate at which radon can escape.

5.5.4. Summary – Production Sludge

Available data show that production sludge can be generated wherever oil and gas operations occur. The primary source of constituent mass in the sludge appears to be deposition from produced water and other fluids that are handled along the production stream. Barite, similar to that found in pipe scale, can be a major component of the sludge. However, other settled solids such as returned fracturing sand, formation solids, and heavier hydrocarbons can also contribute mass. However, the composition of sludge can be highly variable and the lack of characterization data make it difficult to further refine distribution of constituent levels in this waste.

One source of uncertainty associated with the available data are the age of the samples. Zhang et al. (2015) found that radium activity in sludge sampled from a pit increased by two orders of magnitude over the span of three years. Much of the accumulation is attributed to chemical precipitation, as the activity of the produced water did not increase during this interval. This is important because the accumulation of sludge is a gradual process. Thus, grab samples collected at random points during the operational life of a pit or tank could significantly underestimate typical constituent levels in the sludge at the time of disposal.

Another source of uncertainty with the available data are the spatial variability of sludge within the pits and tanks. Solids suspended in produced water can settle out quickly once the velocity of the flow slows at an outfall to a pit or tank. This can result in hotspots of the constituents that concentrate in these solids. Some studies have reported higher levels of both total organic carbon and radium near the point of discharge into pits (Freeman and Deuel, 1984; Pardue and Guo, 1998). Concentrations can also vary based on which piece of equipment is sampled. Heavier solids and organics may settle out in equipment early in the production stream, while chemical precipitation may dominate deposition in pits and tanks used for water storage. Thus, grab samples from a single point in the production stream could underestimate or overestimate the overall constituent levels in the sludge sent for disposal.

5.6. Contaminated Soil and Sediment

Spills and other releases of wastes from exploration and production activities can result in the contamination of various environmental media (e.g., soil, surface water). EPA focused this discussion on soil and sediment because the constituents that precipitate out or adsorb to these media are the most likely to remain in place over time, which allows a more direct comparison of different samples. If undisturbed, contamination may remain in place for years. Constituents in ground and surface water are more mobile and have greater tendency to mix within the media. This makes it difficult to aggregate these data without additional information (e.g., the time elapsed since the release, the flow rate of the water body). Therefore, further discussion of ground and surface water was limited to identification of damage cases based on site-specific information in **Section 8 (Damage Cases)**.

5.6.1. Bulk Content

In total, EPA identified twelve studies that provided data from nine states. The majority of these studies analyzed for radioisotopes. A few also analyzed for other inorganic elements, but none reported data for organic compounds. Barium is the one inorganic element measured with any frequency in these studies. Therefore, EPA chose to present the data for barium and radium together for comparison and discussion. **Table 5-23** presents the 50th and 90th percentile of the available data for barium and radium in contaminated soil and sediment.

Table 5-23. Barium and Radium in Contaminated Media

State	Barium (mg/kg)			Radium 226 (pCi/g)			Radium 228 (pCi/g)		
	n	50th	90th	n	50th	90th	n	50th	90th
California	--	--		16 / 16	0.80	30.4	19 / 19	0.92	29
Illinois	14 / 14	1,320	66,400	24 / 24	8.4	403	21 / 24	3.2	48
Kentucky	17 / 17	3,820	131,242	92 / 92	12	904	79 / 86	2.9	63
Michigan	--	--		20 / 20	153	1,626	11 / 18	2.1	206
New York	--	--		16 / 16	1.1	4.2	16 / 16	1.4	2.9
North Dakota	--	--		23 / 23	0.76	5.4	22 / 22	0.77	8.3
Oklahoma	8 / 8	4,920	416,000	61 / 61	11	406	49 / 60	0.9	15.5
Texas	1 / 1	185,400		34 / 34	14	254	40 / 40	2.0	30
Wyoming	1 / 1	1,600		18 / 18	7.4	42.4	13 / 15	3.2	5.1

n = Number of Samples Detected / Total

The bulk content of contaminated soil has the potential to be one of the most variable wastes generated. This is because it is dependent not only on the initial composition of the waste, but also on the magnitude of the spill and the characteristics of the soil. Many studies collected grab samples around areas of known or suspected contamination based on visible cues (e.g., salt scar, stunted plant growth) or hand-held survey equipment (e.g., spectrometer). As a result, it is not known whether these samples are representative of the overall contamination at each site. Spills are rarely uniform and individual grab samples may capture isolated "hotspots" or miss the impacted area entirely. More comprehensive sample collection would be needed to define the full magnitude and extent of contamination. Yet the available data demonstrate the potential for high radioactivity in contaminated soil and sediment. Maps provided by some studies show that the extent of contamination extends several hundred square meters across multiple locations at each site (U.S. DOI, 1997b; Zielinksi et al., 2000).

Many of the available samples represent releases of sludge and scale, but some are attributed to releases of produced fluids based on the presence of nearby salt scars or waste management pits. To understand whether these different types of spills result in different types of contamination, EPA compared the available barium and radium concentrations in 25 samples. Several studies had reported the presence of barite in the soil and sediment samples (U.S. DOI, 1997a,b; Rajaretnam and Spitz, 1999; Zielinksi et al., 2000). This mineral is known to be present in sludge and scale, but might also precipitate independently from liquid waste. Alternately, the dissolved radium might adsorb directly to the soil independent of barium. The result of this comparison is shown in **Figure 5-9**. Sediment data were not included because the available studies used acid digestion to analyze samples, which can significantly underestimate total concentrations of barium in scale.

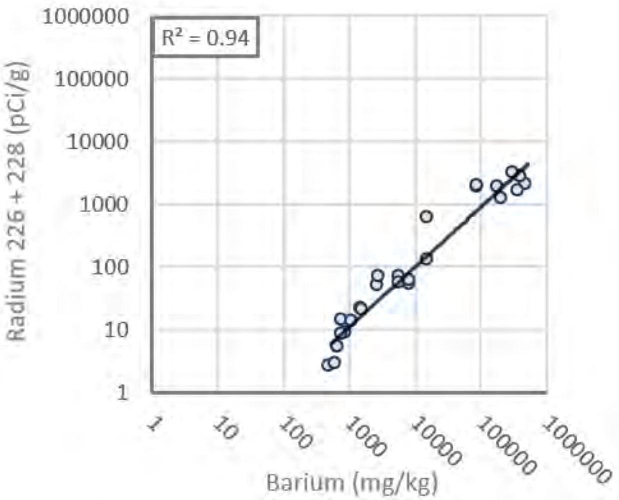

Figure 5-9: Relationship Between Barium and Radium in Contaminated Soil

This graph indicates that co-precipitation with barium is the dominant mechanism for the initial deposition of radium. It also indicates that radium and barium tend to precipitate at a predictable ratio. Previous studies have reported a fixed relationship between losses of barium and radium from solution (Gordon and Rowley, 1957; Zhang et al., 2014). If this relationship reflects a standard rate of radium incorporation, similar relationships would be expected in other precipitated waste (e.g., sludge, scale). Therefore, EPA added an additional 34 samples of other wastes drawn from eight studies to the same graph. The result of this comparison is shown in **Figure 5-10**. Only one study diverged significantly from the relationship identified for contaminated soil (Fisher and Hammond, 1994). Therefore, data are presented without (left) and with (right) the data from this study for comparison and discussion.

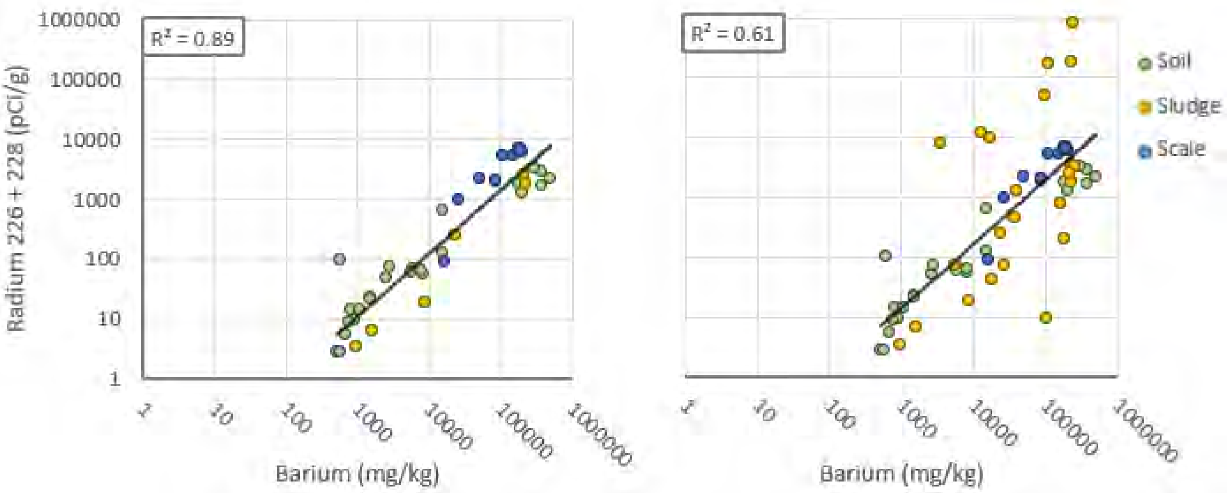

Figure 5-10: Relationship Between Barium and Radium in Different Deposited Wastes

About half the data reported by Fisher and Hammond (1994) agree well with those from other studies. The other half tend to have higher activities than predicted by the other studies, though a similar trend is present with increasing barium. The authors recognized this difference and noted that samples where the barite had deposited as a thin film on the surface of other solids typically had higher activities than those where scale precipitated independently. The authors speculated that higher levels were a result of faster and less-selective precipitation. Fast precipitation can result from changes in temperature and pressure as produced water is transported to the ground surface. This could mean that sludge deposited early in the production stream may have a higher ratio of radium to barium. This would align with the previous finding that the tanks closest to the wellhead tend to have higher total radium activity (U.S. EPA, 1993).

5.6.2. Leachate

EPA identified three studies that analyzed leachate from contaminated soil or sediment. The activities measured in these studies are variable and reflect different wastes that had been mixed with different media. In addition, each study used a different leaching test to estimate potential releases. As a result, the available data are not directly comparable and each study is discussed separately:

- Wilson and Scott (1992) collected three soil samples from around a former pipe cleaning operation in Louisiana. Soil samples had an average activity of 1,485 pCi/g ^{226}Ra. Leachate samples were collected in accordance with EPA Method 1310B (Extraction Procedure Toxicity Test). The study reported leachate activities as the activity in the total volume of fluid, which converted to 3.5 and 5.6 pCi/L. The third sample was non-detect and the detection limit was not reported.

- Pardue and Guo (1998) collected one sample of surface sediment from a water body in Louisiana located downgradient from a pit that held produced water. The sample had an activity of 581 pCi/g ^{226}Ra. The sample was incubated for two months after adjusting the redox conditions to +600 mV (surficial aerobic sediment) and -250 mV (buried reducing sediment), though it was not specified how this adjustment was achieved. The resulting pore water was separated through centrifuge and measured. The study reported pore water activities per gram of sediment, which converted to 49 and 85 pCi/L ^{226}Ra, respectively.

- Rajaretnam and Spitz (1999) collected soil samples from an abandoned drilling site located on a Kentucky farm. The tank batteries on this site contained brine, sludge and other wastes. Two soil samples had an average activity of 880 pCi/g ^{226}Ra. Leachate tests were conducted based on ASTM D5284-93 (sequential batch extraction) with modified extraction fluids containing HCl, NaCl, or Na_2S intended to mimic acid rain, high-salinity produced water, or anaerobic conditions. The study reported releases around 1% of the total mass in the soil samples regardless of the extraction fluid used, which converted to approximately 570 pCi/L. Dissolved activity was similar for both extraction cycles.

Several studies have reported that bacteria have the ability to reduce barite and liberate barium and radium. Some of the same studies also reported a stoichiometric imbalance between the amount of sulfate and barium released into solution following incubation with these bacteria. This imbalance was attributed to either re-precipitation of barium as barium carbonate (witherite; $BaCO_3$) or sorption onto the soil (Phillips et al., 2001; U.S. DOE, 2004). This cycle of dissolution and precipitation in response to changing redox conditions mirrors what is known about barium chemistry during shale formation. It is possible that radium will follow a similar cycle and either re-precipitate with barium or sorb to the soil, which would limit transport away from the point of release. Therefore, the composition of the soil could impact the degree to which radium is retained (IAEA, 2014). Landa and Reid (1982) found that the clay fraction of sediment that had received produced water discharge contained 50% of the radium mass, even though it comprised only 19% of the sediment. Any constituent mass that is adsorbed onto the soil or bound in carbonate complexes is likely to be mobilized more readily than from the original scale.

5.6.3. Air Emissions

Volatile organics and radon are the constituents most likely to be released from contaminated soil and sediment into the surrounding air. EPA did not identify any studies that analyzed for volatile organics, but identified one study that analyzed for radon. As discussed previously, values are commonly expressed as an emanation factor, which represent the fraction of the radon released that is able to migrate out of the material and into the surrounding air. Emanation factors can be used together with the activity of radium present to estimate an overall emission rate. EPA identified a single study that analyzed samples collected from Illinois, Kentucky, Michigan, Oklahoma and Wyoming (U.S. DOE, 1999b). Because the emanation fraction is not a function of activity, EPA combined data from the different states into a single distribution. The ranges reported for each state are similar, which provides additional confidence that these data are representative of potential releases. **Table 5-24** presents the 50th and 90th percentile of the available data for radon emanation from contaminated soil and sediment.

Table 5-24. Radon Emanation from Contaminated Media

Isotope	Emanation Fraction		
	N	50th	90th
Rn-222	65 / 65	0.139	0.243

n = Number of Samples Detected / Total

Emanation fractions measured from contaminated soil all fall within the range reported for disturbed scale. This is expected because many of the samples are mixed with disturbed scale or sludge. Samples with contaminants adsorbed to the surface are expected to release radon at comparable rates because the radium is contained primarily on the surface of the material, which provides more direct contact with the surrounding air. Previous studies of emanation fractions from natural soil reported a similar range of emanation rates (IAEA, 2013). However, releases from soil and sediment may differ in the environment because saturation with water can inhibit releases of radon and other gases.

5.6.4. Summary – Contaminated Soil and Sediment

Each of the wastes discussed in this document (i.e., spent drilling fluid, drilling cuttings or solids, produced water, sludge, scale) have the potential to introduce contaminants into the environment. Reports from Colorado, New Mexico, Oklahoma and Pennsylvania indicate that the most common releases reported to these states are from produced water and drilling fluid (Kuwayama et al., 2017). Few reports were found for releases of sludge, scale and other solids. However, a number of samples reported in the literature are attributed to these wastes. Samples collected in Illinois, Kentucky, Michigan, Oklahoma and Wyoming all identified elevated levels of radium activity in soil attributable to historical contamination. It was estimated that, at the time of sampling, contamination had been present at several of these sites for 30 years or more. The available data show that there are similar concentrations in wastes generated today and so similar potential for contamination exists.

The comparison of barium and radium in contaminated soil indicates there is a consistent relationship between the two precipitated elements. The presence of a predictable ratio indicates that the activity in sludge and scale will be proportional to the amount of barite present in these wastes. With further investigation, it might be possible to use the relationship between barium and radium to attribute historical contamination of unknown origin to spills of exploration and production wastes. Spills are most likely to occur near where the waste is produced (e.g., wellhead) or stored (e.g., reserve pit, tank battery) as a result of equipment failure or human error. As a result, proximity to equipment can be a useful criterion to locate historical spills along with other visual cues (e.g., salt scars). However, samples collected near the point of release will be biased toward contaminants that precipitate out of solution and remain insoluble. Some of the constituent mass may remain in solution because of the high ionic strength of produced fluids and be transported some distance downgradient before settling out. It will be considerably more difficult to locate and attribute this dispersed contamination.

5.7. Conclusions

Both hydraulic fracturing and directional drilling have the potential to impact the composition of E&P wastes. This review shows that there can be orders-of-magnitude variability in the composition of each waste type, though trends are apparent for certain constituents that might be used to predict where elevated constituent levels are more likely to occur. Some inorganic elements (e.g., lithium, molybdenum), organic compounds (e.g., benzene) and radioisotopes (e.g., radium) appear to be correlated with either the organic carbon content of the source rock or the salinity of the formation water. Horizontal wells are frequently drilled a greater distance through high-organic rocks with saline formation water and so higher constituent levels may be more common in the wastes from these wells, but similar orders-of-magnitude levels may also occur in the wastes from vertical wells. Therefore, it is likely that similar regulatory controls would be appropriate for the wastes from both types of wells.

This review focused on publicly-available sources of data. There appears to be a substantial amount of additional data that is not in the public domain. Some studies make reference to databases, which EPA was not able to locate (Dingman and Angino, 1968; Rittenhouse et al., 1968; Collins 1969; U.S. DOE, 1991; Hitchon et al., 2000; U.S. DOE, 2004). Other studies provide summary statistics or qualitative discussion, but not the underlying data. It is often unclear how much data are contained in each database or study. However, the majority of these sources address produced water, which is already the waste with the greatest amount of data available. Therefore, further efforts to assemble existing data are unlikely to substantially improve the characterization of constituent levels (i.e., concentration and activity) present in and released from other wastes.

The majority of available data reflect wastes as generated. However, wastes may then be intermingled with other wastes during storage or treated in preparation for disposal. Limited information is available about the impact that these management practices have on the composition and behavior of the wastes. Available data indicate that certain practices can increase the bulk concentration of some constituents, though the exact cause is not always clear. As a result, an evaluation of potential environmental impacts based on the wastes as generated could underestimate releases to the environment. Further sample collection and analysis would be needed to characterize potential releases to the environment during storage and subsequent disposal of E&P wastes.

There are limited data available on the magnitude of releases through leaching or volatilization for any waste type. The data that are available reflect an assortment of analytical methods that capture different environmental conditions and cannot be reliably aggregated into a single dataset. Although more data are available on the bulk concentrations in these wastes, that alone is not a reliable indicator of how much mass can be released into the environment, particularly for wastes with recalcitrant mass. Further sample collection and analysis would be needed to fully characterize potential releases to the environment during storage and subsequent disposal of E&P wastes.

Despite the various sources of uncertainty, the available data provide an estimate of constituent levels that can be used to determine which constituents are most likely to concentrate in each waste. Taken together with relationships identified among different waste types and different constituents, the data can also estimate where elevated concentrations are more likely to occur. High-organic-content rocks and high-salinity water are well correlated with elevated levels of inorganic and organic constituents and are defining features of hydrocarbon-bearing formations. As a result, elevated constituent levels are unlikely to be geographically isolated.

6. State Programs

States have the primary authority over the disposal of non-hazardous waste within their boundaries. Therefore, it is critical to understand how the different state programs are implemented for E&P wastes. The scope and specificity of state programs is variable. State programs vary, both among states and different regions of a state, to account for regional factors (e.g., formation type, meteorology) that impact the types of waste generated and the appropriate methods to manage those wastes. EPA has previously reviewed state programs, both as part of the 1987 Report to Congress and a more recent effort in 2014 (See **Section 2: Summary of Agency Actions**). However, state programs have continued to evolve to address emerging issues from hydraulic fracturing and other technological advances. Therefore, EPA conducted an updated review to better understand how state regulations currently address E&P waste management and to highlight inconsistencies, lack of specificity, or possible gaps in coverage.

6.1. Methodology

EPA evaluated the state regulations for 28 of the 34 oil and gas producing states, which represent more than 99% of the annual U.S oil and gas production by volume, according to U.S. Energy Information Agency data (U.S. DOE, 2018c,d).[17] The six states with the lowest overall production were not included in this review (i.e., Alabama, Arizona, Maryland, Nebraska, Oregon, South Dakota). For each state, the latest version of E&P regulations were obtained electronically from the source identified on the state oil and gas agency website at the time of the review (February through December 2018). In some cases, such as California and Pennsylvania, the statute or enacting legislation was also obtained because it provided additional clarifying information on the waste requirements. Solid waste and radiation protection regulations were obtained in a similar manner. In addition, readily obtainable guidance and policy documents related to E&P waste were obtained from state agency websites. The review of guidance and other policy documents is unlikely to be as comprehensive as the review of applicable regulations because the Agency cannot guarantee that every potentially relevant document was identified. This review did not evaluate regional or field-specific requirements promulgated by state oil and gas boards. These special rules, often called “Orders” or “Special Field Rules,” may contain additional more stringent requirements for managing wastes and are unlikely to be less stringent than state regulations. Likewise, some counties, notably in Colorado and California, may place additional controls on oil and gas operators that are more stringent than state regulations.

Disposal of RCRA-exempt wastes in Class II injection wells is allowed by permit in most states, and the associated regulatory program may fall under either the oil and gas agency or the environmental

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17) This review of regulations did not include tribal regulations applicable in Indian country, because EPA was unable to conduct a similar review of tribal programs as many do not have the solid waste regulations compiled in a readily searchable online format. Generally, state laws do not apply in Indian country. The amount of tribal land varies across the United States but a majority is concentrated in EPA Regions 8, 9 and 10. EPA is fully aware that oil and gas exploration, development, and production operations take place in these areas, and so will continue to look at regulatory and program management responsibilities in tribal lands specific to managing wastes from these activities.

agency. Several states specifically exempt underground injection control (UIC) disposal facilities, including the pits and tanks associated with these facilities, from the E&P regulations because they are covered under UIC facility rules. While UIC pits and tanks do not fall under E&P regulations in these states, EPA considers them waste management units. However, a comprehensive evaluation of state UIC regulations was outside the scope of this review.

The first step in the review was development of an inventory of potentially applicable state regulations. Oil and gas, solid waste, and radiation protection regulations for each state were reviewed and the regulatory language related to 61 specific technical elements organized into 12 general topic areas were captured verbatim and documented in a spreadsheet (**Appendix C: State Programs**). This spreadsheet reflects the initial capture of regulations potentially applicable to the review. The inventory also included capturing the potentially applicable definitions associated with the regulations, dates of the regulation or subsequent updates (where available) and a link to the original document.

6.2. Uncertainties

EPA used the information compiled in the detailed spreadsheet to review state regulatory programs. These programs were found to vary not only in scope and specificity, but also in the language used to define different wastes and the relevant controls. This variability resulted in uncertainties when defining the regulatory coverage of some states. The following text provides an overview of how the Agency considered and addressed the major sources of uncertainty identified during the review to ensure that it was as complete and consistent as possible.

Specificity: The specificity of state regulations differ for a range of topics, such as signage; groundwater monitoring; financial security; setbacks and location restrictions; run-on/runoff controls; inspections; spill notifications and corrective action. These regulations may specify controls for the individual well, the associated waste management units (e.g., pits, landfills), or site-wide. For record-keeping purposes, any of these requirements were considered evidence that regulatory controls are in place. Many states also include general statements that E&P operations shall not cause pollution to the land, water or air and shall not adversely affect environmental resources. These statements were sometimes part of the definition of "waste" or were stand-alone requirements in various parts of the regulations. States may have great flexibility in interpretation of such requirements, but EPA considered these general requirements to be too broad to address the specific protections for floodplains, endangered species, surface water and groundwater found in 40 CFR 257.3. Therefore, states that only include general protection requirements were listed as not having coverage with respect to 40 CFR 257.3.

Not Allowed versus Not Addressed: EPA did not identify regulations or guidance from certain states for some practices, such as land application, beneficial use, offsite landfills or commercial facilities. In these cases, it was not clear based on the regulatory text whether the practice is prohibited in the state or unaddressed because it is not known to occur in that state. State agencies may have internal policy or case history that provide further guidance for these subjects. However, such documents are difficult to obtain and so these regulations are considered ambiguous. For these situations this review generally considered the practice to not be allowed (for counting purposes), but noted that it could be allowed and controlled on a case-specific basis. In some cases, the practice was mentioned in other parts of the regulation but with unspecified controls, and so the practice was assumed to be allowed.

Specific Requirements versus Supervisor/Agency Approval: Each state had a different approach to the content and level of direction in regulations for E&P wastes. Common approaches included:

- Prescriptive set of rules and regulations with specific technical requirements across many areas that must be followed to receive permit approval or comply with permit by rule (common for high production states)
- General or performance-based requirements that operators must incorporate into planning documents and application submittals that are reviewed and approved by the agency
- Agency defined requirements on a site-specific basis (common for low production states)

Where states provided performance-based requirements, such as "pit and tank bottoms must be impermeable" or "tank construction shall be compatible with waste and not leak," the review considered there to be controls in place for record-keeping purposes.

Deviations Allowed: Many states allow deviations to rules or specifications "with approval of the supervisor or director." Allowance for modification beyond the written regulations can provide state programs with flexibility to address the rapidly changing technology in E&P production and the variability of site-specific conditions. For example, many pit liner regulations specify a material type or minimum thickness but allow the operator to propose an alternative, to be approved by the director. Because there is a specific requirement in place, this review considered the element to be incorporated in the state program and that the deviation did not alter protectiveness specified by the regulation.

Level of Detail: States develop and revise regulations based on the conditions, practices and experiences within the state so it is not surprising that not all states address all topics with the same level of detail. However, it presents a challenge in comparing the comprehensiveness of regulation across states because EPA cannot be as familiar with which specific operations occur in each state. For example, pit definitions and the associated regulations in some states may address only a few types of pits and do not address certain other types. In other states, there are separate detailed requirements for each pit type. In this review for each pit element (e.g., permits, liners, fencing, netting, groundwater monitoring, leak detection), the presence of any topical regulation, regardless of the type of pit, was considered evidence that regulatory controls are in place. For example, if a state defines five types of pits and provides liner requirements for only one, this review concluded that the state did provide regulation on pit liners. Where possible, the state overviews identified the limitations of coverage or missing details.

Definitions and Terms: The review identified several challenges with the definitions and terms used in the regulations. A common challenge was the use of ambiguous or undefined terms. For example, many states require waste to be disposed at an "authorized facility" but do not provide a definition or further details on the specific types of facilities that might be authorized to accept the waste. Other terms such as "significant," or "appropriate," or phrases such as "earthen pit," and "above the water table" were ambiguous and the level of protectiveness could not be identified but were still considered to provide regulatory control. As discussed above, definitions for pits are variable among states. Some states define pits by function (e.g., collection pit, reserve pit, emergency pit), and other states define pits by length of service (e.g., temporary pit, permanent pit) or content (e.g., freshwater pits, high chloride pits). Many states use a combination of classifications. Other reviews of E&P regulations note the same issue of inconsistent nomenclature for pits. STRONGER recognized this issue and provided guidance for consistent nomenclature in their 2017 Guidelines (STRONGER, 2017).

Definitions for a specific term can vary among states. Across the states several terms are used to describe the non-salable liquids generated by producing oil and gas wells: brine, salt water, produced water and produced fluids. The discussions in this summary use the terminology defined by the state when discussing specific examples. The term "brine" is used when a specific state regulation is not being referenced. The review noted many other examples of multiple terms for the same concept. Conversely the review identified some terms that were defined differently by different states. The term waste, as defined in most state regulations, has a dual meaning. In addition to the traditional definition (byproduct or unusable material), it refers to the inefficient production of oil and/or gas such that the resource is lost or not recoverable. Unless otherwise specified, the traditional meaning is implied here. Definitions were used to support the evaluation of the level of detail and the coverage of state regulations. States with many definitions that included technical terms and subdivision of waste unit type (i.e. multiple pits or tank types) were deemed to be more comprehensive because they addressed a wider range of potential risks.

Complexity of Regulations: E&P regulations cover many different technical areas and processes and are necessarily complex. Some state regulations were organized and presented in a centralized and comprehensive manner making it clear what was required and what was prohibited. For example, Oklahoma provided a list of E&P wastes, and a corresponding list of the acceptable disposal methods for each of the wastes. Some state regulations were complex and difficult to navigate because several different agencies had jurisdiction over different parts of the regulations. For example, The California Department of Conservation, Division of Oil, Gas and Geothermal Resources regulates oil and natural gas production in the state. The California Environmental Protection Agency has several departments, such as the Department of Toxic Substances Control, the State Water Resources Control Board and the nine Regional Water Quality Control Boards, and California Integrated Waste Management Board, all of which may be involved in the permitting process for oil and gas operations.

6.3. Analysis of Specific Elements Across States

EPA organized the review of state programs into 12 topic areas, which are further divided into 61 sub-elements. These elements were selected based on a review of elements incorporated for similar waste management units. For each state, an initial binary (yes/no) determination of whether regulations were in place for each of the 61 elements was assigned using the approach described above, supplemented by a second focused review of the regulatory text. The following discussion provides a summary of state programs organized around some of these topic areas. More comprehensive summaries for all topics on a state-by-state basis and the spreadsheet used to document the regulatory text that formed the basis for this review are provided in **Appendix C (State Programs)**. Specific examples provided in this summary are generally intended to demonstrate the range of requirements among different states and should not be interpreted to be representative of states not listed.

6.3.1. Waste Management Location Requirements (Siting and Setbacks)

All states in this review except Missouri and Florida provide some form of location and siting requirements to address where oil and gas operations and associated waste management activities can be located. Siting requirements can be found in either the oil and gas rules or the solid waste rules depending on the nature of the waste operation (onsite versus offsite; temporary use versus permanent disposal). This review included review of state regulations only. Some counties and municipalities may have specific rules for oil and gas setbacks. Siting regulations can be found as broad general overarching requirements, or more commonly as dispersed rules associated with the construction or operation of specific waste units such as pits or tanks. Requirements commonly include setback distances from human and environmental resources including residences, schools, inhabited structures, roads, wetlands, floodplains, groundwater and wildlife habitats. At least five states (e.g., Alaska, Nevada, New Mexico, North Dakota, Utah) also consider seismicity and land stability conditions in siting for landfills or salt water treatment facilities that accept E&P wastes. Alaska also includes permafrost and ground thawing as site conditions to be considered in siting and design of drilling waste monofills. Texas, which accounts for the largest contribution to oil and gas production and number of wells drilled per year, does not have state-wide setback rules for E&P waste, and allows communities to set siting requirements.

Applicability: Most rules focus on the siting of pits and tanks located onsite (within the well pad area) and only a few states discuss siting requirements for offsite commercial and centralized facilities for treating, recycling or reclaiming E&P wastes. Texas and Oklahoma have extensive sections in their regulations addressing siting criteria for offsite commercial and centralized facilities. North Dakota provides siting, construction and operation requirements for salt water handling facilities, which may be located onsite or offsite. Some states do not have siting requirements for drilling, completion and production pits or brine holding tanks because they are considered part of the drilling site/pad and proposed locations are included in the drilling permit application (APD) that is approved by the state. The APD form may include information on pit construction and location. Some states, including Colorado and Michigan have requirements for both the general well facility, and waste unit (pits) setbacks from environmental features such as groundwater or floodplains.

Location and Siting Requirements: A direct comparison if location and siting requirements in different states is challenging because the coverage of waste operations varies among the states. Some states regulate siting based on the type of waste managed. Pits containing completion fluids and flowback water may have more stringent setback requirements than reserve pits and others only address specific situations (e.g., emergency pits). For example, the setback requirement from a continuously flowing watercourse in New Mexico ranges from 100 ft (temporary pits with low chloride fluids) to 300 ft (permanent pits and temporary pits with higher chloride fluids). Arkansas has residential and environmental receptor setbacks for crude oil tank batteries and gas well produced fluids storage tanks but minimum groundwater depth is not specified for all mud, circulation or reserve pits. Several states (e.g., Colorado, Louisiana; Haynesville shale areas only, Ohio) provide different setbacks for urban and non-urbanized areas, as defined by the state. Three states (i.e., Florida, Missouri, Montana) do not provide residential, environmental or depth to groundwater setback distances for E&P wastes and allow the operator to propose locations and provide the distance to lease lines, water resources, buildings and water supplies to be approved by the agency. Michigan requires an environmental assessment of the site including identification of more than a dozen special hazards and conditions within 1,320 feet of the surface facility as part of the well permit process.

Most states have a general rule that prohibits the siting of a well or waste management unit (specifically pits, tanks or landfarms) in a location that could allow pollution or damage to environmental resources. Solid waste requirements for siting landfills that accept E&P wastes may have more stringent requirements. All states with location or siting requirements have rules for siting wells or waste operations near floodplains or surface water resources, however, the definitions of the resources differ. For example, New Mexico and Pennsylvania provide a list of specific types of water bodies and environments for setbacks but many other states only reference setback from the 100-year floodplain. In Arkansas, a closed loop system is required for oil-based drilling fluid pits, mud pits or circulation pits within 100 feet of a pond, lake, stream, extraordinary resource waters, ecologically sensitive water bodies, or natural and scenic waterways. Of the 28 states in the review, only Colorado addressed siting related to endangered species in E&P regulations. Nine states included endangered species in landfill requirements applicable to E&P wastes. Tank battery siting is often included as part of the general well permit, but Arkansas and Idaho have specific setback rules for crude oil and brine tanks. **Table 6-1** provides a summary of state requirements for location restrictions and setback distance.

Table 6-1. Summary of Required Setback Distances in Select States.

Resource	Number of States with Specific Setback Distances	Setback Requirement (Lower Bound)	Setback Requirement (Upper Bound)
Residences/Inhabited Structures	17	100 ft (OH)	1,000 ft (CO, NM) 1 mile (UT)
Floodplains/Surface Water Resources	24	50 ft (OH)	1,500 ft from groundwater intake (IL)
Groundwater	12	20 in below seasonal high groundwater table (9 states)	50 ft below the base of waste (UT)

Siting and location of landfills permitted for disposal of E&P waste are generally regulated by the state solid waste agency. As noted before, the states classify exempt E&P wastes in a variety of ways (solid waste, non-hazardous waste, special waste, and industrial waste), each with different rules for landfill siting and location. Because of the long-term nature of disposal in landfills, solid waste landfill siting rules generally provide more stringent requirements and specificity in guidance for siting and location than oil and gas rules. For example, Class 1 solid waste landfills in Nevada may not be sited where groundwater is less than 100 feet below ground surface, which is more than twice the distance of the most stringent E&P waste rule identified in this study. Similarly, states with rules for commercial operations for recycling or reclaiming oil, or disposal of brine tend to provide detailed siting requirements. Texas, for example, does not allow commercial recycling facilities in the 100-year flood plain, in a streambed, or in a sensitive area (as defined in regulations), and has a setback distance of 150 feet from surface water and supply wells. When reviewing applications for siting a commercial recycling facility, Texas considers waste type and volume, distance to residences and receptors such as wetlands, surface water, coastal resources, groundwater, and water supplies.

6.3.2. Tank Requirements (Onsite/On-Lease)

Tank requirements may apply to one or more types of tanks (e.g., drilling fluid, produced water, oil). In some states, regulations for E&P waste tanks are incorporated in the above ground storage tank regulations. Regulations typically address the tank construction materials, secondary containment, and fluid/waste management practices. For this review, it was assumed that tanks holding crude oil can accumulate waste solids and so are considered potential waste management units.

Tank Berms and Containment Specifications: Approximately 74% of states reviewed (18 of 28) have some requirements for tank berms or secondary containment. Some states require secondary containment for all tanks, while others have certain criteria. For example, in North Dakota, dikes for produced water tanks and berms at salt water handling facilities are required when deemed necessary by the director. In Colorado, secondary containment is required for "all tanks containing oil, condensate, or produced water with greater than 3,500 milligrams per liter (mg/L) TDS (not including water tanks with a capacity of less than 50 barrels) and must be constructed of steel rings or another engineered technology." Nevada regulations state that "dikes or fire walls are required around permanent tanks for the storage of oil located within the corporate limits of any city or town, where tanks for storage are less than 500 feet from any highway or inhabited dwelling, less than 1,000 feet from any school or church or are so located as to be deemed by the Division to be a hazard."

Half of the states with berm requirements (9) provide a specific capacity for the secondary containment with most of them being 1½ times (or 150%) the size of the tank. Florida specifies two times the tank capacity, and New York regulations state that secondary containment must be able "to contain 110 percent of the volume of either the largest tank within the containment system or the total volume of all interconnected tanks, whichever is greater." While the size and dimensions are not specified for any state, Utah regulations indicate "berms of sufficient height and width to contain the quantity" and Colorado regulations indicate the secondary containment "shall be sufficient to contain the contents of the largest single tank and sufficient freeboard to contain precipitation." Regulations for five states (i.e., Colorado, Florida, Mississippi, North Dakota, West Virginia) indicate secondary containment must be impermeable or sufficiently impervious, while Idaho is the only state that provides a specific permeability value (1×10^{-9} cm/sec). In Colorado, operators are also subject to tank and containment requirements under Rules 603 and 604 (safety regulations for location and siting facilities and wells). Two states (Pennsylvania and Wyoming) refer to requirements under 40 CFR Part 112 (Spill

Prevention Control and Countermeasure Plans). Several states address construction and design requirements for piping that penetrates the dike, and the maintenance of the berm and bermed area.

Tank Construction Material Requirements: Some requirements for tank construction are provided in regulations for 11 of 28 states reviewed. These states include general requirements indicating that tanks must be impermeable (i.e., Pennsylvania), constructed with compatible materials (i.e., Illinois, New Mexico, New York, North Dakota), and properly designed/constructed to contain liquids or minimize pollution (i.e., Colorado, Oklahoma, Virginia). Alaska regulations refer to API standards for tank construction, and Ohio regulations indicate that only steel tanks are allowed for burial. Colorado requires a synthetic liner under the entire bermed tank area and compliance with National Fire Protection Association (NFPA) Code 30 for tank construction.

Netting for Open Tanks: Six states require netting for open tanks to protect birds and other wildlife from contacting possible hazardous fluids in open tanks and other open storage vessels (i.e., Arkansas, Illinois, Indiana, Montana, New Mexico, Texas). Oklahoma requires protection for migratory birds but does not make specific mention of netting.

Modular Large Volume Tanks (MLVTs): These temporary tanks are constructed from modular components and used to hold large volumes of water for drilling, completion and production. The figures below are examples of MLVTs used for oil and gas operations. MLVTs are only addressed in regulations for two states. In Pennsylvania, modular aboveground storage structures that exceed 20,000 gallons require prior approval. Siting approval is required for site-specific installation of these modular structures at each well site. North Dakota regulations "allow portable-collapsible receptacles used solely for storage of fluids used in completion and well servicing operations, although no flowback fluids may be allowed." MLVTs must utilize a sealed inner bladder and conform to API construction and installation standards. Tanks must have signage on all sides clearly identifying the fluid within.

Tank Monitoring Requirements: Tank monitoring was found to be required in only a few state regulations. In Florida, "all tanks shall be installed, maintained, pressure tested, and protected against corrosion in accordance with generally accepted petroleum industry standards and practices." Additionally, "tanks containing sour fluids shall be equipped so they can be gauged, sampled and the temperature measured at ground level." Alaska regulations for crude oil tanks require an external method of leak detection and inspections after a significant seismic event, however it is unclear if these regulations apply to E&P waste fluids stored in tanks. Virginia and New York both require tank inspections. Several states require high level alarm and automatic shutoff systems on tank batteries to prevent overflows. Tank inspection requirements are quite variable. Many states do not specify inspections but require tanks to be maintained fluid tight or without leakage. Other states allow self-inspections (including visual observations of bermed areas and sumps) or require prescribed inspections annually (Virginia) or up to every 10 years (Alaska).

Tank Solids Removal: Tank operation and management may include removal of solids (and any intermingled fluids) that accumulate in the bottom of crude oil and salt water tanks. Four states require permits for tank bottom removal (i.e., Kentucky, North Dakota, Pennsylvania, Texas). Although other states may not require permits for tank bottom removal, some do provide procedures for managing tank bottom wastes. In Illinois, a permit is not required but approval may be needed for some non-regulated disposal options. Oklahoma requires permits for commercial tank bottom reclamation facilities. In Colorado, tank bottom removal does not require a permit, but the disposal facility must be permitted. Wyoming regulations indicate "dispose of produced water, tank bottoms, and other miscellaneous solid waste in a manner which is in compliance with the Commission's rules and other state, federal, or local regulations." Regulations for managing tank bottoms are often included in disposal requirements such as beneficial use, land application, and commercial reclamation/recycling. In Kentucky, recycling of tank bottoms is encouraged as a best management practice.

6.3.3. Pit Construction and Operation Requirements

Pits may be used at any stage of E&P operations (e.g., drilling, completion, workover, production). A wide range of both fluids and solids can be stored in pits. All 28 states in this review regulated the construction or operation of pits in some manner. However, one state, Missouri, does not provide technical requirements for pits for any of the topic areas discussed below. Most states have developed regulations based on some type of classification, generally based on the intended use for the pit and/or the type of materials held in the pit. These classifications reflect the anticipated level of risk from use of pits over time. For example, pits used to hold produced water have a higher potential for risk than those that hold fresh water and so may have more stringent design requirements. Additionally, some states classify pits based on their expected time of use (temporary or permanent). Production pits holding brine over long periods of time are generally considered to represent a higher risk of release than pits used during the much shorter drilling process.

Pit Types: The number of types of pits defined in the regulations varies considerably among the states reviewed. At one extreme, Texas regulations describe more than 15 different types of pits using both pit names or pit function. At the other, New York and Pennsylvania only identifies a single category of "brine pits" in the regulations. The different approaches used to define pits makes comparison and analysis of regulations difficult. Because most state E&P regulations are organized by process (e.g., permitting, drilling, production), pit regulations are often dispersed throughout the rules. Many states regulate pits based on the general stage of the process (e.g., drilling, production, disposal). Within these categories there are often further subdivisions that reflect the specific use (e.g., reserve pit, circulating pit, skimming pit, flare pit) or pit contents (e.g., fresh water, drilling fluids, produced water). Some pit types, including emergency pits, burn pits, gas processing plant blowdown pits and centralized or multi-well pits do not fit directly under these categories and are often addressed separately. EPA also identified structures in some state regulations referred to as "impoundments." In West Virginia, an "impoundment" only refers to earthen structures for fresh water. In Alaska, New Mexico and Ohio, an "impoundment" may be lined and hold waste materials. In some states, impoundments greater than a certain size are regulated and permitted as dams.

Many states have revised pit and drilling regulations since 2011 and specifically address existing pits that do not conform with the updated regulations. Generally, non-conforming pits must be closed within 3 to 12 months, brought into conformance, or receive approval for continued use by the state agency. A few states have addressed historical pits ("inactive pits") that may not have been constructed, operated or closed in accordance with current rules, and either provide regulations for inventory of such pits (e.g., Indiana) or a program to address remediation of these pits. The assessment and remediation programs are generally under the direction of the state environmental agency.

Commercial Pits and Centralized Pits: Some states with significant oil and gas production, such as Texas, Oklahoma, Wyoming and New Mexico, have separate regulations that cover commercial E&P waste management facilities. In 6 of the 28 states reviewed, centralized pits used to support multiple wells are regulated separately from individual well site pits primarily because of their large volume and unique design considerations (i.e., Colorado, Pennsylvania, New Mexico, Oklahoma, West Virginia, Wyoming). Centralized pits associated with disposal wells are not consistently addressed in the pit rules in all states. Although Class II disposal wells are regulated under the Safe Drinking Water Act's UIC program, the aboveground pits and other waste management units are not. Oklahoma includes detailed specifications for surface facilities (pits) associated with commercial injection wells, but most other states do not specifically address the subject or make a distinction between salt water holding pits and pits associated with permitted disposal wells.

Prohibited Pits: Almost half the states reviewed (13 of 28) identified specific types of pits that are prohibited; however, no state prohibits pits entirely. Many states include a general prohibition on pits that would cause pollution or release to the environment. The most common prohibitions on specific types of pits are those that contain a specific type of waste (e.g., oil, brine, salt cuttings), that are unlined (sometimes called "earthen"), are permanent (i.e., present longer than a specified duration), and unpermitted. Other specific prohibitions include those constructed on fill material, those associated with particular well types, that are in areas that are hydraulically linked to groundwater or surface water, and that are within a certain distance of specific zones, such as residential areas.

Permits: Permits are required for pits in 16 of the 28 states reviewed; however, in some states permits are only required for certain types of pits. For example, only commercial brine pits in Texas and pits holding greater than 5,000 barrels of fluid in Virginia require permits. In many of the states where a specific pit permit is not required, the pit is permitted as part of the APD or covered as permit by rule. In New York and Alaska, permits are not required but a management plan for drilling fluids (including pit information) is required as part of the well APD permitting process.

Freeboard: Most of the states reviewed (20 of 28) include some requirement for maintaining adequate freeboard. Sixteen of the 20 states include specific requirements, which typically range from 1 to 3 feet. Some states have different freeboard requirements based on various pit types. For instance, Kansas provides different values: drilling, work-over, burn and containment pits have a minimum freeboard of 12 inches, while emergency and settling pits have a minimum freeboard of 30 inches. Some states also only provide values for particular pit types. Utah, for example, specifies a 2-feet of freeboard for evaporation ponds only. Four other states (i.e., Indiana, Ohio, Texas, Wyoming) do not provide specific values for freeboard but rather indicate "adequate" or "sufficient" size/capacity of the pit is necessary. **Table 6-2** provides a summary of state-specific requirements freeboard.

Table 6-2. Summary of Freeboard Requirements for Pits.

Freeboard	States
1 ft	3 – KS (drilling, workover, burn and containment pits), KY, MS (brine pits)
2 ft	11 – AK, AR, CO, ID, LA, MS, OK, PA, TN, VA, WV (centralized pits)
2.5 ft	1 – KS (emergency and settling pits)
3 ft	2 – MT, NM
75% capacity	1 – FL

Signage: Most states (19) require signage for the site, though seven (i.e., Colorado, Indiana, Mississippi, New Mexico, North Dakota, Oklahoma, West Virginia) require signage for pits specifically. Five of these states specify signs for particular pit types. For example, offsite reserve pits and commercial disposal pits in Oklahoma, temporary salt water storage pits in Mississippi, and freshwater in both pits and portable-collapsible receptacles in North Dakota all require specific signs. New Mexico regulations specify that "the operator shall post an upright sign not less than 12 inches by 24 inches with lettering not less than 2 inches in height in a conspicuous place on the fence surrounding the pit or below-grade tank, unless the pit or below-grade tank is located on a site where there is an existing well…that is operated by the same operator."

Fencing and Netting: Eighteen states have fencing requirements for pits. Some states require fencing only for certain pit types. For example, North Dakota requires fencing for open pits and ponds that contain salt water or oil, while fencing is not required for drilling or reserve pits used solely for drilling, completing, recompleting or plugging, except beyond 90 days of operation. Ten states do not have fencing requirements for pits with Mississippi regulations specifically stating that fencing is not allowed to ensure agency field personnel have access to facilities for inspection and regulatory enforcement purposes, that first-responders (fire, sheriffs, emergency medical personnel, etc.) have ready access in the event of emergencies (fires, explosions, etc.), and that site personnel have a ready means of egress or escape from such facilities in the event of emergencies.

Ten of the 18 states that require fencing also require netting. North Dakota regulations state that all pits and ponds that contain oil must be fenced, screened and netted. Colorado regulations state that "where necessary to protect public health, safety and welfare or to prevent significant adverse environmental impacts resulting from access to a pit by wildlife, migratory birds, domestic animals, or members of the general public, operators shall install appropriate netting or fencing." Idaho does not specify fencing or netting directly but rather "site-specific methods for excluding people, terrestrial animals and avian wildlife from the pits." There are no states that require netting without fencing. **Table 6-3** provides a summary of the specific state requirements for fencing and netting. Idaho was counted as both fencing and netting for accounting purposes.

Table 6-3. Summary of Required Fencing and Netting for Pits.

Requirement	Number	States
Fencing Only	8	IL, MI, LA, OH, OK, PA, VA, WV
Fencing and Netting	10	CO, ID, IL, IN, MT, ND, NM, TX, UT, WY

Liners: Twenty-seven of the 28 states require liners for at least some types of pits. Most states (22 of 28) clearly state that liners are required by providing specifications, such as pit types, liner types and liner requirements. Other states, like Nevada, are more indirect and imply that a liner is required by prohibiting unlined pits. Michigan prohibits earthen pits for well completion fluids, produced fluids and tank bottoms but does not define earthen pits so it is unclear if lined pits are included in the prohibition.

Some states provide specifications for liners, including thickness and material. Liner thickness typically ranges from 10 to 60 mils, and materials are often synthetic or materials with equivalent performance, such as compacted clay, as approved in each state. Colorado regulations are substantial and specify different pit types/waste characteristics and associated liner requirements. Idaho regulations indicate that all liners should have a minimum permeability of 1×10^{-9} cm/sec, and thicknesses of 20 mils for reserve, well treatment and other short-term pits and 60 mils for long-term pits. In contrast, New York regulations state that a "watertight material" is required for brine pits. In Tennessee, liner seams should be 4 inches wide and welded. Seams are not allowed in Michigan.

State requirements for liners may vary by pit type. Some states have different requirements for liners based on the material being contained, while others require liners for some liquids but not others. Arkansas regulations, for example, require synthetic or compacted clay liners for reserve pits, synthetic or bentonite liners for drilling mud, and concrete liners for mud and circulation pits. In Illinois, fresh water reserve pits do not require liners but other pits do. Mississippi only requires temporary salt water pits be lined with an approved impervious material. Michigan specifies secondary containment (i.e. liners) for flare pits.

Leak Detection and Monitoring: Ten of the 28 states require leak detection and monitoring, though specifications provided in the regulations varies. For example, leak detection/monitoring is only required for long-term pits (more than one year) in Idaho, for brine pits in Texas, and centralized pits in West Virginia. The type of detection/monitoring also varies by state. For instance, Indiana requires visual inspections while Colorado requires the use of pit level indicators within designated setback locations. Two additional states (i.e., Utah, Wyoming) may require leak detection/monitoring in sensitive areas, as required by the agency or specified in a permit.

Berm Requirements: Seventeen states include requirements for berms with varying degrees of detail. Four have requirements for the site, but not pits specifically (i.e., Florida, Ohio, Virginia, West Virginia). Six states (i.e., Alaska, Indiana, Mississippi, New Mexico, Oklahoma, Texas) have general requirements for pits indicating, for example, that "pits shall be protected from surface waters by dikes and drainage ditches" (Mississippi) or that berms should be "adequately sized" to prevent pit inundation (Indiana). Alaska states that "if practical, confinement diking in construction of a reserve pit must be avoided. If confinement dikes are necessary, they must be kept to a minimum." Five states (i.e., Idaho, Kentucky, North Dakota, Pennsylvania, Tennessee) provide specific berm requirements for pits. For example, berms in Tennessee should have a 2:1 slope and a width of 2 feet. Idaho regulations state that the top of bermed pit walls be a minimum of 2-feet wide and "pits that have constructed berms ten or more feet in height or hold fifty acre-feet or more of fluid must also comply with the dam safety requirements."

Depth to Groundwater: A minimum depth to groundwater for pit siting is required by 12 of the 28 states reviewed. Seven states provide specific depths that range from 20 inches in Pennsylvania and West Virginia to 25 feet in Oklahoma. **Table 6-4** provides a summary of the specific state requirements for depth to groundwater.

Table 6-4. Summary of Required Depth to Groundwater for Pits.

Minimum Depth to Groundwater	States
1.7 ft	PA, WV (centralized pits only)
4 ft	MI
5 ft	KS, LA
10 ft	AR
20 ft	WY
25 ft	OK

Three remaining states provide more tailored requirements. Tennessee regulations state that, "in areas where groundwater is close enough to the surface that it will be encountered in construction of a pit, pits shall be constructed above ground, or the operator shall use a closed-loop system." Utah uses a ranking approach to evaluate potential impacts based on pit location. Surface to groundwater depth is one criterion considered in this evaluation, and if less than 25 feet, a closed-loop system should be considered instead of constructing a pit. In New Mexico, temporary pits containing low-chloride fluid may not be located where groundwater is less than 25 feet below the bottom of the pit.

Groundwater Monitoring: Over half of the states reviewed (15 of the 28) address groundwater monitoring either on a site-wide basis or specific to an E&P waste management unit (e.g., pit, landfill). Eight of the 15 states address groundwater monitoring on a site-wide basis (i.e., Colorado, Illinois, Michigan, Nevada, Ohio, Tennessee, Utah, Virginia), rather than for any specific type of E&P waste management unit. In Wyoming, however, baseline groundwater monitoring is conducted for the entire drilling site and may be also required for an E&P waste pit if it is located in a sensitive area. The remaining seven states (i.e., California, Louisiana, North Dakota, Oklahoma, Pennsylvania, Texas, West Virginia) require some type of groundwater monitoring for specific E&P waste management units. For example, Texas requires groundwater monitoring for commercial recycle/reclaim pits, brine pits and other types of pits if required by a permit. Oklahoma requires groundwater monitoring for flowback pits with capacities greater than 50,000 barrels and brine disposal well pits. Pennsylvania requires groundwater monitoring for centralized impoundments and unconventional well construction. North Dakota states that monitoring is required, which may include groundwater monitoring, for all buried or partially buried structures at treatment plant facilities.

Inspections: Eleven states include requirements for the inspection of pits. The different approaches used to define pits makes it difficult to further summarize the requirements. The regulations often specify the type of pit requiring inspection, which varies considerably among the states:

- Illinois and Indiana require inspection of concrete storage structures, which are allowed to be used as pits for production and waste materials.
- Louisiana requires inspection of reserve pits.
- Mississippi does not require inspection of pits, but the state must be given the opportunity to inspect the pit prior to use.
- New Mexico requires that the state be given the opportunity to inspect pits prior to use. The following inspection activities are required:
    - A minimum of daily inspections for temporary pit containing drilling fluids while the drilling or workover rig is on location, then weekly so long as liquids remain in the pit.
    - Weekly inspections of permanent and multi-well fluid management pits with the use of an on-site log while the pit has fluids at least monthly until the pit is closed. Inspections will include monitoring of the leak detection system during operation and before the system is covered.
    - If netting or screening is not feasible for a permanent pit or multi-well fluid management pit, the operator shall inspect for dead migratory birds and other wildlife on a monthly basis.
- North Dakota requires all reserve pits to be inspected prior to installation of the liner and use.
- Oklahoma requires inspections only for flowback water pits.
- Pennsylvania requires inspections at least once a year for onsite brine or residual waste disposal.
- Texas requires inspections of all brine pits and commercial recycle/reclaim pits, as well as others as specified by permit.
- Tennessee requires pre-permit inspections for all “pollution control structures.”
- West Virginia requires inspections of pits and impoundments with a capacity greater than 5,000 barrels (at conventional wells) and all centralized pits/impoundments prior to placement of any fluid, every two weeks for the life of the pit, and within 24 hours of significant rainfall (2 inches or more within a 6-hour period). For other types of pits, the state must be notified and given the opportunity to inspect prior to use.
- Wyoming requires periodic inspections of pits by the operator (weekly at a minimum) with documentation of such inspections sent to the Supervisor (state) at their request.

6.3.4. Pit Closure Requirements

Regulations were reviewed for several pit closure requirements including removal of waste material prior to closure, timing for pit closure, inspection and sampling. A total of 22 of the 28 states directly address pit closure requirements. One of those states (Kentucky) includes the requirements in an Operator’s Manual instead of regulations. Tennessee regulations do not specifically address pit closure but require removal of fluids from pits “as soon as practical after fluids have accumulated in them.” **Table 6-5** provides a summary of the general types of pit closure requirements identified in this review.

Table 6-5. Summary of Pit Closure Requirements.

Criteria	Number of States	Specific States
Liquids Removal	23	AR, CA, CO, FL, ID, IL, IN, KS, KY, MI, MS, MT, ND, NM, OH, OK, PA, TN, TX, UT, VA, WV, WY
Solids Removal	17	AR, CA, CO, FL, ID, IL, IN, KS, KY, MT, ND, NM, OH, PA, TN, TX, UT, WY
Closure Timeframe	22	AR, CA, CO, ID, IN, KS, KY, MI, MS, MT, ND, NM, NV, NY, OH, OK, PA, TN, TX, VA, WV, WY
Inspections	10	CO, ID, LA, MS, ND, OK, PA, TX, UT, WV

Removal of Liquids and Solids: Most states (23 of 28) require removal of liquids prior to pit closure. Some states specify the types of pits that require liquid removal. For example, drilling, reserve and temporary pits in North Dakota and hydraulic fracturing fluid pits in Ohio must have liquids removed prior to filling and compaction. Details about the method of liquid removal or disposal are provided in some regulations and may include disposal at an appropriate facility, offsite reuse or downhole disposal (i.e. injected liquids and semisolids, or placement of cuttings in the annular space of a plugged well). Illinois regulations specifically state that “all oilfield brine and produced waters shall be removed and disposed of in a Class II UIC well.” In Colorado, Oklahoma, Utah and Wyoming, natural evaporation is an accepted method of removal.

Six of the states that require removal of liquids do not require removal of solids prior to pit closure (i.e., Michigan, Mississippi, Oklahoma, Pennsylvania, Virginia, West Virginia). Michigan regulations state that drilling mud pits with waste in place shall be stiffened (i.e., earthen materials are mixed with the pit contents to provide physical stability and support for the pit cover) prior to encapsulation. Sixteen of the 28 states reviewed require removal of solids in some instances prior to pit closure. Arkansas, Texas and Wyoming specify the types of waste that either require removal or may remain in the pit. North Dakota regulations specify that contents of any earthen pit/receptacle be removed and disposed, while waste in drilling and reserve pits be encapsulated in the pit and covered. Idaho requires all pits to remove and dispose of solids and the pit liners.

Regulations in four states (i.e., Alaska, Missouri, Nevada, New York) do not mention removal of liquids or solids prior to pit closure. However, Alaska regulations include a general requirement that “upon completion the operator shall proceed with diligence to leave the reserve pit in a condition that does not constitute a hazard to freshwater.”

Closure Schedule: A total of 22 of the 28 states provide a schedule for pit closure. Some include specific requirements while others are more general. Timeframes typically range from 30 days to 12 months after the completion of particular site operations. For example, in North Dakota, pits should be reclaimed according to the following schedule: earthen (unlined) pits within 30 days after operations have ceased, reserve pits within 30 days after the drilling of a well or expiration of a drilling permit, and reserve pits within a reasonable time but not more than one year after the completion of a shallow well. Nevada regulations indicate pit closure be conducted “as soon as weather and ground conditions permit, upon final abandonment and completion of the plugging of any well.” Colorado regulations for reclamation are not specific for pits but indicate that reclamation for wells be completed within three months on crop land and 12 months on non-crop land.

Inspection and Sampling: Seven states require some form of inspection and sampling prior to pit closure (i.e., Colorado, Idaho, Louisiana, Oklahoma, Texas, Utah, West Virginia). Idaho regulations state "the owner or operator must notify the Department at least 48 hours prior to removal of the pit liner so an inspection may be conducted." Idaho also requires the testing of residual fluids and any accumulated solids in the pit to determine which disposal facility can accept the material. In Texas, inspections are required for commercial recycling/reclamation pits, or as required by a permit for other pit types. Texas also requires the testing of soils prior to closure. Testing parameters include pH, TPH, BTEX, as well as numerous metals. Colorado requires an inspection for overall drill site reclamation but not for pits specifically. Two states (i.e., Mississippi, Pennsylvania) require inspections, but no sampling. In Mississippi, emergency pits require inspection following the emergency period. Arkansas only requires sampling. Inspection and sampling are not required in Wyoming but may be determined to be necessary based on site-specific conditions. Inspections are not required for North Dakota, but approval is needed prior to pit reclamation. EPA identified no state regulations that require groundwater monitoring or testing subsequent to pit closure, but such a requirement could be included by the state agency in an individual well or pit permit. Several states that require sitewide baseline groundwater monitoring also have requirements for monitoring post well construction. Virginia, for example, requires groundwater monitoring consisting of initial baseline groundwater sampling and testing followed by subsequent sampling and testing after setting the production casing or liner. Pennsylvania requires that bodies of water and watercourse over and adjacent to horizontal directional drilling activities must be monitored for any signs of directional drilling fluid discharge.

Financial Assurance: For all states reviewed, separate financial assurance is not required for pit closure. Instead, if required, it is included in the general permit/bond for the well or overall facility.

6.3.5. Spill Notification and Corrective Action

A total of 26 of the 28 states reviewed included requirements for notification of spills in their regulations. Many of these regulations are not specific to a waste type and can include spills of crude oil or raw materials, neither of which is covered under the RCRA exemption. Some states refer to spills as "releases" or "nonpermitted or unauthorized discharge." New Mexico separately defines "major release" and "minor release," with different requirements for each. Some states (i.e., Idaho, Montana, Nevada, Utah, Wyoming) discuss spills in sections with other accidents or emergencies, such as fires, lightning strikes or blowouts. Other states (i.e., Colorado, Illinois, Indiana, Kansas) have separate "spill" sections. Mississippi regulations only address spill notification and corrective action in offshore rules.

Notification: For the 26 states with spill notification requirements, immediate notification is required following a spill or discharge from a waste management unit, especially for an uncontrolled spill/discharge that enters (or threatens to enter) nearby surface water or impact groundwater. Immediate notification is generally required to the Department/Commission/Division and a timeframe is often specified, ranging from 30 minutes to 24 hours. Some states (e.g., Michigan) do not give a specific timeframe but instead require the incident to be reported immediately or promptly. This initial notification is often communicated verbally, although North Dakota does have an initial online notification system that requires the location, type of incident, cause of the incident, volume released, volume recovered, potential environmental impacts and actions taken. A follow-up written report is typically required within five to 15 days, depending on the state. Additional requirements for initial spill notification can vary based on quantity of material spilled. **Table 6-6** provides a summary of the spill notification requirements for Wyoming and New Mexico.

Table 6-6. Summary of Spill Reporting Requirements in Select States.

State	Spill Type/Material	Quantity	Timeframe/Report Type
New Mexico	Volume that may with reasonable probability be detrimental to water or exceed specified standards	Not specified	Verbal report: immediately, within 24 hours Written notice: 15 days
	Major release	>25 barrels	Verbal report: immediately, within 24 hours Written notice: 15 days
	Minor release	>5 and <25 barrels	Written notice: 15 days
Wyoming	Uncontained spill or authorized release which enters, or threatens to enter, waters of the state	Any/All	Verbal report: by next business day Written report: 15 working days
	Contained spill	<1 barrel (42 gallons)	Reporting not required (maintain record of incident)
	Contained spill	>1 and <10 barrels	Written report: 15 working days
	Contained spill	>10 barrels	Verbal report: Next business day, Written report: 15 working days

States have a minimum spill volume threshold at which notification is required, which range from any amount spilled (e.g., Kansas, North Dakota, Utah) to 2,100 gallons (e.g., Nevada). Most states have a minimum quantity between 210 and 420 gallons (i.e., five to ten barrels). Volume requirements may also vary for the type of fluid spilled. Some states provide general descriptions (e.g., deleterious substances[18]) while others are more specific, such as crude oil, brine or produced water. For example, in both Arkansas and Illinois, immediate notification is required for a spill of one barrel of crude oil and/or five barrels of produced water. The type of notification required can further vary based on different waste characteristics or site conditions. For example, in Montana, immediate notification is required for the following cases: "(a) the spill, leak, or release of more than 50 barrels of oil or water containing more than 15,000 parts per million (ppm) TDS; (b) the spill, leak, or release of any amount of oil or of water containing more than 15,000 ppm TDS that enters surface water or groundwater; (c) the spill, leak, or release of any amount of produced water that degrades surface water or groundwater." Colorado regulations indicate that notification is required within 24 hours of the following: (1) a spill/release of any quantity that impacts or threatens to impact any waters of the state, a residence or

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18) The term "deleterious substance" has a broad range of definitions across the states using the term. For example, in Montana it includes all CERCLA and RCRA hazardous material and waste definitions, and any petroleum product, whereas in Oklahoma and Mississippi the term is more limited to oil and gas operations "…any chemical, salt water, oil field brine, waste oil, waste emulsified oil, basic sediment, mud, or injurious substance produced or used in the drilling, development, production, transportation, refining, and processing of oil, gas and/or brine mining."

occupied structure, livestock or public byway; (2) a spill/release of one barrel or more of E&P waste or produced fluids is spilled or released outside the berms or secondary containment; or (3) a spill/release of five barrels or more regardless of whether the spill/release is within the berms or other secondary containment.

Corrective Action: Twenty of the 28 states reviewed include discussion of corrective action in the regulations. Some states (e.g., Montana, Utah), provide general statements indicating that leaks/spills be contained and cleaned up promptly. Some (e.g., Colorado) include specific cleanup criteria for specified contaminants in soil and groundwater, while others (e.g., Kansas) provide details for the corrective action approach. In Kansas, "the following cleanup techniques shall be deemed appropriate and acceptable to the commission: physical removal, dilution, treatment, and bioremediation." Regulations in Illinois provide detailed approaches for crude oil spills as well as produced water spills, while Texas regulations provide similar details specifically for soil contaminated by crude oil in non-sensitive areas. Additionally, some states (e.g., Michigan, Virginia) include details in a spill management or abatement plan.

Some regulations provide timeframes for performing corrective actions. For example, spills greater than 42 gallons or that pollute or threaten to pollute the waters of Pennsylvania require an initial written report within 15 days and a site characterization report within 180 days to determine the extent of contamination resulting from the spill and document initial response actions. In Idaho, leaks that develop in a pit or closed-loop system require corrective action within 48 hours to include removing all liquid above the damage or leak line.

6.3.6. Offsite Landfills

Regulations for disposal of E&P wastes in offsite landfills may be found in either the state regulations for E&P waste, solid waste or both. To determine if wastes can be placed in offsite landfills it may be necessary to consult both sets of regulations. Therefore, this review considered both E&P and solid waste regulations. However, cross references are sometimes unclear or inconsistent because solid waste regulations often do not specifically discuss E&P wastes or define the type of landfill required for disposal.

Offsite Disposal Allowed: Twenty-five of the 28 states reviewed address offsite landfill disposal of E&P wastes in regulations. The three remaining states (i.e., Missouri, Mississippi, Tennessee) may allow offsite disposal, but it was not clear in the regulations reviewed. For example, Mississippi solid waste regulations delegate exclusive authority for disposal of nonhazardous oilfield waste, both commercial and noncommercial, to the Mississippi Oil and Gas Board, but offsite disposal methods are not addressed in the regulations. A fact sheet regarding disposal of wastes from the BP oil spill indicates that landfills are an acceptable disposal option if waste meet the state and federal definitions of non-hazardous (MSDEQ, 2010).

Some state regulations do not require E&P wastes be disposed in a particular type of disposal facility but rather state "a permitted facility." When the type of facility is specified, municipal solid waste landfills are the most common (e.g., Indiana, Kansas, Montana, Pennsylvania, West Virginia).

Municipal solid waste landfills are designed according to regulations from 40 CFR Part 258, which include liners and groundwater monitoring, among other requirements, and so are generally considered protective provided that the waste meets acceptance criteria. Other offsite disposal options may include industrial landfills, special waste landfills, commercial facilities and recycling facilities. For example, Alaska regulations specify drilling waste monofills as a particular type of permitted landfill. E&P wastes in Colorado may be disposed at permitted commercial disposal facilities, while New Mexico regulations specify recycling facilities. Oklahoma regulations state the type of facility for disposal of E&P wastes is based on either Department of Environmental Quality approval or landfill permit requirements. States generally classify landfills based on the risk from the wastes allowed, and set different protective criteria (design, operation, and monitoring) for each type of landfill.

Details about allowable waste types are provided in some of the state regulations but generally do not address every individual waste type. Ohio regulations indicate that a solid waste facility is acceptable for "drill cuttings that have come in contact with refined oil-based substances or other sources of contamination." In Illinois, waste classified by the state as naturally occurring radioactive material (NORM) with activities at background levels may be disposed at a permitted non-hazardous special waste landfill, while NORM waste above background levels requires disposal at a waste facility permitted by the Illinois Department of Nuclear Safety. Most regulations, however, focus on pit wastes, with less attention to tank wastes and little mention of other exempt wastes (pipe scale, pigging wastes, produced sand, dehydration and sweetening wastes, spent gas plant filter material, and associated wastes). North Dakota appears to be the only state with regulations to explicitly identify filter socks and other filter media in E&P regulations.

Waste Testing: Testing of waste prior to offsite disposal is required in seven of the 28 states reviewed (i.e., California, Idaho, Illinois, Louisiana, New Mexico, Oklahoma, Texas). In Illinois, testing is necessary only for wastes that might have NORM. Idaho requires routine characterization of waste received for facilities permitted to receive E&P waste. Wyoming and Utah do not require testing for all wastes, but it may be deemed necessary by the Supervisor/Division on a site-specific basis. Site specific waste control plans in New York may also include a requirement for testing. Individual disposal facility permits may require testing of wastes prior to acceptance.

Daily Cover: The use of E&P wastes as a daily cover was not specifically addressed in any of the state regulations reviewed. A report prepared for the West Virginia Department of Environmental Protection noted that the drill cuttings received often have too high a moisture content, which makes it difficult to meet specifications for compaction (WVDEP, 2015). However, a report by the ANL noted that stabilized oil and gas wastes have been used as daily cover in Louisiana. (U.S. DOE, 2006). New Mexico and Texas indicate that stabilized, uncontaminated solids may be suitable for use as daily cover at landfills. In New York, such waste also appears able to be used as part of the cap but cannot be within 10 ft of the final cover. In Arkansas, Nevada, Oklahoma, Texas and several other states, regulations allow unspecified alternate materials to be used for daily cover (potentially including drill cuttings, produced sand, petroleum-contaminated materials) if the operator shows that the alternative materials can control wastes without presenting a threat to public health and safety and the environment.

6.3.7. Land Application

Land application consists of applying waste to the land surface as a means of treatment and disposal. More than half of the states in this review (17 of 28) address land application of E&P wastes through regulations. Nearly all these states (15 of 17) provide specific limitations or conditions for application, which may include waste characteristics, site conditions and operational requirements. A number of states have regulations for land application of septic sludges and other industrial byproducts, but the regulations were not incorporated into the current review. For these remaining states, it is unclear if land application of E&P wastes is prohibited.

Waste Types: The types of E&P waste that may be land applied vary by state. Some states allow more than one type of waste to be land applied. **Table 6-7** provides examples of the different types of waste allowed for land application in each state.

Table 6-7. Summary of Wastes Allowed for Land Application.

Waste Type	States
Water-Based Drilling Fluids and/or Cuttings	AR, CO, IN, KS, OK, PA, TX
Oily Waste Including Materials Containing Crude Oil, Condensate or Wastes that Contain Hydrocarbons (Such as Soil, Frac Sand, Drilling Fluids, Drill Cuttings and Pit Sludge)	CO, NM, OK, PA, U
Drilling Fluids, Produced Water and Produced Water-Contaminated Soils, Waste Crude Oil, Sludges, and Oil-Contaminated Soils	WY
Drilling and Production Fluids	VA
Special Waste Defined as "Gas and Oil Drilling Muds, and Oil Production Brines"	KY
Crude Oil Bottom Sediments	IL, IN
Naturally Occuring Radioactive Material (NORM)	MS, TX

Permits: There is a wide range of permit requirements for land application amongst the 17 states. Six clearly require permits (i.e., Arkansas, Indiana, Oklahoma, Pennsylvania, Texas, Wyoming). Two either do not require them (Colorado) or only require under certain conditions (Virginia[19]). Six do not mention permits for land application in state regulations (i.e., Illinois, Kansas, Kentucky, Mississippi, New Mexico, Utah). Of the six states that require permits, Indiana and Texas only require permits for off-lease application of E&P wastes. In Wyoming, permits are issued by the Department of Environmental Quality.

Waste Testing: Almost all of states that allow land application (16 of 17) include some limits or conditions for land application of the waste, though the level of detail varies. Some states provide numerical requirements for land application. Various examples from both Indiana and Virginia include: TDS < 1,500 mg/L, Cl < 1,000 or 5,000 mg/L, Fe < 7 mg/L, Mn < 4 mg/L, Oil and Grease < 15 mg/L, pH: 6-9. Some states place restrictions on physical properties, such as the presence of a visible sheen or free water. Other states (e.g., Texas) specify the limits for the soil after application, such as $^{226+228}$Ra < 30 pCi/g or < 150 pCi/g of any other radionuclide.

Location Restrictions: Most states (14 of 17) have some application site restrictions provided in the regulations. Some of those states only allow land application of wastes on lease property, the site of

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[19] According to the disposal application form, if TDS exceeds 5,000 mg/kg a permit may be required by VA DEQ.

origin, or “lands previously disturbed by well site construction and drilling operations.” Colorado allows for land application onsite or at a centralized waste management facility. Oklahoma and Texas provide specifications for commercial soil farming facilities; some of which are different from or add to those for non-commercial sites. For instance, in Oklahoma, commercial soil farming facilities have setbacks for incorporated municipalities: 3 miles for populations 20,000 or less, or 5 miles if greater than 20,000. A majority of the 14 states also provide operational conditions for land application. Wyoming and Kentucky do not provide specifications in their regulations, while Arkansas includes criteria in a permit. Some states provide buffer zones/setback restrictions for the application site, including distances from surface water bodies and site boundaries, as well as conditions for the site, such as depth to groundwater and soil types. **Table 6-8** provides a summary of the location and siting restrictions for land application of E&P wastes.

Table 6-8. Location and Siting Restrictions for Land Application.

	Siting Restrictions	IN	KS	NM	OK	PA	TX	UT	VA
Location Restrictions	Surface Water Body	X	X		X	X	X		X
	Water Supply	X	X		X	X	X		X
	Site Boundary	X	X	X	X				X
	Highways								X
	Rock Outcrops, Sinkholes								X
	Building		X			X	X		
	Pipeline			X					
	Drainage		X		X		X		
Site Conditions	Depth to Bedrock				X	X	X		
	Depth to Groundwater		X		X	X			
	Soil Type		X		X	X			
	Hydraulic Conductivity							X	
	Slope		X		X	X	X		
	Chloride (in Soil)		X						
	Previous Land Application		X						
	Chloride (in Groundwater)		X						
	Salinity				X				

Examples of weather-related restrictions include prohibiting land application during precipitation events or when ground is frozen or snow-covered. Loading rates are provided for nine states and may include general performance criteria (will not result in runoff or pooling) or values for specific loading rates. The maximum depth of waste applied, and the depth of tilling is specified in nine states. Mississippi required tilling waste into the soil only if precipitation exceeds 25 inches per year. Three states provide regulation on how the waste is to be applied to the soil including the use of injection, pressurized diffusers, disking, or tilling methods and prohibition on gravity feeders, and use of bulldozers and backhoes for incorporating cuttings into soil. **Table 6-9** provides a summary of the operational conditions for land application in specific states.

Table 6-9. Summary of Operational Conditions Required for Land Application.

Operational Conditions/Criteria	Specific States
Resulting Concentration in Soil	CO, MS, TX, UT
Weather-Related Application Restrictions	IN, KS, OK, PA, VA
Rates to Prevent Runoff, Ponding, Erosion	CO, IN, KS, NM, PA, UT, VA
Depth of Incorporation	IL, MS, PA
Maximum Application Thickness	CO, KS, NM, OK, TX, UT
Enhance Bioremediation	CO (oily waste), NM
Timeframe for Application	CO, KS, NM, UT (Hours/Day after Received) IN (Only Daylight Hours)
Loading Rate	NM, OK, PA
Specific Method of Application (Type, Vehicle, etc.)	IL, OK, UT

6.3.8. Beneficial Use

EPA defines beneficial use to be the substitution of non-hazardous industrial secondary materials, either as generated or following additional processing, for some or all of the virgin, raw materials in a natural or commercial product (“analogous product”) in a way that provides a functional benefit, meets product specifications, and does not pose concerns to human health or the environment” (U.S. EPA, 2016c). State agencies have the primary authority to determine whether beneficial use of a non-hazardous material is allowed within the state and may use definitions that differ from EPA. For example, some states may classify the processing of waste for oil recovery to be beneficial use. A survey of state management practices for E&P wastes in 2013 included questions about beneficial use (ASTSWMO, 2015). A total of 11 states indicated that they had approved various beneficial uses for drill cuttings (concrete, road base, grading), drilling fluid (concrete), sludge (road application), produced water (dust suppressant, de-icing agent) and other wastes. There is little information available about the frequency of different uses or the volumes of waste involved. However, states have developed requirements for certain beneficial uses of E&P wastes.

Types of Waste: Eleven of the 28 states included in this review have requirements that address beneficial use of E&P wastes. Seven states have requirements incorporated into regulations, three provide guidelines (i.e., Alaska, Pennsylvania, Texas), and one outlines requirements in an agreement between the state Division of Highways and Department of Environmental Protection (i.e., West Virginia). The most common use is road application of E&P waste fluids to control dust, stabilize unpaved surfaces, and de-ice road surfaces. **Table 6-10** provides a summary of the uses allowed for each type of waste in these states.

Table 6-10. Summary of Waste Types Allowed for Beneficial Use.

State	Type of Waste for Beneficial Use		Type of Beneficial Use
	Fluid	Sludge/Sediment/Solids	
AK	None	Drill Cuttings	Construction of Roads, Pads and Berms on Oil and Gas Properties Owned or Operated by the Company
AR	None	Crude Oil Tank/Pit Solids	Oiling (Lease Roads)
CO	Produced Waters (Flowback Fluids Prohibited)	None	Dust Control (Lease Roads)
LA	Brine	None	Roadspreading, Deicing
MI	Brine	None	Dust and Ice Control, Road Stabilization
NY	Brine (Flowback and Marcellus Shale Water are Prohibited)	None	Dust Control, Unpaved Road Stabilization, Ice/Snow Reduction
OH	Brine (Horizontal Wells Prohibited)	None	Dust and Ice Control
PA	Production or Treated Brine (Not from Shale Formation)	None	Dust Control, Road Stabilization
TX	Treated Fluid	Oily Waste Waste Solids	**Treated Fluid:** Any Approved Re-Use That is Not Considered Disposal **Oily Waste:** Roads (Lease or County), Firewalls **Other Waste Solids:** Concrete Bulking Agents, Landfill Cover or Capping Material, Landfill Berms, Construction Fill Material or Treated Aggregate, Closure or Backfill Material, Firewall, or Other Construction Fill Material
WV	Brine	None	Prewetting, Anti-Icing, Deicing
WY	Drilling Fluids, Produced Water	Produced Water-Contaminated Soils, Waste Crude Oil, Sludge, Oil-Contaminated Soils	Roadspreading, Road Application

Testing Requirements: These 11 states include a wide range of requirements for waste characteristics and operational conditions. Wyoming requires slightly different analyses for particular waste types. **Table 6-11** provides a summary of common testing requirements for beneficial uses in select states. Additional analyses may be required by certain states. Colorado requires sampling of soil adjacent to road application and includes a list of 18 organic compounds and three additional parameters (electrical conductivity, sodium adsorption ratio and pH). Texas requires testing of one sample from each 200 cubic yards of treated products.

Table 6-11. Summary of Beneficial Use Testing Requirements.

Parameter	AK	AR	CO	MI	NY	TX	WV	WY		
								Drilling Fluid and Cuttings	Petroleum-Contaminated Soil	Produced Water and Contaminated Soil
TPH	X					X		X	X	X
TDS			X		X		X	X		X
SO_4					X					
H_2S				X						
Cl					X	X	X			
Ca				X	X		X			
Na, Fe					X		X			
Ba, Pb	X				X	X	X	X	X	X
Ag, As, Cd, Cr, Hg, Se	X					X		X	X	X
Ra-226										X
Oil/Grease					X		X			
Benzene				X	X	X	X	X	X	X
Toluene				X	X		X			
Ethylbenzene				X	X		X			
Xylene				X	X		X			
TOX								X	X	X

TOX – Total Halogenated Organics

Limitations on Use: States also provide specific restrictions for the site of use, such as distance from surface water body and grade of the roadway. Some provide more general description for the site. For example, Colorado regulations state that roadspreading may be conducted on lease roads outside "sensitive areas." Six of the 10 states also provide operational conditions for beneficial use. New York and Pennsylvania specify setbacks from surface water bodies of 50 and 150 feet, respectively. In New York and Pennsylvania (when brine is used for dust control or road stabilization), a maximum roadway grade of 10 percent is allowed and brine may not be applied to wet roads during rain or when rain is imminent. Brine may not be applied between sundown and sunrise, except for ice control in Ohio and when applied for dust control/road stabilization in New York. Michigan, Texas and Wyoming do not include such requirements in their regulations.

Application rates for natural gas brines in West Virginia are "limited to 10 gallons per ton for pre-wetting use, 50 gallons per lane mile for anti-icing use, and 100 gallons per lane mile for de-icing use." Ohio regulations state "the maximum uniform application rate of brine shall be 3,000 gallons per mile on a 12-foot-wide road or 3 gallons per 60 square feet on unpaved lots." Pennsylvania regulations indicate "The road should initially be spread at a rate of up to one-half gallon per square yard (typically after the road has been graded in the spring). The road should subsequently be spread at a rate of up to one-third gallon per square yard no more than once per month unless–based on weather conditions, traffic volume or brine characteristics–a greater frequency is needed to control dust and stabilize the road. The application rate for race tracks and mining haul roads should be determined for each site and should not exceed one gallon per square yard." New York regulations do not provide a numerical value but state that "the brine application must not be used at a rate greater than needed for snow and ice control."

Vehicle requirements are provided for three states. In Pennsylvania, "brine must be spread by use of a spreader bar with shut-off controls in the cab of the truck…and each vehicle used to spread brine shall have a clearly legible sign identifying the applicator on both sides of the vehicle." Ohio regulations specify "the discharge of brine through the spreader bar shall stop when the application stops…the applicator vehicle shall be moving at least five miles per hour at all times while the brine is being applied…The maximum spreader bar nozzle opening shall be three-quarters of an inch in diameter…the angle of discharge from the applicator vehicle spreader bar shall not be greater than sixty degrees from the perpendicular to the unpaved surface…only the last twenty-five per cent of an applicator vehicle's contents shall be allowed to have a pressure greater than atmospheric pressure; therefore, the first seventy-five per cent of the applicator vehicle's contents shall be discharged under atmospheric pressure." When brine is used for dust control or road stabilization in New York, "a spreader bar or similar device designed to deliver a uniform application of brine must be used; the application vehicle must have brine shut-off controls in the cab…when the application vehicle stops, the discharge of brine must stop; and the vehicle must be moving at least five miles per hour when brine is being applied."

Some states provide additional details in their regulations. Arkansas, for instance, states "immediately following completion of the application, all liquid fractions shall be immediately incorporated into the road bed with no visible free-standing oil; and no lease road shall be oiled more than twice a year." In Michigan, the well owner may not use brine for beneficial use but may convey or transfer it for use by another party. In addition, the administrative requirements for beneficial use of E&P waste vary amongst the states reviewed. For example, Ohio requires a permit, Texas requires a permit for off-lease only, New York requires a written petition, and Kansas requires an application. Ohio also provides detailed information about the approval process, and the Texas permit application provides detailed requirements for treating and recycling oil and gas solid waste for commercial or industrial use. **Table 6-12** provides a summary of common restrictions on the placement of brine and other waste liquids on roadways.

Table 6-12. Summary of Restrictions on Placement of Waste Liquids on Roadways.

Site and Operational Restrictions		Specific States
Site Restrictions	Distances to Surface Water Bodies	NY, PA
	Grade	NY, PA
	Within 12ft of Structures Crossing Water Bodies or Crossing Drainage Ditches	NY, OH

Table 6-12. Summary of Restrictions on Placement of Waste Liquids on Roadways.

Site and Operational Restrictions		Specific States
Operational Restrictions	Weather-Related (Flooded, Snow Covered, Frozen Ground)	NY, PA
	Prevent Pooling/Runoff, Impact to Surface Water Bodies	AR, CO, PA
	Time of Day	NY, OH (except for ice control)
	Specific Loading Rate	NY, OH, PA, WV
	Vehicle Requirements	NY, OH, PA
	Avoid Vegetation	NY, OH

6.3.9. NORM and TENORM

The wastes generated during drilling, completion, production, workover and closure may contain elevated concentrations of certain radioactive elements (“radionuclides” or “radioisotopes”). EPA uses the general term “technologically enhanced radioactive materials (TENORM)” to refer to these wastes. EPA defines TENORM as "naturally occurring radioactive materials that have been concentrated or exposed to the accessible environment as a result of human activities such as manufacturing, mineral extraction, or water processing. Technologically enhanced means that the radiological, physical, and chemical properties of the radioactive material have been altered by having been processed, or beneficiated, or disturbed in a way that increases the potential for human and/or environmental exposures.” State regulations use terminology that includes TENORM, NORM, and naturally occurring and/or accelerator-produced radioactive material (NARM). There can be important distinctions between these different terms, as some states specifically exclude wastes classified as NORM from state radiation regulations. The current discussion uses TENORM for all wastes that have the potential to have elevated activity, unless referring to the regulations of a specific state. **Table 6-13** provides a summary of the different terminology typically used by different states in regulatory text.

Table 6-13. Summary of Terminology for Radioactivity

Terminology	Specific State
NORM	AR, IL, IN, MS, NM, TX, WY
TENORM	KY, MT, ND, NY, VA, WV
NARM	FL, NY, NV, TN
NORM and TENORM	CO, ID, OH, PA
Naturally Occurring Material	MI

Radiation Regulations: Most of the states reviewed (22 of 28) address radioactivity somewhere in the state regulations. Only ten states discuss radioactivity within the E&P regulations, though some (e.g., Tennessee) simply refer back to the state’s radiation regulations. Of the top five producing states (i.e., Texas, Pennsylvania, Alaska, Oklahoma, North Dakota), Texas and North Dakota have the most extensive regulations. Pennsylvania requires a comprehensive radioactive material action plan for any onsite treatment of fluids or drill cuttings. Alaska and Oklahoma do not specifically address this topic. In nearly all of the states, primary responsibility for regulating TENORM lies with the state health department (ten states) or environmental agency (includes solid waste agencies). For example, radioactivity in New Mexico is regulated by the Oil and Gas Conservation Division, and Texas is regulated primarily by the Railroad Commission and supported by the Department of State Health Services. Texas regulations include a clear and comprehensive description of the jurisdiction of the two agencies. The delineation of roles is less clear in the regulations of other states with split jurisdiction, though several states (e.g., Colorado, North Dakota) provide fact sheets to help operators navigate the regulations. Because of the fragmented nature of E&P regulations on radioactivity, it was challenging to construct a complete picture of the coverage of all aspects of regulation across the country.

EPA found that state regulations touch on a wide range of issues including planning requirements, operational activities at the well or production site, closure activities, or characterization and disposal (includes onsite, downhole and offsite landfills). However, few states cover all these areas and the relevant regulations are often scattered across different agencies and sections of regulatory text. The most comprehensive regulations related to solid waste landfill requirements and downhole well disposal. A few states addressed radioactivity associated with waste management unit operation and closure.

Action/Management Plan: Four states (i.e., Illinois, Indiana, Louisiana, New Mexico) require an action/management plan to manage radioactivity, but the required content varies. For instance, in Illinois, E&P waste is considered low-level radioactive waste and disposal is managed under the Central Midwest Interstate Low-Level Radioactive Waste Commission Regional Management Plan, but a site-specific action plan addressing handling and testing of E&P waste is required as part of the Illinois oil and gas permitting regulations. The Action Plan required in Pennsylvania, however, is specific to oil and gas operations and must include procedures for monitoring and responding to radioactive materials produced by the treatment process and procedures for training, notification, recordkeeping and reporting. Some states appear to require action or management plans as part of the radiation safety protection regulations (under the public health division or solid waste division) but it is often unclear how or if these regulations apply to operation and disposal at oil and gas operations.

Storage Requirements: Eight states include some type of storage requirements for NORM/TENORM wastes. For example, North Dakota provides detailed requirements for management and inspection of containers and tanks containing TENORM waste. Wyoming guidelines indicate NORM wastes "should be stored in enclosed containers, durable synthetic fiber 'super sacks' or equivalent" for periods not to exceed 90 days, 180 days or up to 1 year depending on the activity and volume of the waste. In addition, West Virginia requires an annual registration form and Arkansas refers to general "NORM radiation requirements" for storage.

Disposal Screening: Eleven states require screening for radioactivity prior to disposal either onsite or at the landfill. Although many regulations do not provide detailed requirements for testing, New York includes a specific regulation for screening when cuttings with NORM/TENORM are disposed. Pennsylvania requires radiation testing for disposal at offsite municipal landfills but not for NORM/TENORM wastes specifically. While Colorado does not require screening at the landfill prior to disposal, testing of each waste shipment by the facility generating the waste is required prior to transport. Illinois and several other states require testing of soil and residues before pit closure. Site-specific landfill permits may include requirements for screening of incoming materials for radioactive materials or provide specific acceptance criteria.

Disposal Options: Most states (23 of 28) discuss disposal options for these wastes, which may vary depending on waste activity. The most common option is offsite disposal at facilities permitted for general radioactive waste or more specific NORM/TENORM. Disposal at solid waste or hazardous waste facilities is allowed in some states in accordance with specific thresholds. Other options include downhole injection, land spreading, onsite burial and reuse. Some states may allow more than one type of disposal. Ohio regulations, for instance, state "lawful disposal" of wastes is required, which may include reuse, injection and out-of-state disposal. Florida regulations are complex but appear to allow NORM/TENORM disposal by a variety of methods.

Administrative requirements such as notification, reporting and permitting also vary by state. For example, Indiana regulations require notification and a disposal plan but not a permit for NORM disposal. Permits are required for disposal in some states, such as Mississippi and New York. In New York, no permit is required for disposal of NORM but disposal of TENORM is highly restrictive. States governed by interstate agreements or compacts for low-level radioactive waste often include an additional layer of regulations regarding import and export of radioactive materials for disposal.

Disposal Limits: Nearly all (20 of 23) states that explicitly allow disposal present activity limits. Based on the regulations reviewed, numerical thresholds typically range from 3 picocuries per gram (pCi/g) of $^{226+228}$Ra (Colorado) to 200 pCi/g $^{226+228}$Ra (Kentucky). In many states, wastes classified as NORM are exempt from regulations if the materials contain concentrations less than 5 pCi/g of $^{226+228}$Ra or 100 pCi/g of other naturally occuring radionuclides. Colorado currently has three landfills permitted for TENORM disposal with different acceptance criteria, while solid waste facilities may be used only if stringent testing and radioactivity criteria are met.

The type of facility where disposal is allowed may depend on the waste activity. Wyoming regulations allow disposal at a solid waste facility for waste up to 50 pCi/g ^{226}Ra while wastes with levels greater than 50 pCi/g ^{226}Ra must be managed at out-of-state facilities authorized to accept low-level radioactive waste. In Michigan, disposal of waste up to 50 pCi/g ^{226}Ra is allowed in a hazardous waste or Type 2 landfill, but wastes greater than 50 pCi/g ^{226}Ra must be disposed in a licensed radioactive waste facility. No limits are presented for downhole disposal of waste.

6.4. Conclusions

The review of state regulatory programs focused on 61 specific elements organized into 12 general topic areas. Each of these elements (e.g., location restrictions, inspections) was chosen based on a review of existing federal solid waste management programs. The selected elements are those that EPA considers to be broadly applicable, regardless of waste type, and so provide a reasonable basis for comparison among different programs. Yet the absence of a particular element in this review does not necessarily mean a state program is deficient. Some states may not address a particular practice in regulations because issues are handled on a case-by-case basis (e.g., beneficial use) or the practice is does not occur within the state boundaries (e.g., centralized pits). In some cases, professional judgment was required to interpret how regulatory language would be implemented by the relevant state agencies. It is possible that separate guidance documents and individual permits further elaborate on requirements in the regulatory text; however, these documents may not be posted publicly or may require foreknowledge of specific wells or management units to locate. Therefore, this regulatory review, while not fully comprehensive, does provide a great deal of information about the scope of coverage (e.g., the wastes and activities), and the level of detail and precision in the requirements to determine where these programs are equivalent to or expand upon current RCRA Subtitle D requirements.

EPA reviewed the text of regulations from 28 of the 34 states with reported production of oil and gas tracked by the EIA. Together, these states represent over 99% of the total oil and gas production in the United States. **Table 6-14** provides a summary of the states reviewed, organized by the estimated percent of national crude oil and natural gas production in 2016 (by volume expressed in barrels).

Table 6-14. Ranking of State Oil and Gas Production

Percent Production	State	Percent Production	State	Percent Production	State	Percent Production	State
32.0%	Texas	4.6%	New Mexico	1.0%	Kansas	0.04%	Indiana
11.5%	Pennsylvania	4.4%	Louisiana	0.4%	Montana	0.04%	New York
8.4%	Alaska	3.4%	Ohio	0.4%	Mississippi	0.03%	Florida
7.3%	Oklahoma	3.1%	West Virginia	0.3%	Michigan	0.01%	Idaho
6.0%	North Dakota	2.8%	California	0.3%	Virginia	0.01%	Tenessee
5.1%	Colorado	1.8%	Arkansas	0.2%	Kentucky	0.01%	Nevada
4.9%	Wyoming	1.2%	Utah	0.1%	Illinois	0.01%	Missouri

Generally, EPA found that state regulatory programs for E&P waste include a majority of the elements relevant to the management of solid wastes. The scope and specificity of regulatory programs varied among states; however, some general trends were observed relative to the amount of oil and gas production in the states. The 11 highest-producing states account for more than 90% of national production. These states tend to have regulatory programs tailored specifically to the management of E&P wastes, which can include specific requirements by well type (e.g., conventional, unconventional), waste type or management practice. These states are also more likely to have centralized infrastructure dedicated to the storage and disposal of E&P wastes mainly due to the sheer volume of waste generated and the possibility of overwhelming the capacity of other disposal options (e.g., municipal solid waste landfill). The remaining 17 states account for around 9% of total oil and gas production. It appears that these states tend to have more general programs that address E&P waste management under the same or similar regulatory framework as other non-hazardous solid wastes. These states are more likely to manage E&P wastes, as appropriate, within existing landfills and may not have requirements that specifically reference E&P wastes. **Table 6-15** provides a summary of the prevalence of each element in state programs based on Agency review. Each specific regulatory elements within a topic area is ordered from greatest to least coverage.

Table 6-15. Summary of State Program Regulatory Elements

General Topic	Specific Element	Percent of National Production	State Count
1	**Consistency with 40 CFR Part 257.3 – Coverage**		
	1) Groundwater	94%	25
	2) Surface Water	94%	24
	3) Floodplains	93%	23
	4) Endangered Species	31%	9
2	**Waste Management Location Requirements (Siting and Setbacks)**		
	5) Environmental Receptors (Surface Water, Wetlands, Watercourses)	91%	22
	6) Residential	73%	17
	7) Depth to Groundwater	42%	13
3	**Tank Requirements (Onsite/On-Lease)**		
	8) Tank Berms and Containment Specifications	74%	18
	9) Requirements for Tank Construction Material	50%	11
	10) Tank Bottom Removal Permit Required	50%	4
	11) Netting for Open Tanks Required	46%	7
	12) Requirements for Modular Large Volume Tanks	18%	2
	13) Tank Monitoring Required	12%	4
4	**Pit Construction and Operation Requirements**		
	14) Requirements for Pit Liners	99%	27
	15) Multiple Pit Content/Use Types Specified	88%	23
	16) Temporary Pit Requirements	88%	17
	17) Requirements for Fencing	87%	18
	18) Freeboard Requirements	86%	20
	19) Berm Requirements	84%	17
	20) GW Monitoring Required	81%	15
	21) Run-On and Run-Off Controls	80%	19
	22) Inspections	74%	11
	23) Discharge Permits Required	72%	11
	24) Permit Required	70%	16
	25) Prohibited Pits	69%	13
	26) Non-Commercial Fluid Recycling Pits	62%	5
	27) Netting	57%	11
	28) Leak Detection/Monitoring Required	55%	10
	29) Depth to Groundwater Specified (Minimum)	40%	12
	30) Centralized Pits	37%	6
	31) Pit Signage	27%	7
5	**Pit Closure Requirements**		
	32) Liquids Removal Required	87%	23
	33) Closure Schedule Specified	85%	22
	34) Inspections Required	71%	10
	35) Solids Removal Required	64%	17
	36) Sampling Required	55%	8
	37) Financial Security Required	3%	1

Table 6-15. Summary of State Program Regulatory Elements

General Topic	Specific Element	Percent of National Production	State Count
6	**Spill Notification and Corrective Action**		
	38) Spill Notification Required	91%	26
	39) Corrective Action Plan Required	78%	20
7	**Offsite Landfills**		
	40) E&P Waste Allowed in Offsite Landfills	99%	25
	41) Testing of Waste Required	51%	7
	42) Use of E&P Wastes as Daily Cover Allowed	7%	2
8	**Land Application**		
	43) Land Application Allowed	81%	17
	44) Specific Limitations/Conditions for Land Application	79%	16
	45) Location Restrictions	69%	14
9	**Beneficial Use**		
	46) Road Spreading Allowed (Specify if Permit is Required)	68%	11
	47) Testing Requirements for Beneficial Use	64%	10
	48) Specific Limitations/Conditions for Road Spreading	62%	9
10	**Waste Minimization and Best Management Practices**		
	49) Closed Loop Drilling Requirements	25%	7
	50) Produced Water Recycling Requirements	0%	0
11	**Commercial On/Off Lease and Stationary Recycling/Reclamation Facilities**		
	51) Commercial Facilities Regulated (Specify if Permit is Required)	58%	7
	52) Financial Security/Closure Required	50%	4
	53) Offsite Reclamation Manifest Required	50%	4
	54) Monitoring and Testing Required During Operation	50%	4
12	**NORM and TENORM**		
	55) State Regulations Address Radioactivity	79%	22
	56) Disposal Allowed	71%	23
	57) Disposal Limitations and Conditions	67%	20
	58) Onsite or Landfill Testing/Screening Required	60%	11
	59) E&P Waste Regulations Address Radioactivity	47%	8
	60) Storage Requirements	28%	8
	61) Action Plan/Management Plan Required	9%	4

The level of coverage for each element is variable. This is expected, as the scope and specificity of state programs can vary in response to regional factors that impact the types of waste generated and the appropriate methods to manage those wastes. However, several elements are present in regulations for nearly every state reviewed. Many of these elements are more standardized requirements intended to either prevent releases to the environment (e.g., pit liners) or ensure that releases are identified and addressed (e.g., spill reporting, groundwater monitoring). Other elements have substantial coverage, but from a relatively small number of states, which indicates these elements (e.g., centralized disposal) are concentrated states with higher production. The elements with the lowest coverage (e.g., tank signage, financial assurance, produced water recycling) tend to be those that do not directly address potential environmental releases, but are considered best management practices. There is no indication from this review that there are widespread gaps in the scope of the written regulations. Any gaps that are identified for individual states might be better addressed through outreach and other targeted actions.

States have continued to periodically update regulatory programs that address issues raised by increased production, emerging environmental issues, and ongoing reviews from third parties. At least 24 states out of the 28 reviewed have revised their regulations related to E&P wastes in the past six years, with some revisions as recent as 2018. **Table 6-16** provides a summary of the most recent updates for each state.

Table 6-16. Most Recent Updates to State Programs

State	Percentage of Production	Most Recent Updates Identified
Texas	32.0%	2013
Pennsylvania	11.5%	2016
Alaska	8.4%	2017
Oklahoma	7.3%	2017
North Dakota	6.0%	2015
Colorado	5.1%	2016
Wyoming	4.9%	2016
New Mexico	4.6%	2016
Louisiana	4.4%	2014
Ohio	3.4%	2005
West Virginia	3.1%	2016
California	2.8%	2015
Arkansas	1.8%	2012
Utah	1.2%	2016
Kansas	1.0%	2013
Montana	0.4%	2018
Mississippi	0.4%	2015
Michigan	0.3%	2015
Virginia	0.3%	2016
Kentucky	0.2%	2007
Illinois	0.1%	2014
Indiana	0.04%	2017
Florida	0.03%	2013
New York	0.04%	Unknown
Idaho	0.01%	2015
Tenessee	0.01%	2013
Nevada	0.01%	2014
Missouri	0.01%	2016

Based on this review, EPA concludes that the scope and specificity of regulatory programs varies among the states based on a number of factors, such as the quantity of oil and gas produced in the state and the prevalence of hydraulically fractured wells. Despite this variability, the existing state programs incorporate a majority of elements found in federal waste management programs, which indicates that the scope of the written state regulations is robust. However, the way in which these regulations are interpreted and implemented are also important considerations. To better understand which practices may pose concern, EPA reviewed the assembled literature for existing evaluations that had drawn conclusions about the potential for adverse effects from management of E&P wastes.

7. Review of Existing Evaluations

EPA reviewed the available literature to identify evaluations that had previously quantified the risk of adverse effects associated with the management of E&P wastes. The purpose of this review was to determine whether the data and analyses that underpin the findings of these evaluations are of sufficient quality to draw conclusions about the current management practices. EPA identified two evaluations that provide quantitative estimates of potential risk:

- Technical Support Document Onshore Oil and Gas Exploration, Development, and Production: Human Health and Environmental Risk Assessment (U.S. EPA, 1987d)
- Potential Radiological Doses Associated with the Disposal of Petroleum Industry NORM via Landspreading (U.S. DOE, 1998)

EPA reviewed the data relied upon and analyses conducted for these evaluations to identify any major sources of uncertainty. Moreover, EPA considered how the information that has become available since the completion of these evaluations might affect reported risks. Based on this review, EPA determined whether these evaluations support any conclusions about the types of management practices that could result in adverse effects.

7.1. U.S. Environmental Protection Agency (1987d)

In the 1987 *Technical Support Document Onshore Oil and Gas Exploration, Development, and Production: Human Health and Environmental Risk Assessment* (1987 TSD; U.S. EPA, 1987d), EPA evaluated the risks that might result from the management of E&P wastes from exploration and production. The potential release routes examined were leaching from pits with and without liners and caps, inadvertent discharges to groundwater through well failure and direct discharges to surface water from wells. The following discussion focuses only on waste management in pits. Discharges from waste management units to water bodies are classified as point sources and regulated under the Clean Water Act. Disposal through injection wells is regulated under the Safe Drinking Water Act. Therefore, these management practices are not further discussed in the context of RCRA.

7.1.1. Evaluation Summary

To characterize wastes generated for the 1987 TSD, EPA initially collected 100 samples of drilling and production waste from 49 sites across the country. Sampling locations included centralized treatment facilities (3 sites), central disposal facilities (4 sites), drilling operations (19 sites), and production facilities (23 sites). EPA analyzed the collected samples for 534 constituents and parameters that included 444 organic compounds, 68 inorganic elements, 19 water quality parameters, and 3 RCRA characteristics.[20] EPA initially limited the quantitative evaluation to 36 inorganic elements and 25 organic compounds based on frequency of detection in waste samples and availability of toxicity values.

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20) Water quality parameters include pH, total suspended and dissolved solids and biological oxygen demand. RCRA characteristics include corrosivity, ignitability and reactivity.

This list was then further refined based on anticipated mobility of constituents in groundwater (i.e., likelihood to reach receptors). Constituents ultimately retained for fate and transport modeling included benzene and arsenic for cancer risk; cadmium, chromium and sodium for noncancer risk; and boron, cadmium, chloride, chromium and sodium for aquatic toxicity and environmental resource damage.

The 1987 TSD modeled fate and transport from pits. A range of disposal unit sizes and distances to receptors were considered. Risks were found to be below levels of concern for all modeled exposure scenarios. For waste disposed in reserve pits, the majority of modeled cancer risks were less than $1{\times}10^{-7}$ and none were greater than $1{\times}10^{-5}$. Only two percent of model runs for unlined pits resulted in noncancer risks from sodium. However, EPA concluded that the high salt content of produced waters would result in noticeable and unpleasant changes to the taste of water concurrent with any elevated risks, which would alert residents and limit exposures.

7.1.2. Uncertainties

As with any evaluation, there are uncertainties associated with the 1987 TSD. Some may arise from the practical limitations of models and data available at the time, while others are driven by changes to industry practices in the decades since the evaluation was finalized. The following discussion summarizes key uncertainties identified during this review and, where practicable, how consideration of more recent data might affect the evaluation findings.

Waste Types Evaluated

The reserve pits modeled in the 1987 TSD contained wastes generated from drilling with water-based fluids. The main types of waste managed in these pits are cuttings and drilling mud. There are a number of other wastes generated during exploration and production (e.g., produced water, sludge) and, as shown in this document, these wastes may contain higher concentrations of some constituents than drilling solids. EPA acknowledged in the 1987 TSD that these other wastes might potentially result in adverse effects to human health and the environment. However, the Agency did not have adequate data at the time on the chemical composition, sources, volumes and management practices for these other waste types to permit evaluation of the associated risks. As a result, no conclusions can be drawn from this evaluation about the risks associated with these additional wastes.

Waste Composition

The largest shift in drilling practices in the past three decades has been the adoption of directional drilling. Although hydraulic fracturing has been used since the 1950s, the practice was not as widespread until the 2000s when advances in directional drilling allowed greater access to formations that had been previously deemed uneconomical (Soeder et al., 2014). This shift in drilling practices resulted in greater volumes of waste due to the greater distance drilled and the large volume of water needed for fracturing. To better understand the extent to which the composition of these wastes may also have changed since 1987, EPA compared the constituent concentrations used in the 1987 TSD and those assembled in the current E&P database.

In 1986, EPA was able to sample only a limited number of facilities due to time and resource constraints. To provide a best estimate of typical waste concentrations from these samples, EPA first weighted selection of sample locations based on indicators of waste generation from previous reports. Drilling site selection was weighted based on total wells drilled in each state, while production site selection was weighted based on annual hydrocarbon production in each region. Samples from the north slope of Alaska were omitted from summary statistics because this region was handled in a separate qualitative evaluation.

The current produced water dataset is based on a review of available literature and so the Agency did not have any control over the type or number of samples available. This resulted in uneven sampling in different regions of the country. Therefore, EPA weighted the available data by the annual hydrocarbon production in each region of the country. All samples within a given region were given the same weight. **Table 7-1** provides a comparison of the 50th and 90th percentile concentrations from vertical wells in the 1987 TSD and horizontal wells in Pennsylvania (the only state with data available) in the current dataset.

Table 7-1. Comparison of Constituent Data for Produced Water

Constituent	1987 Vertical Data			Current Vertical Data			Current Horizontal Data		
	N	50th	90th	N	50th	90th	N	50th	90th
Arsenic	9 / 24	0.02	1.7	51 / 65	0.01	0.20	--	--	--
Benzene	16 / 21	0.47	2.9	27 / 32	0.23	4.9	--	--	--
Boron	24 / 24	10	120	1,369 / 1,370	39	115	192 / 195	21	46
Chloride	21 / 21	7,300	35,000	39,766 / 39,766	27,500	132,048	291 / 291	71,200	132,000
Sodium	24 / 24	9,400	67,000	39,138 / 39,138	15,375	62,678	291 / 291	34,700	52,322

N – Detection Frequency

The two vertical datasets ostensibly reflect the same waste and so should be similar if all sources of variability have been captured. Both high-end and median concentrations of benzene, boron and sodium are similar and median concentrations of arsenic are similar. The similarities between the two datasets provides some confidence that the overall distributions for these constituents. The greatest difference between the datasets is chloride. It is not clear why chloride in the 1987 TSD is lower than both chloride in the current vertical dataset and sodium in the same dataset. This indicates that the 1987 TSD may underestimate concentrations of certain constituents.

The current dataset for drilling fluid was assembled through the same literature review as produced water. However, unlike produced water, there was not sufficient data from across the country to weight the data by region to obtain a more representative national distribution. Instead, EPA conducted a more limited comparison with horizontal data from a single state. **Table 7-2** provides a comparison of the 50th and 90th percentile concentrations contained in the 1987 TSD and the current dataset for horizontal wells in Pennsylvania.

Table 7-2. Comparison of Constituent Data for Drilling Fluid

Constituent	1987 Vertical Data			Current Horizontal Data		
	N	50th	90th	N	50th	90th
Arsenic	6 / 17	ND	0.16	12	0.03	0.18
Cadmium	13 / 17	0.04	1.4	--	--	--
Chloride	17 / 17	3,500	39,000	35	17,000	89,000
Chromium	14 / 17	0.43	290	13 / 21	0.25	1.3
Sodium	17 / 17	6,700	44,000	33	11,400	33,900

N – Detection Frequency
ND – Non-Detect

Some of the trends observed for produced water are also present in the data for drilling fluid. Both high-end and median concentrations of arsenic and sodium are similar, while chloride concentrations in the 1987 TSD are lower than both the current dataset and sodium in the same dataset. Chromium is substantially higher in the 1987 TSD, which might be attributed to the additive chrome lignosulfonate that was historically used to deflocculate clay particles and to reduce fluid viscosity (NRC, 1983). There are reports that this additive is used less frequently in current drilling operations and is often replaced by iron or calcium lignosulfonate (Schlumberger, 2018). However, to the extent the chromium-based additive is still used, the current dataset may underestimate chromium concentrations.

Based on this comparison of datasets, EPA concludes there is general agreement between the two datasets for several constituents. Other constituents were found to be higher or lower in the 1987 TSD, though there is no evidence of a consistent bias in either direction. The greatest difference between the datasets is for chloride. It might be possible that lower chloride levels in the 1987 TSD are the result of analytical error due to improper calibration for high concentrations. There is not enough data available to determine whether other constituents that have a strong relationship with chloride (e.g., strontium) are also lower in this dataset. This remains a source of uncertainty.

Additional Constituents

The 1987 TSD analyzed for 444 organic compounds. A majority of these compounds were not detected in any samples. However, some were later detected at low concentrations in more recent studies. It is possible that the 1987 TSD failed to identify some compounds present because of higher detection limits. It is also possible that some of these compounds were not present in 1987 and were introduced into recent samples by hydraulic fracturing additives. Between 1,400 to 2,500 compounds have been tentatively reported in samples of produced water by different studies. Some of the compounds detected in recent studies were not analyzed for in the 1987 TSD. Therefore, there is potential for additional risks from additives that were not considered in the 1987 TSD.

The 1987 TSD did not address radiation from E&P wastes. Public health concerns were initially raised when pipe scale with high activity was identified in drilling equipment around the Gulf Coast (API, 1989). EPA began efforts to characterize the occurrence and potential impacts of NORM and TENORM in the late 1980s (U.S. EPA, 1993). A draft report was reviewed by the EPA Science Advisory Board (U.S. EPA, 1994), but was not finalized based on the need for additional data to address remaining uncertainties. Around the same time, several states began to collect data on radioactivity in E&P wastes (e.g., WVDEQ, 1990; MIDNR/DPH, 1991; TXBEG, 1995; CADHS/DC, 1996; NYDEC, 1999). To assist states with the management of these and other TENORM wastes, the Conference of Radiation Control Program Directors developed suggested regulations (Part N) that address a structure for licensing programs, worker protection, release limits and conditions for regulatory exemption. These suggestions have been revised and updated on an ongoing basis, most recently in 2004. A number of states have incorporated these suggestions into regulatory programs for E&P wastes (ASTSWMO, 2015). Further discussion of state regulations is provided in **Section 6 (State Programs)**. However, renewed concerns have recently arisen due to the expansion of directional drilling (e.g., U.S. DOE, 2014; WVDEP, 2015; PADEP, 2016). Both the increased waste volume and the potential for higher activities pose additional management challenges. To understand whether and how recent changes in drilling practices might affect the composition of E&P waste, EPA compiled data on radioisotope activities in the E&P Database. The available data indicate that elevated activities of uranium or radium can be present in waste from both vertical and horizontal wells. These elevated activities are not isolated to specific formations and, thus, are likely to have been present at similar levels in samples analyzed for the 1987 TSD.

Model Duration

The 1987 TSD refined the ultimate list of constituents evaluated based on mobility in the environment, focusing on those anticipated to reach receptor wells within 200 years of the initial release. Wells were assumed to be present at distances of 60, 200, and 1,000 meters away from waste pits. This constraint resulted from limitations in the Landfill Liner Model. More recent model runs with the EPA Composite Model for Leachate Migration with Transformation Products on coal ash ponds found that that median time for peak concentrations of arsenic to reach the nearest wells at similar distances ranged from 2,000 to 10,000 years, depending on chemical speciation (U.S. EPA, 2014d). The results of this risk assessment cannot be directly transposed onto E&P wastes. However, it is clear that the 200-year limit is likely to underestimate potential long-term risks.

Constituent Mobility

Partitioning coefficients (K_d) are ratios of constituent mass that is bound to the soil and dissolved in the aqueous phase at equilibrium. Higher values reflect greater retention on the soil and lower mobility through the subsurface. In the 1987 TSD, EPA reviewed the available literature to identify values for each modeled constituent and selected single values intended to be representative for each constituent. However, partitioning coefficients can be affected by a number of environmental factors that are not constant. Some key factors known to affect K_d values include the concentration of the constituent in groundwater, the pH and ionic strength of the solution, the degree of soil saturation, and the type and amount of different sorbents present within the aquifer.

EPA developed the Metal Speciation Equilibrium for Surface and Ground Water Model in 1999 to calculate K_d values for a wider range of environmental conditions and provide a better estimate of constituent mobility for different types of waste (U.S. EPA, 1999a). The most recent version of this model was released in 2006 (Version 4.03). To understand the extent to which single K_d values may overestimate or underestimate constituent mobility, EPA compared values used in the 1987 TSD with those calculated for municipal solid waste landfills (U.S. EPA, 1999b) and coal combustion residual (CCR) landfills (U.S. EPA, 2014d). These calculated values incorporate variability from different aquifer pH, ionic strength, organic matter and iron oxide sorbents. Because these values can vary widely on a national-scale, EPA selected high and low bounds for comparison. **Table 7-3** presents the result of this comparison. It is anticipated that E&P wastes will most closely resemble CCR data because of the similarly high ionic strength of the wastes.

Table 7-3. Comparison of Saturated Zone Partitioning Coefficients (ml/g)

Constituent		1987 TSD	Municipal Solid Waste		CCR Waste Landfill	
			Low	High	Low	High
Arsenic (III)	Unsaturated	5.0	5×10^{-3}	3.0	9×10^{-8}	0.64
	Saturated		2×10^{-3}	3.0	5×10^{-7}	1.1
Arsenic (V)	Unsaturated	5.0	0.2	10,000	1.9	1,100
	Saturated		0.6	10,000	1.0	450
Boron	Unsaturated	3.0	--	--	$< 1 \times 10^{-10}$	0.80
	Saturated		--	--	1×10^{-6}	3×10^{-5}
Cadmium	Unsaturated	6.5	0.1	10	$< 1 \times 10^{-10}$	2.3
	Saturated		0.1	3.0	0.2	7.3

-- Constituent not modeled

In several cases, the entire range of modeled K_d values are lower than the individual value used in the 1987 TSD, often by several orders of magnitude. The major exception is arsenic (V), which ranges from slightly lower to several orders of magnitude higher. Based on this comparison, the groundwater model in the 1987 TSD will tend to underestimates the potential mobility of the modeled constituents.

7.1.3. Findings

U.S. EPA (1987d) found limited potential for risk from disposal of drilling solids in pits. However, there are several uncertainties associated with the analysis conducted that may, on the whole, result in an underestimation of risk. The greatest uncertainties are waste types, management practices, constituents and release pathways that could not be evaluated due to a lack of data. The extent to which the analysis might underestimate actual risks is not clear and EPA did not attempt to update the model results as part of this review. A number of states now have regulations in place that require use of liners and other controls for pits that would potentially mitigate releases from these wastes. Therefore, there is not enough information available from this existing evaluation to draw conclusions about the current disposal practices for E&P wastes.

7.2. U.S. Department of Energy (1998)

In 1998, the U.S. DOE Argonne National Lab modeled exposures that may result from land application of E&P wastes that contain TENORM. This report expands on previous analyses reported in Smith et al. (1995). The practice of disposing of E&P waste in surface soil has been referred to by various terms that describe a range of practices with substantial overlap (e.g., landspreading, landfarming, land application, land treatment). These practices may involve spreading waste on top of the soil or mixing it into the soil column. Application of the waste may occur all at once or in multiple iterations. The primary goal of these disposal practices is the natural attenuation of organic compounds combined with the dilution and immobilization of other contaminants. To this end, nutrients or other soil amendments may be spread along with the waste to promote degradation of organics and the soil may be periodically tilled to improve aeration (API, 2000).

Surface disposal is generally limited to solid or semi-solid wastes such as drill cuttings, pipeline scale and pigging waste, tank and pit sludges, and contaminated soil. Surface disposal of one or more of these wastes at offsite facilities has been reported in at least 11 states (U.S. DOE, 2006). However, this is not assumed to be a comprehensive list because it is based on voluntary responses and does not include onsite disposal. The most common restrictions identified during the review of state programs involve the levels of chloride or TPH in the waste or the resulting soil-waste mixture. Some states also include restrictions on the activity of radioisotopes with limits set anywhere from 5 pCi/g above background to 30 pCi/g total activity, though a number of states have no documented limits. Further discussion of state-specific regulations is provided in **Section 6 (State Programs)**.

7.2.1. Evaluation Summary

Argonne National Laboratory used RESRAD (Version 5.782) to model the doses that may result from direct gamma exposure, inhalation of radon, and ingestion of local soil and produce. The evaluation considered multiple receptors that include residents, industrial workers and recreational users. The most significant differences between the modeled receptors is which exposure pathways are complete (e.g., ingestion of local produce) and the duration of exposure. The primary radionuclide of concern modeled in the evaluation was radium because these radioisotopes and the immediate progeny are those most likely to concentrate in these wastes and drive risk. Because exposures to radiation can be scaled based on the activity present, the evaluation used a unitized activity of 1 pCi/g ^{226}Ra. The immediate, short-lived progeny (half-life less than a year) were assumed to be in secular equilibrium with the applied radium. To address uncertainty about the final soil activity, ANL modeled doses were adjusted to values ranging between 5 and 2,000 pCi/g ^{226}Ra. As part of a sensitivity analysis, additional contributions from ^{228}Ra were estimated as 30% of the activity of ^{226}Ra.

U.S. DOE (1998) found that a surface soil activity of 5 pCi/g ^{226}Ra above background resulted in an additional 30 mrem/yr exposure from gamma radiation. Radon accumulation in the home increased the modeled doses to 60 mrem/yr. All other pathways contributed less than 5% to the total dose. Based on these results, the authors recommended that states that allow landspreading of E&P waste to activities greater than 5 pCi/g above background should consider establishing policies that will restrict future land use or, at a minimum, ensure that future land owners are advised of the activities and the potential associated health risks.

7.2.2. Uncertainties

As with any evaluation, there are uncertainties. Some may arise from the practical limitations of models and data available at the time, while others are driven by changes to the industry practices in the decades since the evaluation was finalized. The following discussion summarizes key uncertainties identified during this review and, where practicable, how consideration of more recent data might alter the evaluation findings.

Total Radium

The lowest identified state limits of 5 pCi/g reflect the combined contributions from ^{226}Ra and ^{228}Ra. U.S. DOE (1998) did not account for this limit on combined activities. Instead the authors assumed that the activity of ^{228}Ra was a third of the longer-lived ^{226}Ra isotope. Therefore, a ^{226}Ra activity of 5 pCi/g would result in a total activity of approximately 6.7 pCi/g $^{226+228}$Ra. This has the potential to result in an overestimation of risk in areas where such limits are enforced.

Erosion

ANL assumed a uniform rate of erosion of approximately 0.04 in/yr that resulted in the eventual depletion of both topsoil and applied waste over time. This rate of soil erosion may occur around fields that are in active rotation where the soil is periodically disturbed, but may overestimate losses in areas adjacent to and particularly underneath a building. The presence of continuous vegetation and man-made structures that shield the soil will limit erosion from wind and encourage suspended soil particles to settle out of overland runoff. Thus, the assumed rate of erosion may underestimate long-term risks.

Dose

ANL compared modeled doses to the National Council on Radiation Protection and Measurements recommended annual dose limits for the general public of 100 mrem above background and concluded that exposures below 5 pCi/g were generally acceptable. The use of dose does not provide information about the magnitude of excess cancer risk. A dose rate of 100 mrem would result in risks considerably higher than the upper bound of the risk range used by RCRA of 1×10^{-6} to 1×10^{-4}. Differences between dose and risk are attributable to how competing mortality risks and age-dependent radiation risk models are handled, the weighting of individual organs, as well as other dosimetric and toxicological assumptions (U.S. EPA, 1999c; 2014e; ISCORS, 2002). ANL did attempt to translate modeled doses to risk of fatal cancer based on conversion factors developed by the International Commission on Radiological Protection (ICRP, 1991). However, the risk of fatality will always be lower than the risk of cancer incidence that is the basis for the RCRA risk range.

7.2.3. Updated Analysis

The review of the previous analysis indicates that some assumptions may overestimate or underestimate the magnitude of exposures on a case-by-case basis, though the largest uncertainty is the use of dose. Therefore, EPA updated the analysis with current models and data to estimate potential risks. EPA used RESRAD-OFFSITE version 3.2 (U.S. NRC, 2013) because the similar model framework allows a more direct comparison with the previous model results.[21] The current version of RESRAD calculates risk with cancer slope factors based on the data from *Biological Effects of Ionizing Radiation (BEIR) VII Phase 2: Health Risks from Exposure to Low Levels of Ionizing Radiation* (NRC, 2006). This allows a direct comparison of results using the RCRA risk range. EPA selected model inputs based on data from

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21) Use of this model does not represent an endorsement by EPA for use in other applications. EPA offices may evaluate similar exposure scenarios with other models based on the specific needs and requirements of each program.

the literature and Agency documents. For some inputs, particularly those related to waste properties and building design, insufficient data are available to construct full distributions. Instead, EPA selected high and low values to provide a bounding analysis. For inputs based on policy or that are considered less variable, EPA selected a single value to manage the number of model runs required. **Table 7-4** presents a comparison of data used in the current analysis and U.S. DOE (1998).

Table 7-4. Comparison of Inputs for RESRAD Model

Parameters	Current	U.S. DOE (1998)
Human Exposure Factors		
Fraction of Time Spent Indoors (%)	0.8	0.5
Fraction of Time Spent Outdoors (%)	0.096	0.25
Exposure Duration (years)	48	30
Inhalation Rate (m^3/day)	23	23
Waste Characteristics		
Radium Isotopes Ratio (^{228}R/^{226}Ra)	0.33 - 3.0	0.3
Radon emanation coefficient (unitless)	0.05 - 0.22	0.04
Application Depth (m)	0.02 - 0.2	0.2
Application Area (m^2)	4,047	8,093
Building Characteristics		
Residential Air change per hour (1/hr)	0.18 - 1.26	0.5
Room Height (m)	2.7	2.5
Room Area (m^2)	100	100
Floor Thickness (m)	0.13	0.15
Effective radon diffusion coefficient of floor (m^2/s)	2.1×10^{-8} - 5.0×10^{-6}	3.0×10^{-7}
Density of floor and foundation (kg/m^3)	2,600	2,000
Total porosity of floor and foundation (unitless)	0.16	0.10
Gamma Shielding Factor (unitless)	0.2 - 0.7	0.7

The total range of values can sometimes span multiple orders of magnitude. This is because the current evaluation aims to provide both an upper and lower bound on highly exposed individuals. However, many of the selected values are similar to or encompass those used in the 1998 analysis. Further discussion of each variable and the data sources is provided below:

- **Inhalation Rates** is the volume of air inhaled by an individual over a specified period of time. It determines the amount of radon taken into the lungs. The selected value is a weighted average of the 95th percentile inhalation rates for adults between the ages of 16 and 71 years old reported in Table 6-16 of the *2011 Exposure Factor Handbook* (U.S. EPA, 2011).
- **Exposure Duration** is the number of years that the receptor lives at a single residence. It determines the total amount of time a receptor is near the waste and potentially exposed. The selected value is the 90th percentile for resident farmers from Table 16-92 of the *2011 Exposures Factors Handbook* (U.S. EPA, 2011).

- **Time Spent Indoors/Outdoors** is the fraction of a day that a receptor spends indoors and outdoors while at home. It determines the fraction of time a receptor is exposed to external radiation with shielding from the walls of the house. It also determines the fraction of time a receptor is exposed to radon that accumulates within the home. The selected values are the reported averages for ages 18 to 64 reported in Table 16-22 of the *2011 Exposure Factor Handbook* (U.S. EPA, 2011). The remaining time not accounted for between these two fractions is assumed to be spent away from home.

- **Radon Emanation Coefficient** is the fraction of the generated radon that escapes from the waste matrix and is able to migrate into the surrounding air prior to decay. It determines the fraction of radon that is released and is available to enter a home. Emanation rates were drawn from available data for scale, sludge and contaminated media (API, 1990; Wilson and Scott, 1992; White and Rood, 2000). The lower end of values reflects intact pipe scale, while the higher end of values reflects disturbed scale and production sludge.

- **Radium Ratio** is the relative amount of ^{228}Ra and ^{226}Ra isotopes in the applied waste. This is not a variable required by the RESRAD model. Instead, EPA used it along with the assumption to define initial radium activities. EPA reviewed available data from the literature (**Appendix B: Constituent Database**) to determine a range of radium ratios. Of those sources that reported activities for both isotopes, the ratios for scale ranged between 0.01 to 2.5 with an average of 0.7, while reported ratios for sludge ranged between 0.01 and 4.7 with an average of 0.5. Based on these data, EPA selected ratios of 1:3 and 3:1 to provide a reasonable range.

- **Application Area** is the lateral extent over which the waste is spread. EPA selected 1-acre (4,047 m^2), based on the assumption that the residence is centrally located. It is anticipated that waste application could cover an area considerably larger than a single acre. However, for the purpose of this model, this area is sufficiently large approximate an infinitely wide source. Increasing the area further will have negligible impacts on the calculated risk. For example, U.S. DOE (1998) found that decreasing the area from 4 to 0.2 acres decreased exposures by only five percent.

- **Application Depth** is the depth below ground surface that the waste is incorporated into the soil. This mixing can dilute the activity of the waste and may contribute some additional shielding from overlying soil. EPA considered two values for the thickness of the contaminated zone. The first depth is 2 cm and represents surficial spreading without any active mixing. The second depth is 20 cm that represents soil tilled with a standard disk tiller. Both values are based on the recommended values in the *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities* (U.S. EPA, 2005).

- **Room Height** is the vertical measurement of an average room in the residence. It determines the volume of air in the house in which radon can accumulate. The selected value was drawn from the U.S. Housing and Urban Development Residential Structural Design Guide (U.S. HUD, 2000).

- **Room Area** is the floor area of an average room in the residence. It determines the volume of air in the house in which radon can accumulate. The selected value is the RESRAD default.
- **Air Exchange Rate** is the number of times that the total volume of air in a housing unit is exchanged with outside air during a given time period. It determines the extent to which radon is able to accumulate in the home before it is cycled out. The selected values are the national 10th and 90th percentile values drawn from Table 19-24 of the *2011 Exposure Factors Handbook* (US EPA, 2011).
- **Concrete Thickness** is the distance that radon must migrate through the floor before it enters a home. It determines the rate at which radon can accumulate in a home. The selected values were drawn from the *U.S. Housing and Urban Development Residential Structural Design Guide* (U.S. HUD, 2000).
- **Concrete Density and Porosity** are the compactness of the floor and the relative volume of void spaces through which radon can travel. These variables determine the rate at which radon can accumulate in a home. Values were drawn from *Characterization of Radon Penetration of Different Structures of Concrete* (U.S. DOE, 1996).
- **Shielding Factor** is the fraction of the gamma ray energy that is absorbed by walls and other obstacles located between the waste and receptor. The shielding factor is applied only when the receptor is indoors. The lower value was drawn from *Generic Procedures for Assessment and Response During a Radiological Emergency* (IAEA, 2000). The higher value is the RESRAD default value. Denser materials, such as concrete and brick, offer higher shielding factors compared to other building materials, such as wood.

EPA limited the scope of this analysis to a single scenario of a resident farmer living around the field where the wastes had previously been applied. EPA only modeled exposures to external radiation and radon because these were previously identified as the primary exposure pathways and there are greater uncertainties associated with other type of releases (e.g., leachate). EPA modeled risks up to 1,000 years following initial disposal of the waste with negligible losses to surface erosion or subsurface leaching. Available data indicate the fraction of radium leached from these wastes is often minimal. Anoxic conditions that may promote releases are not likely to form in the topsoil and any mass that is released may sorb onto surrounding soil. Therefore, the assumption of negligible losses is considered appropriate at this stage.

The model was run deterministically with each combination of the inputs listed in **Table 7-4**. The model results are presented in **Figure 7-1**, plotted as a function of final soil activities ranging from 1 to 100 pCi/g. Given the radium activities measured in the various associated wastes, any of these soil activities could result from surface disposal in the absence of relevant restrictions. Each line on the graph reflects a different combination of inputs, with the top and bottom-most lines reflecting combination of all high-end and low-end inputs, respectively.

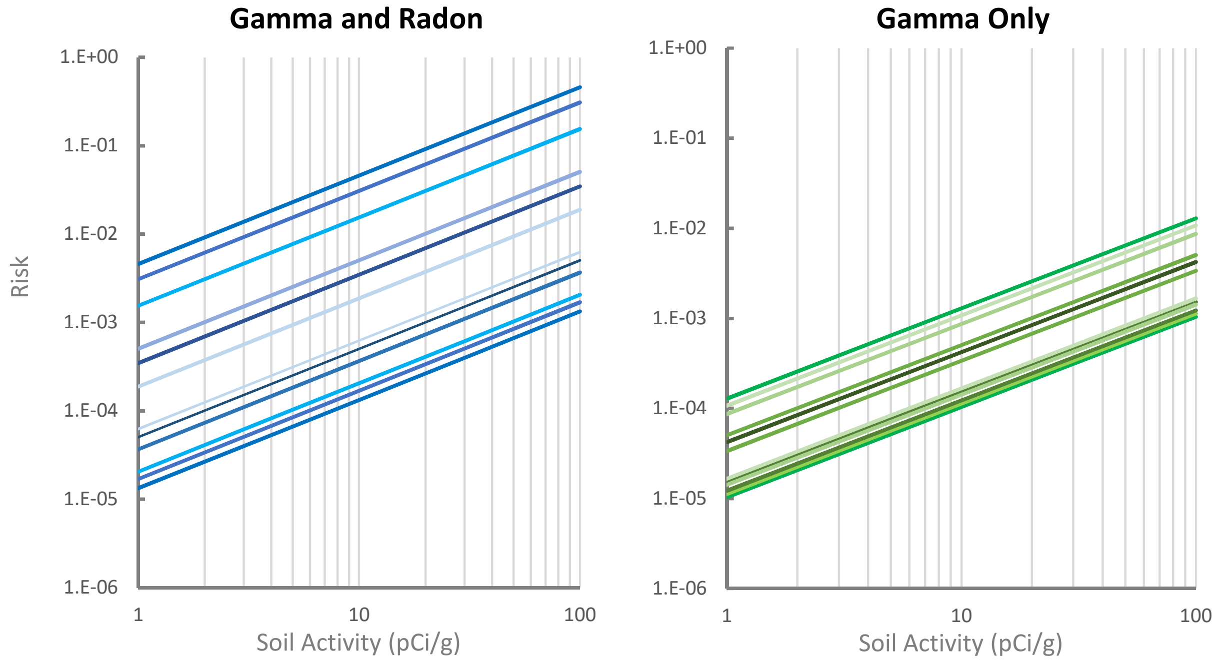

Figure 7-1: RESRAD Model Results With and Without Radon Exposure

Potential risks from gamma radiation and radon greater than 1×10^{-5} are possible at every modeled soil activity. However, the model results do not provide any information about which of these results are most likely. It is possible that some of the modeled combinations are not realistic. For example, the lower radon emanation factor is associated with intact scale. However, removal from the well and mixing with the soil will inevitably disturb the integrity of scale, making higher emanation rates more likely. The range of potential risks from gamma radiation alone (right) is narrower than for combined gamma and radon (left). This is because many model inputs affect radon release and transport. Exposure to gamma radiation is a more direct pathway. The lower bound on modeled risks in both graphs are similar and attributed primarily to direct gamma exposure.

7.2.4. Findings

U.S. DOE (1998) found that soil activities greater than 5 pCi/g can result in exposures greater than the dose limit of 100 mrem/yr recommended for the general public by the International Commission on Radiological Protection. The results of this update to that analysis confirm that exposure to these activities has the potential to result in doses that correspond to risks outside of the Office of Land and Emergency Management risk range. However, this update does not provide a likelihood that such risks will occur from current practices. Based on the activities measured in different E&P wastes (**Section 5: Waste Characterization**), uncontrolled land application of E&P wastes have the potential to result in soil activities at or above 5 pCi/g. However, it is not clear from available information which wastes are currently land applied. Past reports reference application of drill cuttings, drilling fluid, produced water and sludge. A number of states now have regulations in place that limit the activity in waste that can be applied. Even if a higher activity wastes are applied, it is not possible to estimate the resulting soil activity without more information on application rate and frequency. Therefore, there is not enough information available from this existing evaluation to draw conclusions about the current disposal practices for E&P wastes.

7.3. Conclusions

The two identified evaluations indicate that adverse effects are possible from uncontrolled releases of E&P waste. Similar risks have been previously documented in historical damage cases. However, the majority of state regulatory programs now include specific requirements intended to prevent or substantially mitigate these types of risk. For example, the majority of states currently require some form of liner for pits that hold E&P waste and place limits on both where and how land application is allowed. Therefore, these types of uncontrolled releases are less likely to occur. To better understand the potential magnitude and frequency of environmental releases associated with current waste management practices, EPA reviewed the available literature for documented damage cases.

8. Damage Cases

As part of the 1987 Report to Congress (RTC), EPA gathered information on instances where ongoing management practices of E&P wastes had resulted in damage to human health and the environment. The Agency found evidence at the time that damages could occur in instances where these wastes were managed in accordance with applicable regulations. However, there have been considerable changes to both the oil and gas industry and state regulatory programs over the last thirty years. To better understand the effects of these changes, EPA conducted an updated review of recent damage cases that occurred in state, federal or tribal jurisdictions. The following section details the approach used to identify damages and the conclusions that can be drawn from the available information.

8.1. Review of Recent Damage Cases

EPA conducted a review of summary reports and other sources that had either been submitted to the Agency or identified through an independent literature search. Based on this review, EPA identified the following initial sources that had not previously been reviewed:

- *Oil Field Produced Water Discharges into Wetlands in Wyoming* (U.S. DOI, 2002);
- *U.S. EPA Region 8 Oil and Gas Environmental Assessment Effort 1996-2002* (U.S. EPA, 2003);
- *2016 Notice of Intent to Sue for Violation of Nondiscretionary Duties under the Resource Conservation and Recovery Act with respect to Wastes Associated with the Exploration, Development, or Production of Oil and Gas*.
- *Compendium of Scientific, Medical, and Media Findings Demonstrating Risks and Harms of Fracking (Unconventional Gas and Oil Extraction)* (CHPNY and PSR, 2018); and
- Individual news articles, scientific journals and state enforcement orders (Ramirez, 2010; Fehling, 2012; Vengosh et al., 2014; PADEP, 2014a,b; Flesher, 2015; ADSBRL, 2016; Fears, 2016; Lauer et al. 2016; Schladen, 2016; AP, 2018; Geeza et al., 2018; Pappas, 2018).

The scope of damages considered in this review is broad and includes adverse health effects to humans and wildlife, impairment of habitat, and degradation of natural resources. However, it is important to note that this review only considered cases where a reasonably clear link of cause and effect exists between the waste management practice and the resulting damages. Because this review relied on well-documented cases by necessity, it is not expected to be exhaustive. For example, damage claims that were settled outside of court are unlikely to be available in the public record. As a result, this review is not intended to provide a statistically representative sample of the type or frequency of damages that may occur. Instead, it aims to summarize the nature and extent of known damages and to highlight specific management practices that might warrant further review.

8.1.1. Review Criteria

The Agency relied on a number of criteria to determine whether each of the reported incidents fell within the scope of the current review. Incidents that did not meet all the criteria were not retained for further consideration. EPA first applied the “tests of proof” used in the 1987 RTC to determine whether a reported incident qualifies as a damage case (U.S. EPA, 1987a,b,c). An incident was retained if there was sufficient information to classify it under one or more of the following categories:

- **Scientific Investigation:** Damages were found to exist as part of the findings of a scientific study. Such studies could be extensive formal investigations supporting litigation or a state enforcement action, or they could, in some instances, be the results of technical tests (such as monitoring of wells) if such tests were a) conducted with state-approved quality control procedures and b) revealed contamination levels in excess of an applicable state or federal standard or guideline.
- **Administrative Ruling:** Damages were found to exist through a formal administrative finding, such as the conclusions of a site report by a field investigator, or through existence of an enforcement action that cited specific health or environmental damages.
- **Court Decision:** Damages were found to exist through the ruling of a court or through an out-of-court settlement.

EPA further focused the scope of the current review to incidents that occurred between 2012 and 2018. During the most recent review of damage cases in 2010 (See: **Section 2: Summary of Agency Actions**), EPA concluded that a number of incidents had occurred years before the state in question had established relevant regulations and that enforcement of current regulations would prevent the vast majority of identified incidents from reoccurring. Therefore, EPA excluded older incidents both because of the timeframe of the previous review and the fact that older incidents are less likely to be representative of current waste management practices. This is consistent with the Agency’s review in the 1987 RTC that limited the review to the previous five years.

The damage cases assembled in the 1987 RTC were broad and often included incidents that extend beyond the jurisdiction of RCRA. However, the scope of the current review is limited to whether revisions to RCRA Subtitle D regulations are necessary to address ongoing risks from the management of E&P wastes. Therefore, EPA focused the current review to include only management units that E&P wastes currently exempt from regulation under RCRA Subtitle C. For example, the current review did not address release incidents that result from disposal down injection wells. Nor did it address releases of salable petroleum products, unused chemical feedstock, and other non-wastes.

EPA reviewed the release incidents reported in the identified sources based on the above criteria to ensure that the damage cases are both reliable and relevant to the current review. When an incident was judged not to be relevant, it was not retained for further review. When an incident was judged to be relevant or potentially relevant, EPA assembled as much specific information as possible about the location of the release, dates over which the release occurred, type and amount of waste released, the contaminants of concern, type of management unit from which the waste was released, cause of the release, whether the release occurred during operations allowed under state regulations, regulatory response, and any criminal or civil penalties that resulted. However, many sources contain incomplete documentation of the incidents. When insufficient information was available to determine the nature of the release or the associated damages, EPA attempted to collect additional information from other available sources, such as references cited in the initial source document, state websites, and broader web searches. If the Agency was not able to find enough information to meet the test of proof, then these incidents were not retained for further review.

8.1.2. Findings

Of the incidents reviewed, only eight met all the criteria and demonstrated a clear link between the management of E&P wastes and the resulting damages. **Table 8-1** provides a summary of the available information for each of these incidents. A broader list of both the relevant and potentially relevant incidents considered in this review are provided in **Appendix A (Damage Cases)**.

Table 8-1. Summary of Relevant Damage Cases, 2012 – 2018

Location	Release Dates	Waste Type	Reported COCs	Unit Type	Source	Reported Damages
Kern County, CA	1960 - 2018	Produced Water	B, Cl	Evaporation Pit, Spray Irrigation	Seepage from Disposal Unit, Spray Irrigation	Contaminated GW
Pittsburgh, PA	2011 - 2012	Produced Wastewater	Cl	Pit	Liner Leakage	Contaminated GW & SW, Impacted Vegetation
Chartiers, PA	2012	Frac Fluid, Produced Water	Cl, Mn	Pit	Liner Leakage	Contaminated Soil
Hopewell, PA	2013	Reuse Water	Cl	Pit	Unspecified Leak	Contaminated Soil & GW
Amwell, PA	2013 - 2014	Frac Fluid, Produced Water	Cl	Pit	Pump Leak, Liner Leakage	Contaminated Soil
Mount Pleasant, PA	2014	Frac Fluid, Produced Water	Not Reported	Pit	Unpermitted Discharge	Soil Erosion, Deposition to Sediment in SW Body
Yeager, PA	2014	Frac Fluids, Produced Water	TDS, Cl	Pit	Unspecified Release	Contaminated Soil & GW
Midway, TX	2016	Frac Fluid, Produced Water	Not Reported	Wastewater Storage Tanks	Flooding, Tank Failures	Contaminated Soil & SW

Eight incidents involved management of produced water (e.g., wastewater, flowback fluid, brine, reuse water) in pits and tanks. The magnitude of reported releases was highly variable, ranging in volume from approximately 1,300 gallons to over 500,000 gallons. Few sources provided information on the extent of contamination that resulted from these releases, but this may not have been known at the time damages were first identified. Available information shows that corrective action efforts have begun or been ordered to begin at each of these sites. In one case, a fine of $4.5 million was also levied against the facility.

Each of the eight incidents resulted in contamination of one or more environmental medium (i.e., soil, groundwater, surface water, sediment). Most damages were identified from measured concentrations, though few sources indicated what contaminant levels were present or what benchmarks were used for comparison. All of the reported contaminants are inorganic elements commonly found in produced water at elevated concentrations (**Section 5: Waste Characterization**). The most common contaminant was chloride. It is unclear if the contaminants reported served as an initial basis to identify damages or if the list reflects the full extent of contamination considered. There is potential for a number of other inorganic elements and organic compounds to be present in produced water and other E&P wastes, so partial characterization of the spill might result in incomplete remedial efforts.

Four of the identified incidents were associated with units that were not in compliance with existing laws or regulations. For example, one incident (Pittsburgh, PA) involved the management of produced water in a pit that was only permitted to store fresh water. Another incident (Hopewell, PA) involved a pit that did not install the groundwater monitoring wells required by permit and so failed to identify subsurface leaks in a timely manner. A majority of the remaining incidents were a result of faulty or degraded equipment (e.g., poorly installed liners, tank collapse, leaks from pumps).

It is noteworthy that a majority of the identified incidents occurred in Pennsylvania. However, it is highly unlikely that the actual frequency of releases is so disproportionately high in Pennsylvania compared to other states. Instead, given the high level of scrutiny that has been applied to the state in recent years due to increased concerns about drilling in the Marcellus shale, it is more likely to be a result of better documentation and communication with the public. Thus, the lack of damage cases identified in other states does not necessarily mean that none have occurred, nor does it mean that other states have not taken appropriate steps to address the environmental impacts from releases. However, the lack of available data for other states make it difficult to draw conclusions about the representativeness of the identified damage cases.

8.2. Spill Reporting

During the search of state websites associated with E&P waste regulatory programs, EPA identified four states that maintain centralized databases of spills that occur during site activities (i.e., Colorado, New Mexico, North Dakota, Wyoming). Although several other states collect information on spills, the data are extremely difficult to aggregate because specific information, such as the facility location (latitude and longitude) or the facility name is required to search the data (e.g., Oklahoma, Pennsylvania, Texas, West Virginia). The effort needed to assemble and review data for these additional states was prohibitive at this time. Regulations in these states require that spills above a set volumetric threshold be reported to the state within a certain timeframe. Identification and cleanup of the spills is conducted in accordance with state requirements for corrective action and so sites are typically not subjected to fines in response. Because the releases are generally contained and addressed onsite without the need for enforcement action,[22] these spills were not classified as damage cases. EPA reviewed the spill databases from the four states to identify data related to spills of E&P waste from waste management units (e.g., pits, tanks). **Table 8-4** provides a summary of the available data over a 3-year period between 2014 and 2017.

Table 8-2. Summary of Reported Spills for Select States, 2014 – 2017

State	Unit Type	Number of Active Units	Number of Reported Releases	Number Reported with Volume	Total Reported Volume (BBLs)	Average Reported Volume (BBLs)	Most Frequent Spill Causes
Colorado	Pits	3,417	51	17	21,159	1,245	Not Reported (31), Equipment Failure (12), Human Error (8)
	Tanks	1,441	529	206	14,150	69	Equipment Failure (251), Not Reported (235), Human Error (34)
	Central Disposal	41	11	10	1,290	129	Human Error (6), Equipment Failure (4), Not Reported (1)
New Mexico	Pits	NR	5	5	127	25	Not Reported (5)
	Tanks	NR	516	433	82,262	190	Not Reported (197), Equipment Failure (169), Human Error (24)
Wyoming	Total	NR	408	407	203,566	500	Equipment Failure (349), Human Error (38)

NR – Not Reported
Colorado: http://cogcc.state.co.us/cogis/IncidentSearch.asp
New Mexico: https://wwwapps.emnrd.state.nm.us/ocd/ocdpermitting//Data/Incidents/Spills.aspx
Wyoming: http://deq.wyoming.gov/admin/spills-and-emergency-response/

A similar number of total spills were identified across several states, though the typical volume released varied more widely. The most common waste reported by each state was produced water, which is also the largest volume waste generated during well production. Other wastes include drilling mud and tank bottoms. The reported spills can be generally categorized as resulting from equipment failure (e.g., damaged liner, breached berm, corrosion), weather events (e.g., flooding, lightning), and human error (e.g., overfilling). However, root causes do not always fall into neat categories, as equipment failure may sometimes be a form of human error due to poor maintenance or lack of planning. Nearly half of the incidents had no reported cause. The types of spills identified in this review align well with the findings of previous reviews of spills in other regions of the country (U.S. EPA, 2015b; 2016a).

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22) For example, it has been reported that around 80% of spills in North Dakota are contained onsite (King and Soraghan, 2015).

Although the reported spills were identified between 2014 and 2017, that does not mean all of the spills originated during this timeframe. Some of the "historic" spills occurred at some earlier time, but were only identified during decommissioning of a tank battery, replacement of subgrade equipment, or other routine facility maintenance. Subsurface releases are more difficult to identify and this may explain the greater number of spills recorded for tanks. While groundwater monitoring may help to eventually detect leaks, contamination may not reach the installed wells before the unit is taken out of service for repair or decommissioned.

Only one state, Colorado, provided information on how corrective action is implemented at spill sites. Colorado requires that the extent of soil and groundwater contamination be identified by sampling of soil and groundwater assisted with photoionization detector and the installation of temporary groundwater monitoring wells. Chemical analyses are generally limited to TPH, BTEX and select inorganics. Soil remediation typically involves excavation of the contaminated soil and/or in-situ treatment (e.g., stabilization). Groundwater remediation typically involves in-situ treatment (e.g., chemical oxidation, bioremediation), natural attenuation, and/or pumping groundwater to an offsite treatment facility. Sites are required to sample groundwater quarterly until relevant maximum contaminant levels are achieved. Of the 149 spills found to have reached groundwater between 2014 and 2017, 142 (95.3%) were considered resolved as of late-2017.

8.3. State Inspection and Enforcement

EPA searched the websites of thirty-five states for information on releases of E&P waste. During this search, EPA identified three states that published summary reports on the number of inspections and resulting enforcement actions taken on a yearly basis. These actions included both informal notices of the violation and formal enforcement orders. EPA did not include these violations in the list of damage cases because a number of violations identified did not involve actual releases to the environment. Rather, these other violations involved non-compliance with specific state requirements, such as failure to adequately label tanks or remove equipment from around inactive wells. Enforcement of these requirements helps prevent minor infractions from potentially becoming major releases. The violations that did result in releases are a clear result of non-compliance with state regulations, though there was not enough information available to define the type of waste involved, the cause of the release, or the resulting damages. Therefore, it is difficult to aggregate individual violations in a meaningful way. However, these reports still provide information that can be used to better understand the structure and implementation of state programs. **Table 8-2** provides a summary of the available information for these three states. The number of inspectors was from state websites. EPA did not include supervisors or support staff (e.g., quality assurance officer) in the list of inspectors.

Table 8-3. Summary of State Inspections and Enforcement Actions in 2018

State	Source	Number of Inspectors	Number of Inspections	Number of Violations	Penalties Assessed
Colorado	CODNR (2019)	20	Not Reported	163	$9,832,096
Pennsylvania	PADEP (2018)	100*	35,556	2,290	$9,590,432
Texas	TXRRC (2018)	158	130,064	29,964	$5,718,143

* Most recent data available from IPAA (2013).
Colorado Inspectors: https://cogcc.state.co.us/about.html#/staffmaps
Texas Inspectors: https://www.eenews.net/energywire/2017/02/09/stories/1060049755

State inspectors work to ensure compliance with applicable state regulations at both drilling sites and centralized waste disposal operations. Therefore, the number of inspectors and enforcement personnel employed by states is a useful metric that can be compared with different measures of enforcement (e.g., number of inspections) or production (e.g., number of wells) to better understand how the state programs are currently implemented. A greater number of inspectors relative to the number of facilities that require inspection is generally considered desirable because it would allow more regular inspection of individual sites. Infrequent inspections may allow violations to go unnoticed, particularly in remote or unpopulated areas, which may eventually result in environmental releases.

Data for these states indicate that in 2016 each inspector visited an average of 356 wells in Pennsylvania and 781 wells in Texas. Data on the number of inspections was not identified for Colorado; however, the state reported that each inspector visited an average of 1,000 wells in 2015 (COOGTF, 2015). At these rates, it would take between 2.2 and 2.7 years to visit every well in these states, though it is unlikely each of the wells would be visited with the same frequency. States can and do place greater emphasis on inspections of certain operations. The Colorado Department of Natural Resources reports the use of a risk-based strategy to prioritize inspection of the phases of E&P operations considered most likely to experience violations (CODNR, 2014). A study conducted with data from the Pennsylvania Department of Environmental Protection found that the average time between inspections in this state increased from 0.3 years for newly installed wells to 2.8 years for those in operation for nearly a decade (Ingraffea et al., 2014). This compares well with the calculated average of 2.2 years for all wells.

There is, however, no apparent correlation between the number of inspections conducted and the number of violations identified across the different states. States with fewer reported violations tended to levy higher individual fines. Larger fines may be used as a deterrent to compensate for fewer staff or less frequent inspections. However, it is not clear how states keep track of violations. The total number reported might capture each individual violation identified or only the sites where violations occurred. Therefore, it is difficult to draw meaningful comparisons among the states.

As part of the 1987 RTC, EPA compared the number of inspectors and enforcement personnel in 12 states with the number of active oil and gas wells in the states. EPA updated this comparison for 11 of the same states based on the most recent data available. Data were not identified for Kansas and so it is not included in the current comparison. **Table 8-3** provides estimates of the number of inspectors employed relative to the number of active wells in each state. Recent estimates align well with the estimates for western states made in 2015 (COOGTF, 2015).

Table 8-4. Summary of Inspection and Enforcement Personnel in Selected States, 1987 - 2018

State	1984-1986			2017-2018			Change to Wells per Inspector
	Active Wells	Number of Inspectors	Wells per Inspector	Active Wells	Number of Inspectors	Wells per Inspector	
Alaska	1,295	16	81	2,421	5	484	**↑ 498%**
Arkansas	11,982	9	1,331	11,563	3	3,854	**↑ 190%**
California	56,645	31	1,827	50,874	40*	1,271	↓ 30%
Louisiana	40,259	68	592	35,839	31	1,156	**↑ 95%**
New Mexico	40,294	10	4,029	57,868	18	3,215	↓ 20%
Ohio	60,553	66	917	42,059	36	1,168	**↑ 27%**
Oklahoma	122,667	52	2,359	81,822	50	1,636	↓ 31%
Pennsylvania	44,789	34	1,317	78,842	100*	788	↓ 40%
Texas	278,811	120	2,323	305,895	158	1,936	↓ 17%
West Virginia	48,395	15	3,226	55,912	18	3,106	↓ 4%
Wyoming	14,438	12	1,255	33,366	11	3,033	**↑ 142%**

* Most recent data available from IPAA (2013).
Alaska Inspectors: http://doa.alaska.gov/ogc/reports/reportsAndStudies/AOGCC_Statement_to_Gov.pdf
Arkansas Inspectors: http://www.aogc.state.ar.us/about/staff.aspx
Louisiana Inspectors: http://www.dnr.louisiana.gov/index.cfm/page/558#Engineering-Regulatory-Division-Direct
New Mexico Inspectors: http://www.emnrd.state.nm.us/OCD/about.html
Ohio Inspectors: http://oilandgas.ohiodnr.gov/inspectors
Oklahoma Inspectors: http://www.occeweb.com/contactlist/ogcontacts.htm
West Virginia Inspectors: https://apps.dep.wv.gov/oog/contact_new.cfm
Wyoming Inspectors: http://wogcc.wyo.gov/home/contacts

EPA noted in the 1987 RTC that enforcement of regulations was made more difficult in some regions of the country by the limited availability of state inspection and enforcement personnel. However, multiple states have decreased the number of inspectors over the past three decades. States that increased the number of inspectors are often those that have seen recent increases in production from tight oil and shale gas reservoirs. The magnitude of change in the well-inspector ratio ranges between a 40% decrease to a nearly 500% increase. Although the percent change is useful to track trends within a state, it does not provide a meaningful comparison between states as the state with the greatest increase (i.e., Alaska) still maintains the lowest overall ratio. In addition, statistics based on number of active wells may not adequately reflect the waste management units and other equipment associated with the wells that must also be inspected. There can be multiple pits and tanks present at a single drilling site. There can also be pits, tanks, and other management units (e.g., land application) at offsite disposal locations. Yet, as discussed in **Section 4 (Waste Management)**, information available on the total number and location of such units in each state is limited.

Based on inspection rates previously estimated for Colorado, Pennsylvania and Texas, it could take the remaining nine states anywhere from 0.3 to 10.8 years to cover all of the active wells with the current number of inspectors. It is not apparent whether an ideal ratio of wells (or other metric) to inspectors exists. The same number of wells may need greater or fewer inspectors in different states based on a number of regional factors, such as the average distance between wells and the use of other methods to limit violations (e.g., spill reporting requirements, groundwater monitoring, higher fines).

The frequency of inspections is an important consideration, but how inspectors interpret and enforce the state regulations are also important considerations. Therefore, it is critical that the inspectors are adequately trained to ensure both an understanding of the issues that may be encountered around E&P sites and consistent identification of and response to violations. This may accomplished through development of training standards, inspector certification programs or other technical assistance efforts. Some states have standardized training programs in place and some have taken public steps in recent years to invest additional resources. West Virginia developed a standardized observation checklist and an operations and maintenance questionnaire for the inspection of pits and tanks to ensure the field observations were recorded in a consistent method in response to a study in 2013 commissioned by the state legislature (WVDEP, 2013). In 2016, California awarded a contract to TOPCORP, an educational consortium composed of the Colorado School of Mines, Pennsylvania State University and University of Texas at Austin, to train inspectors through a combination of online training, classroom instruction and field experience.

8.4. Conclusions

EPA reviewed the release incidents that had been submitted to the Agency, as well as additional incidents identified during this review, to understand the type and frequency of releases from waste management units containing E&P wastes. Altogether, this review identified eight confirmed damage cases. During the damage case review, EPA also identified several state databases that provide information on the number of violations identified during inspections or reported spills. The databases include thousands of additional incidents; however, these incidents were not counted as damage cases because there was no evidence provided of adverse effects. Reported violations did not always involve releases to the environment. A number involved non-compliance with specific state requirements, such as failure to adequately label tanks or remove equipment from around inactive wells. Reported spills did involve releases to the environment; however, these releases were often limited by secondary containment and were addressed upon discovery without the need for state enforcement action. The conclusions that can be drawn from available data on violations and spills are more limited because these datasets primarily represent instances where the existing regulations were successfully enforced. However, the types of releases observed from spills align well with findings identified in both in this current review for damage cases and a previous reviews of spills conducted by the Agency (U.S. EPA, 2015b; 2016a).

EPA studied the available data to determine whether patterns exist in the type and frequency of releases. It does not appear that any one type of waste management unit is more likely to result in releases; however, little information was identified for some types of waste management units (e.g., land application). The available data indicated that a greater proportion of the identified damage cases involved pits and a greater proportion of reported spills involved tanks. It is possible that releases to the subsurface from pits and buried equipment make it more difficult to identify releases from equipment failure. However, routine maintenance and inspections during the operational life of the unit, as well as requirements to survey the area when a unit is taken out of service for periodic cleaning or repair can help to ensure that releases are identified and remediated.

EPA found no indication that the types of uncontrolled releases from waste management units identified in historical damage cases are common. The two main causes of releases identified from E&P operations are now equipment failure (e.g., corrosion) and human error (e.g., overfilling tanks). These types of releases can be mitigated within the framework of existing state programs through increased enforcement of existing state regulations. However, some states appear to have reduced the number of inspectors relative to the number of active wells over the past three decades. This indicates that there is an opportunity to improve compliance through greater resources toward enforcement.

9. Summary and Conclusions

In 1988, EPA issued a regulatory determination that exempted wastes associated with the exploration, development and production (E&P) of crude oil, natural gas and geothermal energy from Subtitle C of RCRA (53 FR 25446). Over the last three decades, there have been significant advancements in the production of crude oil and natural gas from hydraulic fracturing and directional drilling used to access black shale, tight oil and other "unconventional" formations. This document reviews the information currently available to the Agency about the generation, management and ultimate disposal of E&P wastes, assesses the likelihood of adverse effects to human health or the environment from current practices and presents EPA's determination of whether revisions to federal regulations are necessary to address the identified risks. This review focused primarily on E&P wastes from crude oil and natural gas, as available data indicate that geothermal production remains limited to a few states and has not undergone a similar surge in production. This section summarizes the findings of EPA's review and documents the Agency's rationale for why revisions to regulations for E&P waste management are not necessary at this time, based on the currently available information.

In the 1988 Regulatory Determination, EPA laid out a multi-pronged strategy to identify and address issues posed by the management of E&P wastes, that included working to improve state programs as well as addressing gaps in federal Subtitle D regulations. The Agency has since taken a number of steps to improve existing waste management programs by supporting independent reviews of state programs (e.g., State Review of Oil and Natural Gas Environmental Regulations) and compiling existing guidance and information on best management practices (e.g., U.S. EPA, 2014b). These efforts have resulted in substantive changes to state regulations for pits, tanks, offsite disposal, centralized facilities, spill reporting, corrective action, remedial standards, and other areas. EPA has also undertaken a number of important efforts and actions related to E&P operations under other Agency programs, such as a study of the potential impacts of hydraulic fracturing on drinking water resources (U.S. EPA, 2016a) and new regulations that address effluent limitation guidelines and pretreatment standards for oil and gas operations (44 FR 22069, 58 FR 12454, 61 FR 66086, 66 FR 6849, 81 FR 41845).

In 2016, EPA was sued for its alleged failure to review and, as necessary, revise its federal non-hazardous solid waste regulations for E&P wastes. This lawsuit was based on section 2002(b) of RCRA, which requires every regulation promulgated under the Act to be reviewed and, where necessary, revised not less frequently than every three years. In response to the lawsuit, EPA entered into a consent decree to conduct the review and formally document whether revisions are necessary at this time. To support this effort, EPA conducted an extensive literature review of government, industry and academic sources to supplement the information available from previous Agency actions. EPA also conducted a review of available information on factors such as management practices, waste characteristics, state programs and damage cases in order to determine whether changes to the federal solid waste regulations are necessary.

In sum, the combined use of hydraulic fracturing and directional drilling has altered the energy production landscape in the United States. Production in some states, such as North Dakota and Pennsylvania, has increased by nearly an order of magnitude in the past decade. As of 2017, horizontal wells accounted for nearly 13% of active wells in the United States (U.S. DOE, 2018e). Although the number of newly installed wells has declined sharply in recent years, production has continued to increase as a result of higher production rates from the horizontal wells (IPAA, 2017; U.S. DOE, 2018c,d). Increased production has the potential to generate greater volumes of waste. Some states collect and maintain data on the volumes of E&P wastes generated within their respective borders, but the methods and metrics used to collect these data are not uniform and so waste volumes reported at a national scale are only estimates. It is clear from available data that produced water accounts for the vast majority of the wastes generated, followed distantly by wastewater treatment residuals, spent drilling fluid and drill cuttings (API, 2000). A number of other waste liquids and solids are generated at far lower volumes and may be comingled in the same pits and tanks as higher-volume wastes prior to disposal.

Available data indicate that a considerable fraction of both liquids and saturated solids are disposed through injection into deep formations; however, this disposal method falls outside the scope of the RCRA Subtitle D regulations in 40 CFR Part 257. There are a number of other options available for both onsite or offsite management of the remaining wastes, depending on the local infrastructure and state regulatory requirements. States with higher oil and gas production are more likely to have centralized or commercial facilities designated specifically for the treatment and disposal of E&P wastes. States with lower production are more likely to utilize existing infrastructure for non-hazardous wastes. However, the way that wastes are ultimately managed is primarily a decision made by industry within the bounds of applicable state and federal regulations.

Both hydraulic fracturing and directional drilling have the potential to impact the composition of E&P wastes. EPA reviewed publicly available data on the composition and behavior of these wastes. This review shows that there can be orders-of-magnitude variability in the composition of each waste type, though trends are apparent for certain constituents that might be used to predict where elevated levels are more likely to occur. Some inorganic elements (e.g., lithium, molybdenum), organic compounds (e.g., benzene) and radioisotopes (e.g., radium) appear to be correlated with either the organic carbon content of the source rock or the salinity of the formation water. Horizontal wells are frequently drilled a greater distance through organic-rich rocks with saline formation water, and therefore higher constituent levels may be more common in the wastes from these wells, but similar orders-of-magnitude levels can be possible in the wastes from vertical wells. Therefore, it is likely that similar regulatory controls would be appropriate for the wastes from both types of wells. However, waste composition is not static. Wastes may be intermingled during storage or treated in preparation for disposal, which may result in dilution or concentration of constituent levels. Therefore, it is important to understand the waste composition and behavior at the time of disposal to determine whether the wastes are being managed appropriately.

EPA reviewed state regulations for E&P wastes to determine the scope of coverage (e.g., the wastes and activities), and the level of detail and precision in the requirements. This analysis provided an understanding of state programs and whether each program includes elements that are part of comprehensive waste management programs (e.g., waste containment, monitoring, unit closure), and that would likely be elements of a revised federal solid waste regulation were that deemed to be necessary. EPA reviewed 28 of the 34 states with reported oil and gas production, which together account for over 99% of oil and gas production in the United States. The result of this review shows that states are actively engaged in addressing the challenges posed by increased E&P operations, and have been responding in part by updating their waste management programs. A total of 24 states, which account for approximately 95% of national production, have updated their regulations applicable to E&P wastes since 2013. The scope and specificity of regulatory programs varies among the states, based on multiple factors such as the quantity of oil and gas produced in the state and the prevalence of hydraulically fractured wells. Despite this variability, EPA found that states incorporate many of the regulatory elements that are important components of waste management programs, such as requiring liners for pits, secondary containment and groundwater monitoring. This provides confidence that the scope of current state programs is robust. However, the way that regulations are interpreted and implemented is also important considerations.

To better understand which practices may pose concern, EPA also reviewed the assembled literature for existing evaluations that had drawn conclusions about the potential for adverse effects from management of E&P wastes. Two existing evaluations identified potential adverse effects associated with uncontrolled releases from pits and land application. EPA reviewed both to determine whether the data and analyses that underpin these findings are of sufficient quality to support conclusions about the current management of E&P wastes. Based on this review, EPA concluded that the identified risks are possible when no controls are in place, as has been previously documented in historical damage cases. However, many state programs now include specific requirements that address issues, such as liners for pits, limits on land application, and other standards that address the risks associated with historical damage cases. Therefore, EPA also reviewed available data on recent environmental releases to better understand the current performance of state programs.

EPA reviewed the release incidents that had been submitted to the Agency, as well as additional incidents identified during this review, to understand the type and frequency of releases from E&P waste management units. EPA considered releases from these units that resulted in documented adverse health impacts to humans and wildlife, impairment of habitat or degradation of natural resources. EPA further focused this review to releases that had occurred or were ongoing in the past six years to best reflect current management practices. Applying these criteria, this review identified eight damage cases. During the review of damage cases, EPA also identified several state databases that provided information on the number of violations identified during inspections and reported spills. The databases include thousands of additional incidents; however, these releases were not counted as damage cases because there was no evidence available of adverse effects. Reported violations did not always involve releases to the environment. A number involved non-compliance with specific state requirements, such as failure to adequately label tanks or to remove equipment from around inactive wells. Reported spills did involve releases to the environment; however, these releases were often limited by secondary containment and were addressed upon discovery without the need for state enforcement action. EPA reviewed the available data to determine whether patterns exist in the type and frequency of releases and found no indication that the types of uncontrolled releases identified in historical damage cases are common. Instead, human error (e.g., overfilling tanks) and equipment failure (e.g., liners damaged during solids removal) are the two main causes identified from the available data. These types of releases can be appropriately and more readily addressed within the framework of existing state programs through increased inspections, improved enforcement and other targeted actions than through the imposition of addition requirements under subtitle D of RCRA.

Based on the information gathered for this review, EPA concludes that revisions to the federal regulations for the management of E&P wastes under Subtitle D of RCRA (40 CFR Part 257) are not necessary at this time. The oil and gas industry has undergone a significant transformation in recent years from the use of directional drilling and hydraulic fracturing to access unconventional formations, but states have also revised their regulatory programs to adapt to the challenges posed by these technological advancements; some within the last year. While higher constituent levels may occur more frequently in wastes from newer horizontal wells, similarly high levels are also possible in wastes from vertical wells. Therefore, it is likely that similar regulatory controls are appropriate for the wastes from both types of wells. Based on EPA's review, current state programs incorporate the majority of elements that are important components of waste management programs, which indicates that the scope of existing regulatory programs is robust. There is considerable diversity in how these elements are incorporated in the different state programs, and so how the programs are implemented is also an important consideration. EPA therefore also examined the implementation of state programs based on the frequency, magnitude and extent of recorded releases. Historical damage cases and evaluations have shown that adverse effects can result from uncontrolled releases of E&P wastes. However, there is currently no evidence that these types of releases are common, as majority of the recently identified releases were well-contained and addressed onsite. The primary causes identified for these releases were human error and non-compliance with existing state regulations. The available information does not indicate that new federal solid waste regulations would prevent or substantially mitigate these types of releases. Instead, human error and non-compliance can be appropriately and more readily addressed within the framework of existing state programs through increased inspections, improved enforcement and other targeted actions. EPA will continue to work with states and other organizations to identify areas for continued improvement and to address emerging issues to ensure that E&P wastes continue to be managed in a manner that is protective of human health and the environment.[23]

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23) EPA signed a memorandum of understanding with STRONGER on November 19, 2018 to collaborate and improve both environmental protections and economic outcomes through enhanced enforcement and compliance efforts for E&P waste management.

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Appendix A: Damage Cases

This appendix provides a summary of the Agency's review of damage cases discussed in **Section 2 (Summary of Agency Actions)** and **Section 8 (Damage Cases)** of the main text. EPA reviewed the release incidents that had been submitted to the Agency, as well as any additional incidents identified during this review, to understand the type and frequency of releases from the waste management units that contain E&P wastes. EPA considered releases from these units that resulted in documented adverse health impacts to humans and wildlife, impairment of habitat or degradation of natural resources. EPA further limited this review to releases that had occurred or were ongoing in the past six years to best reflect current management practices.

- **Attachment A-1:** provides a list of sources on alleged release incidents of E&P waste provided by the Natural Resources Defense Council in the 2010 *Petition for Rulemaking Pursuant to Section 6974(a) of the Resource Conservation and Recovery Act Concerning the Regulation of Wastes Associated with the Exploration, Development, or Production of Crude Oil or Natural Gas or Geothermal Energy*.
- **Attachment A-2:** provides the result of the Agency's review of damage cases, which includes summaries of release incidents found to meet all of the review criteria, as well as those that appeared to meet the criteria but did not have sufficient information to determine the cause of the release, the adverse effects, or other pertinent information.

Attachment A-1:

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Attachment A-2:
Summary of Recent Damage Cases

[Due to the file size, this spreadsheet is maintained as a separate file.]

Appendix B: Constituent Database

This appendix provides a summary of the data collection efforts conducted in support of this document. The intent of the literature review is to assemble existing data that can form the basis for conclusions about the composition and behavior of wastes generated by exploration, development and production (E&P) operations. The data review process, as well as the rationale for exclusion of any data from the assembled sources, is discussed in the following sections. The citations in this appendix address only those sources cited in the body of this appendix. The E&P Database contains a full list of the citations associated with the dataset.

- **Attachment B-1:** provides the E&P Database, which contains the constituent data relied upon in tis review to characterize concentrations present in and released from the different waste types.

B.1. Data Collection

EPA reviewed the available literature for studies that contained information on E&P waste. This initial review focused on publicly available data that that could be reasonably assembled without more formal information collection efforts. The purpose of this current effort was to determine whether the available data is sufficient to draw conclusions about E&P wastes and where additional data is needed to understand the impacts to human health and the environment that may result from the current management practices for these wastes.

Some potentially relevant sources were already available from previous Agency investigations. EPA supplemented these sources with reports drawn from the webpages other federal and state agencies with jurisdiction over oil and gas well permitting, operation and/or waste management. EPA first reviewed these sources to develop a baseline understanding of the current universe of waste types, waste composition and drilling practices to focus further searches. EPA then queried multiple databases of peer-reviewed literature, such as Science Direct, with various combinations of descriptive keywords to capture the different wastes (e.g., produced water), constituents (e.g., radium) and drilling practices (e.g., hydraulic fracturing). Finally, EPA reviewed the citations from each study to identify any additional sources that had not yet been captured during the review. Once the citations list had been exhausted, EPA reviewed the identified studies, updated the baseline search terms, and repeated the literature search. This process was repeated until no new sources of information were identified.

B.2. Data Quality Review

EPA reviewed all the literature sources assembled to ensure that the data from each were of sufficient quality to form a basis for conclusions on the composition and behavior of E&P waste. The following subsections detail how the Agency applied the data quality assessment factors outlined in *A Summary of General Assessment Factors for Evaluation the Quality of Scientific and Technical Information* (U.S. EPA, 2003). The following subsections detail the review for each major assessment factor. When it was determined that data from a particular study was not relevant, it was excluded from the database.

When individual data points or entire studies were found to introduce an unacceptable level of uncertainty, these data were filtered out from the dataset prior to any analyses. However, these data were left in the database for future reference.

B.2.1 Evaluation and Review

Evaluation and review is the extent to which the findings of a given study have undergone sufficient independent verification, validation and peer review. An independent review is one conducted by technical experts who were not associated with the generation of the work under review either directly through substantial contribution to its development, or indirectly through significant consultation during the development of the work. Independent review is intended to identify any errors or bias in how data are collected, handled or interpreted, and also to ensure that the findings are accurate and reliable.

Data reported in grey literature has not necessarily undergone formal peer review, though some have been made publicly available for review and comment as part of past Agency rulemakings. Most of the data were collected in accordance with standardized analytical methods that have been validated. EPA relied primarily on raw data from these studies. Any further analyses of the data were only considered as supplementary lines of evidence to corroborate conclusions drawn from the data. External review of each study in isolation would not provide any indication whether the raw data are appropriate for the current application. Instead, EPA relied on other quality metrics to determine whether data was fit for purpose. EPA only excluded data from one study as a result of the level of evaluation and review. One study reported a large amount of leachate data for various wastes collected by a secondary source, but noted that only a subset of the data had been independently validated (LADNR, 1999). EPA retained all of the reported data in the E&P Database, but filtered our all non-validated samples prior to any analyses.

B.2.2 Applicability and Utility

Applicability and utility is the extent to which the data are relevant for the intended use. This means the purpose, design and findings of the study support the intended application of the data. EPA reviewed the assembled studies to ensure that the data contained in each are representative of generated E&P wastes and environmental conditions relevant to anticipated waste management scenarios.

Waste Type:

Data collection was focused on the wastes generated from E&P activities. Some studies reported data for samples outside of this scope. These data often reflected wastes generated at downstream refineries. These wastes may be similar in appearance to those generated at the drilling site, but the composition can be different as a result of losses during storage (e.g., volatilization) or treatment at the refinery to produce a salable product. This represents a major source of uncertainty and so these data were excluded from the E&P Database.

EPA further focused the literature review on the waste types with the greatest amount of data available. These tended to be those either generated in the greatest volume (e.g., produced water) or those that pose specific management issues (e.g., well scale). There are a number of additional wastes generated during the course of E&P activities, such as rig wash (U.S. EPA, 2002). Little characterization data was identified for many of these additional wastes and so no conclusions could be drawn about the typical composition of these additional wastes.

Many studies reported data on individual E&P waste types as generated (e.g., drill cuttings), but others reported data on E&P wastes after management with other E&P wastes (e.g., drilling solids) or treatment in anticipation of disposal (e.g., stabilization/solidification). All of these samples can provide useful information about the impact of management practices on waste composition and behavior. Therefore, EPA retained all the different sample types in the database, but flagged the relevant differences to facilitate comparison.

Country of Origin:

When reviewing the available literature, EPA drew data from any well drilled in North America. The country of origin was labeled for each sample in the E&P Database. It is unknown whether wastes from Canada or Mexico are substantially different from those in the United States given the sparseness of available data. However, if relationships exist between geology and waste composition as anticipated, then these data can still provide useful information. Therefore, EPA included data from Canada and Mexico in the E&P Database. These data were used to identify relationships between constituents, but were not incorporated in any summary statistics. Data from countries outside of North America were not incorporated in the database, but were considered as a secondary source of information to supplement discussion and corroborate findings. These international sources are cited in the main text where applicable.

Well Type:

EPA drew data for all well types during the review of the available literature, including wells used as a source of potable water and brine where the water produced is a valuable product instead of a waste. Some of these wells fall outside the scope of this document, but if relationships exist between geology and waste composition as anticipated, these data can still provide useful information. EPA incorporated the data for these other wells in the E&P Database with the well type flagged. Because these other well types are only used to supplement the waste data, EPA did not aim for a comprehensive review of the literature. Therefore, care should be taken when drawing any conclusions from the database about typical water composition from these wells.

B.1.1 Soundness

Soundness is the extent to which the methods employed by a literature source are reasonable and consistent with the intended application of the data. This means that any methods used to collect and measure data have demonstrated the technical ability to reliably and repeatedly achieve desired levels of accuracy and precision, and that any methods used to analyze and interpret data, such as equations;

models and simplifying assumptions, are adequately justified and rooted in accepted scientific principles.

Analytical Methods:
EPA reviewed the analytical methods used by each study to measure constituent levels in each waste. The purpose of this review was to determine whether the uncertainties associated with reported data could affect the conclusions in this document. The methods used by different studies varied based on the focus of the study and the equipment available to the authors. A few studies did not report the methods used or only noted that the samples had been sent to the U.S. Department of Interior Geological Survey or another certified laboratory for analysis.

One consideration in this review was whether the methods used by a study accurately measured the constituent levels in an E&P waste. Methods that are not well-suited for high ionic strength wastes may result in imprecise data. For example, methods that dilute the waste prior to measurement can result in high detection limits for minor constituents (MSC, 2009), while those that precipitate constituent mass out of solution prior to measurement may underestimate constituent levels as a result of matrix interference (Nelson et al., 2014). The extent to which these uncertainties might affect the data is not known. Therefore, at this stage of investigation, EPA relied on other metrics, such as charge balance and agreement with observed relationships, to identify potential data quality concerns and avoid exclusion of useful data. If data from these studies were incorrectly measured, the error is likely to be reflected in the calculated charge balance. Therefore, EPA did not filter out any data solely because of the specific analytical method reported.

Another consideration in this review was whether the study provides data appropriate for the intended use. Some analytical methods are designed to measure different aspects of waste composition. For example, non-destructive methods (e.g., neutron activation analysis) measure the total constituent mass within the sample matrix, while digestion methods (e.g., mass spectrometry) measure the constituent mass that can be liberated from the matrix with a combination of heat and acid. Both types of data can provide useful information on waste composition and behavior. Total concentrations measured by non-destructive methods better reflect the entire waste and can be used to demonstrate relationships among constituents in the total waste. The acid-extractable concentrations measured by digestion methods better reflect the fraction of the waste that is available to be released into the surrounding environment and can be used to estimate exposures. The resulting data are not necessarily equivalent and care should be taken before combining these data in a single dataset. Therefore, EPA compared data collected with different methods to determine if substantial differences exist. When such differences were identified, EPA separated the data out for further review and discussion in the text of this analysis.

B.1.2 Clarity and Completeness

Clarity and completeness is the degree to which a study transparently documents all assumptions, methods, results, and other key information. An evaluation that is both clear and complete provides enough detail that an outside party with access to the necessary resources can replicate the analyses.

Units:

Studies reported the data in variable units. Some expressed concentrations in terms of mass or molarity, while others reported concentrations per unit of volume or mass. All concentrations were converted into units of milligrams (mg) or picocuries (pCi) per liter (L) or kilogram (kg), based on the relevant media. Sometimes this conversion required the use of additional data or assumptions. For example, when density was not reported for an aqueous sample expressed per unit of mass, a density of 1.0 kg/L was used to convert to a volumetric concentration. This may result in an underestimation of concentration for some samples, as produced water density has been reported as high as 1.3 kg/L. However, the magnitude of this uncertainty is small in comparison to the orders-of-magnitude variability observed among the larger dataset. Any time that additional data or assumptions were required to calculate the concentration, the approach was flagged in the notes column of the database. In instances where data was insufficient to convert the reported units to mg/L with any certainty (e.g., reported in units of chemical activity), the samples were excluded from the database entirely.

EPA identified two separate studies with indeterminate units for some samples. Both of these studies reported data for produced water. The first study, USEPA (2016a), reported data obtained from the Wyoming Oil and Gas Conservation Commission. Despite outreach to the Commission, EPA could not confirm units for many minor constituents. As such, EPA filtered out the constituents with uncertain units prior to the any analyses. The second study, U.S. DOI (2016), is a database compiled from sources assembled by the United States Geological Survey and other organizations.[B1] In this second study, all of the data is reported to be in units of milligrams or picocuries per liter. Yet during the literature review, EPA identified one source document (U.S. DOI, 1975) that had since been included into a dataset flagged in the database as "USGSBREIT." All the values reported in this study are identical to those in the database, but the minor constituents are reported in µg/L. Given that the units of the major ions are correct and the number of minor analytes reported are limited, the calculated charge balance may not always be sufficient to screen out this type of error. Therefore, EPA filtered out all minor constituents from USGSBREIT data prior to calculation of summary statistics. For clarity, only the USGSBREIT data was labeled as U.S. DOI (2016) in the E&P Database. Other data for which the original source could be located were incorporated in the E&P Database under that citation and flagged as originating from U.S. DOI (2016) in the notes column.

Raw Data:

During review of the assembled literature, EPA found that some authors chose to provide summary statistics instead of full datasets. EPA made an initial effort to reach out to a few authors to obtain the underlying data, but received few responses. While summary statistics provide some understanding of the overall distribution of a dataset, it is difficult to incorporate these data along with other individual data points. In particular, the presence of extreme values (e.g., maximum, minimum) can greatly skew analyses. The highest value for one constituent may not correspond to the highest value for another,

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[B1] This database is periodically updated and has been at least once since the E&P database was compiled. The most recent version of the database was not incorporated into the current analysis due to time constraints. However, it is not anticipated to affect the conclusions of this document.

and so extreme values may mask relationships within the data. Therefore, while all of the reported summary statistics were incorporated into the E&P Database, extreme values were filtered out prior from all current analyses. The limited number of mean or median values were incorporated into the analyses as individual data points. When known, the total number of individual samples captured by the summary statistics is also reported in the notes column of the database.

Drilling Method:

The largest shift in drilling practices in the past several decades has been the adoption of directional drilling in formations previously considered uneconomical to access. The greater consolidation that occurred in these formations trapped the natural gas in isolated small, poorly connected pore spaces that make it difficult to liberate. This consolidation also results in greater evaporation of water from the formation, which may result in higher dissolved constituent levels (concentration and activity) in the remaining water. In addition, the greater distance drilled through high organic and metal shale during horizontal drilling could further concentrate constituent mass in the resulting waste. Therefore, where possible, EPA separated out samples from vertical and horizontal wells for further review and discussion in the main text. Some studies did not specify the orientation of sampled wells and so, unless otherwise specified, EPA assumed all samples collected prior to the year 2000 were from vertical wells. Although horizontal drilling has been an available technology for nearly a century beforehand, it was not in widespread use until the early 2000s (EIA, 2018a). It is known that vertical wells can also be sited in lower-permeability formations and that some are hydraulically-fractured. However, few studies noted whether or not a vertical well had been fractured. Therefore, this remains a source of uncertainty in the dataset. However, the greater tendency for vertical wells to be sited in more permeable formations makes it likely that any differences that exist based on the type of formation will still be apparent in comparisons.

The equipment used to install and operate wells may also affect the waste composition. For example, additional constituent mass may be intentionally injected into a well or inadvertently leached from pipes and other equipment in contact with the waste. However, it can be difficult to attribute elevated constituent levels to one of these sources because studies often do not report the specific equipment and practices used at each site. In the case of additives, this information may not be available because it is often claimed as confidential business information (U.S. EPA, 2016b). Yet, even if this information were available, it would be difficult to attribute moderate increases in constituent levels to specific sources without representative samples from wells with and without those sources. In instances where one or more samples were found to be considerably higher than the remaining dataset, EPA reviewed the available information on drilling methods and the available literature to identify and discuss any potential sources.

B.1.3 Variability and Uncertainty

Variability and uncertainty is the extent to which a literature source effectively characterizes, either quantitatively or qualitatively, these two factors in the procedures, measures, methods or models used. Proper characterization of the major sources of variability and uncertainty provides greater confidence that the data are can form the basis for sound conclusions. The data drawn from each literature source is limited in the number of samples or geographical scale. Therefore, no single study can be said to provide a statistically representative sample. However, there is no reason to exclude any individual sample because it does not fully capture the variability of a waste. More data ensures better characterization of the waste types. Therefore, EPA retained data from all of the available studies found to be of sufficient quality.

Age of Sampled Waste:

The composition of a waste is not always static. For example, water present in hydrocarbon formations often exists under reducing conditions, as well as high temperature and pressure. As a result, the conditions surrounding the water will change dramatically before it can be analyzed in a laboratory. Some of these changes occur rapidly, but others can occur gradually over the days or months that the waste is stored. One example is the gradual transfer of CO_2 and O_2 between produced water and the atmosphere, which can shift the water pH and result in production of insoluble oxides and carbonates (DOE, 2004). Barium has been shown to precipitate as barite over the course of months, long after the temperature and pressure of the water has equilibrated (Kraemer and Reid, 1984). This precipitate will gradually add to the mass of sludge and scale. Over the same time, organic compounds and radioisotopes in the wastes will degrade through natural processes.

Many samples reported in the literature are collected soon after generation; however, E&P wastes can be stored on-site for some time prior to disposal. Studies rarely specify the amount of time that has elapsed since the waste was generated. This type of information may not have been made available to the samplers. In addition, waste generation is an ongoing process and so samples collected from downstream pits and tanks will reflect a mixture of the waste generated over some period of time. This represents a major source of variability and uncertainty that is difficult to address. EPA identified one instance where anomalous data can be attributed to sample age. The comparison of ^{226}Ra and ^{228}Ra activities in produced water found the ^{228}Ra activities reported by Shih et al. (2015) to be low relative to the remaining samples. This study reported secondary data from the Pennsylvania Department of Environmental Protection, which did not provide information on the age of the samples. ^{228}Ra has a predictable half-life (5.8 years), which is far less than the corresponding half-life for ^{226}Ra (1,600 years). Thus, as the sample ages, ^{228}Ra will become depleted relative to ^{226}Ra. Given the isolation of these low values to a single study and the strong correlation observed in the remaining studies, EPA concluded that sample age is the most likely explanation. Therefore, EPA filtered out the samples of ^{228}Ra from this study prior to any analyses. Samples of ^{226}Ra were retained because the much longer half-life eliminates the likelihood of similar issues from decay.

Age of Reported Data:

The studies identified with relevant characterization data were published over the span of a full century between 1917 and 2017. The oldest studies predominantly sampled produced water that was analyzed only for major constituents (e.g., chloride). These older studies may include samples drawn from formations that are no longer in production. It is possible the wastes from these formations differ from those generated today. However, available data show a considerable overlap in the major ion composition of produced water from various states. Thus, while there is some uncertainty associated with older studies, it is believed the data can still provide a reasonable order-of-magnitude estimate of major constituent levels that can be generated by a well. Furthermore, there is an equal amount of uncertainty associated with formations that have yet to be drilled. Therefore, inclusion of data from older formations can help ensure that the range of potential constituent levels is captured in the dataset. Therefore, EPA did not filter out any data solely as a result of the date the study was completed.

Sample Collection Location:
More than 10,000 new oil and gas wells are drilled each year in the United States (EIA, 2018b). It is not feasible to collect waste samples associated from every well currently in production and so any analysis must aim for a representative subsample. However, some authors do not have the authority to compel sampling and relied on the cooperation of facilities to obtain access to drilling sites. Other authors selected sample locations based on areas known to have elevated constituent levels. As a result, the sample locations reflected in the data are not truly random. This has the potential to bias the reported data, but the extent to which this uncertainty might affect the overall dataset is not known.

Another source of uncertainty is the spatial variability of wastes within the sampled pits and tanks. Solids suspended in produced water can settle out quickly once the velocity of the flow slows at the outfall to a pit or tank. This may result in hotspots of some constituents within the management units. Concentrations can also vary based on which piece of equipment is sampled and where. Heavier solids and organics are likely to settle out in equipment early in the production stream, while precipitation is likely to dominate deposition in pits and tanks used for water storage. Although constituent levels may be higher in some areas, it is unknown to what extent this will impact the overall composition of the waste when it is aggregated for disposal.

B.3. Data Management

Once all of the identified data were assembled in the E&P Database, some additional management steps were taken prior to analyses. The following steps were taken to mitigate sources of variability and uncertainty that could be reliably identified and effectively managed.

Charge Balance:
Aqueous solutions must be electrically neutral. Thus, the net charge of positive ions (i.e., cations) and negative ions (i.e., anions) must be equal. The charge balance of a solution is the difference between the measured charge of cations and anions in a sample, expressed as a percentage of the total charge. If the calculated charge balance is not zero, it might indicate there was an error during measurement. One potential source of error associated with fluid E&P wastes is high total dissolved solids, which can interfere with measurements if instruments are not properly calibrated.

There are a number of reasons why the charge balance calculated for a sample is not exactly zero. A study may not analyze for every constituent that contributes charge or there may be interference from other constituents during measurement. Therefore, it is common to calculate the charge balance with a select set of dominant ions and value to a cutoff somewhat higher than zero to determine whether there are concerns about the reported concentrations. EPA selected a cutoff of ±15% for this document based on the previous work in the National Produced Waters Geochemical Database (U.S. DOI, 2016). Prior to any analyses of aqueous wastes, EPA filtered out all samples with a charge balance outside of this range.

It is clear that the high charge balance calculated for some studies is primarily the result of the absence of data for one or more of the major ions (e.g., chloride). This was typical when the focus of a study was a specific set of constituents, such as radioisotopes. This does not necessarily mean there are concerns about the quality of these data, but it is not possible to demonstrate otherwise. Therefore, EPA still filtered out any samples that did provide chloride or sodium concentrations, but flagged these samples in the database. Further review found that inclusion of these additional samples did not substantially shift the calculated summary statistics and so these samples are not further discussed in this document.

Redundant Data:

Some studies reported secondary data drawn from other studies. This has the potential to bias the overall dataset toward samples reported across a greater number of studies. Some studies also do not provide relevant background information for secondary data. Therefore, where possible, EPA obtained and cited to the original source of the data for reference. Any data found to be redundant between two or more studies was removed from the database. In instances where multiple studies provided data for different constituents from the same sample, EPA combined the data from the studies into a single entry in the E&P Database and cited to both studies.

To identify redundant data, EPA reviewed the text of each study for citations associated with the reported data. However, some studies did not specify that the reported data was drawn from other studies, particularly in cases where the author(s) built on previous work. To identify this type of redundant data, EPA compared individual samples in the database to identify cases where two or more samples had almost the same value for all of the major ions. To instances where authors rounded exact values. When concentrations were found to be close, other information about the samples was used to confirm that the samples were redundant (e.g., sample date, county).

Detection Limits:

A detection limit is the lowest quantity or concentration of a constituent that can be reliably detected with a given analytical method. When a constituent is not detected above this limit, the analytical results are typically reported as less than the detection limit because the potential still exists for the constituent to be present at lower levels. Such values are referred to as “left-censored.” The detection limit varies among studies because of differences in the methods used to prepare samples, the sensitivity of analytical instruments, and interference from solid media or other chemical constituents. EPA incorporated all left-censored data in the E&P Database and flagged it with “<” in front of the reported detection limit.

Ideally, left-censored data should be the lowest values in a given dataset. However, there are instances in the database where detection limits are higher than any measured samples. This does not mean that the data are of poor quality. For example, the sequential dilution necessary to analyze highly saline water can result in high detection limits for minor elements. High detection limits introduce a great amount of uncertainty into the evaluation and can bias the overall dataset high. To mitigate this uncertainty, EPA filtered out any non-detect values that greater than the 90th percentile of detected data prior to analysis. This cutoff was selected to strike a balance, as elimination of all non-detect data would only bias the remaining dataset even higher. EPA incorporated the remaining non-detect values using half of the reported detection limit based on the recommendations in *Risk Assessment Guidance for Superfund Part A* (US EPA, 1989) and with the *Guidance on Handling Chemical Concentration Data near the Detection Limit in Risk Assessments* (US EPA, 1991). More robust methods are available to manage non-detect data, though these methods often rely on detected data to help backfill censored data, which can be confounded by a small datasets. Therefore, the selected approach is considered reasonable for current purposes of providing a first-order summary of available data.

In a few instances, concentrations were reported at higher concentrations than could be measured by analytical instruments. This typically occurred when an element, such as iron or barium, comprised a majority of the mass in samples of drill cuttings, sludge and well scale. EPA incorporated these data in the E&P Database flagged with ">" in front of the reported detection limit. The range of potential concentrations greater than a specified value is typically far wider than those below and so the uncertainty associated with right-censored data is often greater. Therefore, all right-censored data were filtered out prior to any analyses. Given the small number and types of samples with such high concentrations, it was determined that the removal of these samples would not affect the conclusions of this document.

Some studies flagged non-detects only as "ND" and did not report the associated numerical detection limit. It is not possible to draw conclusions about likely constituent levels in these samples. EPA incorporated the data as "ND" in the E&P Database to show that the study had analyzed for that constituent. However, these samples were not included in sample counts presented in the main text.

Duplicate Samples:

Duplicate samples are two or more field samples intended to represent the same source, which are collected and analyzed in a comparable manner. For a number of reasons, such as heterogeneity of the source material and precision of analytical equipment, values measured for these samples may not be identical. EPA treated all samples collected from the same location (e.g., wellhead, storage tank) as duplicates, regardless of whether the samples were collected as part of separate studies or at different times. This was done to avoid biasing the summary statistics towards wells that had been more heavily sampled. Prior to any analysis, EPA averaged all duplicate values for each well. Where duplicates data were a mixture of detect and non-detect values, the non-detect values were set to half the detection limit and averaged along with detected values. The resulting, averaged value was flagged as a detected value for the summary statistics.

One study provided discharge monitoring reports over time (U.S. EPA, 2013). This database includes data for multiple states, but only the data for Wyoming was found to be useful based on the reported analytes. The database included a number of sample collected at different dates, but the samples were not always measured for the same analytes. This would likely cause many of the individual samples to be filtered out as a result of a high charge balance. Further review of the data found that the constituent levels reported over time did not vary dramatically. Therefore, to make best use of the available data and to keep data entry manageable, EPA averaged all of the data reported for a single location prior to incorporating the data in the E&P Database.

A few studies reported a large number of samples with many apparent duplicates (U.S. EPA, 2016; U.S. DOE, 2017; U.S. DOI, 2017). However, none of these studies flagged duplicate samples. Instead, EPA inferred the presence of duplicates from other available information, such as well names. These studies did not always maintain consistent reporting for well names and so matching by name would have to be conducted manually. Instead, EPA first matched samples based on GIS coordinates. The resolution of the reported coordinates is unknown and so this approach may combine multiple wells that are located in close proximity, but the uncertainty associated with this error is considered minimal because the wells still reflect the same general region. Where GIS coordinates were not available, EPA manually compared the reported well names and flagged those with similar names (e.g., Well #1 and Well Number One). When neither GIS coordinates or well names were available, samples located in the same county were flagged a duplicates.

B.4. Data Summary

The current literature review identified over 700 unique studies, of which 228 contained some relevant data that were included in the E&P Database. Each study reported data on a different combination of constituents based on the focus of that individual study. As a result, the total amount of data available for each constituent can be quite variable. Some inorganic constituents were not reported in any of the studies and so are not listed in the database. However, the absence of data does not necessarily indicate these constituents are not present. Conversely, there a large number of organic compounds reported sporadically in the literature that are not included in the database. The limited amount of data for a large number of compounds limits the conclusions that can be drawn from the data. Therefore, EPA focused data collection efforts on benzene, toluene, ethylbenzene and xylene because these compounds are known byproducts of hydrocarbon formation and are the most commonly measured compounds in the literature. EPA chose to provide a qualitative discussion on the magnitude and frequency of detection of other organic compounds.

During the review of assembled data, EPA identified multiple major sources of uncertainty. Yet because the range of reported constituent levels varies by orders of magnitude, it can be difficult to distinguish between measurement uncertainty and natural variability. Therefore, EPA did not attempt to define fully representative distributions for any constituent. Instead, the statistics presented in this document are intended only to summarize the available data and allow a more general order-of-magnitude comparison between datasets. Despite the uncertainty associated with the current dataset, EPA identified strong trends among the data that indicate the existence of relationships between different constituents that are tied to chemistry and geology, rather than the unique features of individual formations. The likelihood that such strong relationships would erroneously emerge from the noise of numerous independent studies is exceedingly small. Therefore, EPA concludes that the sources of uncertainty in the dataset do not impact the main conclusions in this document and that the data are fit for purpose. Although these data provide useful information for the current discussion, inclusion of a particular study in the database at this stage does not indicate that it will form the basis for future conclusions about waste composition and behavior as more data become available.

B.5. References

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Attachment B-1:

E&P Constituent Database

[Due to the large file size, this database is maintained as a separate file.]

Appendix C: State Programs

This appendix provides a summary of the Agency's review of state programs discussed in **Section 6 (State Programs)** of the main text. The intent of this review is to better understand how state regulations currently address management of wastes from exploration, development and production operations and to highlight inconsistencies, lack of specificity, or possible gaps in coverage. The following text provides a summary of state programs, broken out into 12 general topic areas and 61 specific elements. The summaries in this appendix are organized by each individual state, presented in order of production (highest to lowest) based on the 2016 production data from the U.S. DOE Energy Information Agency.

- **Attachment C-1:** provides the results of the Agency's binary (yes/no) determination whether regulations related to each of the 61 regulatory elements are in place for the states reviewed.
- **Attachment C-2:** provides a detailed spreadsheet that contains excerpts from state regulatory text, organized by topic area and with links to the full regulatory text, that form the basis for this review. All links provided in the spreadsheet were active at the time the spreadsheets were compiled.

C.1. Texas

In 2016, Texas accounted for approximately 32% of the nation's oil and gas production according to the U.S. Energy Information Agency. It is by far the largest oil and gas producing state in the U.S. with almost three times more production then the second largest producer, Pennsylvania. Because of its long history in oil and gas production, Texas sustains a large amount of conventional production, and continues to pursue conventional reserves, both shallow and deep. Modern shale and tight oil unconventional reserve development began in Texas in the 1990's and recent discoveries in the Permian Basin suggest that this will be a significant part of future exploration and production. The Oil and Gas Division of the Railroad Commission of Texas (RRC) regulates oil and natural gas production in the state. E&P wastes are regulated by the RRC under a memorandum of agreement with the Texas Commission on Environmental Quality (TCEQ). The Department of Environmental Quality, Land Protection Division is responsible for management of solid waste. NORM related to oil and natural gas production is regulated by RRC under a memorandum of agreement with Texas Department of State Health Services (DSHS).

Texas maintains an extensive set of regulations for oil and gas that address a wide range of environmental issues. RRC rules (Title 16, Part 1) include 15 sections including two that address waste management requirements (Oil and Gas Division Rules, Chapter 3, and Environmental Protection, Chapter 4). Chapter 3.8 (Water Protection) contains most of the waste management regulations, and Chapter 4 addresses commercial E&P waste recycling and NORM. Several chapters of the regulations have been updated as recently as 2016; Chapter 3.8 and most of Chapter 4 were most recently updated in 2013. **Table C-1** provides a summary of the regulations identified for E&P wastes in Texas.

Table C-1. Summary of Regulations for E&P Wastes in Texas

Topic Area	Summary
Definitions	Section 3.8 includes 47 definitions related to waste and water protection, and more definitions are included within other parts of the rules. The regulations define 16 different types of pits and TRC has grouped the pit regulations by addressing nine types of pits. Additionally, five types of commercial recycle/reuse operations (on and off lease) are addressed in Chapter 4.
Waste Unit Location Requirements	Regulations pertaining to siting waste management units in floodplains are dispersed in the reserve pit section and all five sections of recycling operations regulations and indicate that "all authorized pits shall be constructed, used, operated, and maintained at all times outside of a 100-year flood plain." Regulations for surface water and groundwater are overarching and state "No person conducting activities subject to regulation by the commission may cause or allow pollution of surface or subsurface water in the state." No specific criteria for siting or operation using the term "groundwater" was found. However, throughout the Pit Permit requirements in §3.8 (Water Protection) the director may only issue permits if "the activity does not result in waste of oil, gas, or geothermal resources or pollution of surface or subsurface water." Siting and location requirements related to endangered species are not specifically addressed. The only siting requirements provided in the regulations are a 100-foot setback distance from sensitive areas for commercial recycling plants, and a 150-foot setback from surface water and water supply wells for on-lease commercial waste recycling. Sensitive areas are defined as "by the presence of factors, whether one or more, that make an area vulnerable to pollution from crude oil spills. Factors that are characteristic of sensitive areas include the presence of shallow groundwater or pathways for communication with deeper groundwater; proximity to surface water, including lakes, rivers, streams, dry or flowing creeks, irrigation canals, stock tanks, and wetlands; proximity to natural wildlife refuges or parks; or proximity to commercial or residential areas." Minimum depth to groundwater for waste units is not specified.
Tank Requirements	TRC regulations do not address many aspects of tanks used for waste management and TCEQ tank regulations (§334.123. (a)(7) Exemptions for Aboveground Storage Tanks (ASTs) exempts oil and gas tanks. General requirements are provided for protection of birds for open-top storage tanks that are eight feet or greater in diameter and contain a continuous or frequent surface film or accumulation of oil. These tanks must be screened, covered or otherwise rendered harmless to birds; however, temporary, portable storage tanks that are used to hold fluids during drilling operations, workovers, or well tests are exempt. Recycling facilities, which may contain tanks, also require bird protections and require design and construction of storage areas, containment dikes and processing areas to prevent pollution of surface and subsurface water. Modular large volume tanks, construction materials, and monitoring are not specifically addressed in the regulations. Permits are required for removal of tank bottoms or other hydrocarbon wastes from any producing lease tank, pipeline storage tank, or other production facility.

Table C-1. Summary of Regulations for E&P Wastes in Texas

Topic Area	Summary
Pit Construction and Operation Requirements	Short term use pits including reserve pits, mud circulation pits, completion/workover pits, basic sediment pits, flare pits, fresh makeup water pits, fresh mining water pits, non-commercial fluid recycling pits, and water condensate pits are authorized by rule and no permit is required when specified conditions in Rule 3.8 are met (also called permit-by-rule). Permits are required for longer term storage pits, salt water pits and disposal pits such as saltwater disposal pits; emergency saltwater storage pits; collecting pits; skimming pits; drilling fluid storage pits (other than mud circulation pits); drilling, fluid disposal pits (other than reserve pits or slush pits); washout pits; and gas plant evaporation/retention pits. Pits associated with certain recycling facilities are included as part of the facility permits. Storage of oil in pits of any type is prohibited. Design and construction requirements for permit-by-rule pits are not explicitly defined in most pit regulations. Only non-commercial fluid recycling pits include specifications. For these pits, liner materials may vary and must have a permeability less than 1×10^{-7} cm/sec. For permitted pits requirements such as dike design, minimum depth to groundwater, liner material and thickness, schedules, and fences, are specified in the permits. In addition, skimming pits and collecting pits must be screened, covered or otherwise rendered harmless to birds. General freeboard and berm requirements are provided for non-commercial fluid recycling pits stating that "All pits shall be sufficiently large to ensure adequate storage capacity and freeboard taking into account anticipated precipitation." and "All pits shall be designed to prevent stormwater runoff from entering the pit. If a pit is constructed with a dike or berm, the height, slope, and construction material of such dike or berm shall be such that it is structurally sound and does not allow seepage." Signs are required for the general well location and are not pit specific. Inspections and groundwater monitoring are required for commercial recycle/reclamation pits, brine pits, and as specified in a permit. Permits and leak detection/monitoring are required for brine pits only. Discharge from pits requires a letter of request but no application or permit is necessary. Centralized pits are not specifically addressed in the regulations, but they may fall under non-commercial fluid recycling pits located offsite.
Pit Closure Requirements	Most drilling fluids and cuttings can be disposed in the original pit by burial. Liquids removal is required prior to pit closure for high chloride fluids. Completion and workover wastes (including fluids and solids) can be buried on site in their original pits, as can solids generated from non-commercial recycling pits. The closure schedule varies depending upon pit type, and details are provided in the regulations. Generally, drilling pits must be backfilled and compacted within one year, and all other pits (completion, workover, basic sediment and others) must be backfilled within 120 days. Liners for non-commercial fluid recycling pits must be inspected annually by the operator unless a double liner with leak detection is used. Storage areas for commercial recycling/reclamation pits must be inspected as indicated by permit. Sampling is necessary for stationary solid waste recycling facilities, waste separation facilities, reclamation facilities, or as specified by permit. For wells, financial security is not pit-specific but rather provided by the general APD bond. Financial security bonds are required for all five categories of recycling facilities in Chapter 4.

Table C-1. Summary of Regulations for E&P Wastes in Texas

Topic Area	Summary
Spill Notification	Unpermitted discharge from any pit requires the operator to take any measures necessary to stop or control the discharge and report the discharge to the district office as soon as possible. For other waste management units (tanks) immediate notification of a fire, leak, spill or break is required followed by a letter giving the full description of the event, and the volume of crude oil, gas, geothermal resources, other well liquids, or associated products lost.
Corrective Action	Response actions for crude oil and condensate releases are addressed in the regulations, but the corrective action process for exempt wastes is not described in the regulations. According to the Memorandum of Understanding between RRC and TCEQ, RRC is solely responsible for the control and disposition of waste and the abatement and prevention of pollution of surface and subsurface water in the state from activities associated with the exploration, development, and production of oil and gas. RRC Cleanup Orders appear to be used to identify actions and timelines for remediating releases of waste.
Off-site Landfills	Disposal of E&P waste is allowed in offsite pits and require a permit. Commercial pits require testing of waste and groundwater monitoring wells. Disposal of exempt waste in municipal solid waste landfills is not discussed in the regulations but appears to be allowed with concurrence from TCEQ (TXCEQ, 2014). Use as daily cover is not specifically addressed in the regulations.
Land Application	Land application (landfarming) of E&P waste on-lease property is allowed for low chloride muds and cuttings and does not require a permit (considered permit-by-rule). Other than the chloride content, there are no specific limitations/conditions for landfarming. Off-lease application requires a disposal permit, which includes site specific limitations/restrictions for use.
Beneficial Use	Non-commercial recycling or reuse of treated fluid is allowed and does not require a permit. Commercial recycling facilities are subject to location and operating conditions provided in the regulations and facility permit. Beneficial use of basic sediment is allowed for application to lease roads, and a permit is required for off-lease applications only. Roadspreading of brine does not appear to be explicitly allowed under the regulations, but the RRC has flexibility to approve applications for alternate disposal and use of brine. Disposal of oil and gas NORM waste on roads is prohibited.
Waste Minimization/ Management	Waste minimization practices, such as closed loop drilling and mandatory recycling of produced water are not specifically addressed in the regulations. The RRC Waste Minimization Guide and guidance on the RRC website encourage the reduction, reuse and recycling of wastes.
Commercial Recycling and Reclamation Facilities	RRC Chapter 4 presents the regulations for five different types of commercial recycling facilities including: ▪ On-Lease Commercial Solid E&P waste Recycling Facilities ▪ Off-Lease Commercial Solid E&P waste Recycling Facilities ▪ Stationary Commercial Solid E&P waste Recycling Facilities ▪ Off-Lease Commercial Recycling of Fluid ▪ Stationary Commercial Recycling of Fluid Regulations for each facility type are addressed in the regulations and all require permits and financial security. Many of the technical specifications are contained in the operating permits, which are based on information provided during the permit application process.

Table C-1. Summary of Regulations for E&P Wastes in Texas

Topic Area	Summary
NORM and TENORM	Oil and gas NORM waste is regulated in Texas by RRC under memorandum of agreement with DSHS, and such waste is addressed in the oil and gas regulations. Testing of NORM wastes is required prior to disposal, which may include burial at generation location or landfarming if waste does not exceed 30 pCi/g Radium-226 combined with Radium-228 or 150 pCi/g of any other NORM radionuclide. Off-site disposal and injection are also options for NORM.

C.2. Pennsylvania

In 2016, Pennsylvania accounted for approximately 11.5% of the nation's oil and gas production according to data provided by the U.S. Energy Information Agency. Much of the production is from unconventional reserves in the Marcellus (beginning around 2003), and the remaining is from shallower conventional wells associated with oil and gas producing intervals since the mid 1800's. In 2017, a total of 2,028 unconventional permits were issued and 203 conventional permits were issued (PADEP, 2018). Part of Pennsylvania is underlain by the Utica Shale, which is a potential target for future unconventional oil and gas production. The Office of Oil and Gas Management in Pennsylvania's Department of Environmental Protection (PADEP) regulates oil and natural gas production in the state. The PADEP also regulates solid and hazardous wastes. NORM/TENORM is not specifically addressed in state oil and gas regulations. Pennsylvania substantially updated its E&P regulations by adding Chapter 78a to address unconventional wells in 2016. The new section provides more stringent requirements for many waste management activities including pits, modular tanks and centralized pits. **Table C-2** provides a summary of the regulations identified for E&P wastes in Pennsylvania.

Table C-2. Summary of Regulations for E&P Wastes in Pennsylvania

Topic Area	Summary
Definitions	Approximately 150 definitions are provided between Chapters 78 and 78a of the regulations; some appear in both chapters. Pits are defined generally, but specific types are not defined or addressed in the regulations. Text in the regulations note that pits are temporary, and pit and tank contents may include wastes generated from drilling, altering, completing, recompleting, servicing and plugging the well including brines, drill cuttings, drilling muds, oils, stimulation fluids, well treatment and servicing fluids, plugging and drilling fluids. Regulations regarding oil and gas activities distinguish the drill cutting type based on origination, either from above the surface casing seat (uncontaminated drill cuttings, tophole water or fresh water) or below the surface casing seat (contaminated drill cuttings and associated fluids).

Table C-2. Summary of Regulations for E&P Wastes in Pennsylvania

Topic Area	Summary
Waste Unit Location Requirements	Regulations regarding protection of floodplains, surface water and groundwater are dispersed throughout the various technical regulations for pits, tanks and other activities. An analysis of the well's impact on endangered species is required in the permit application and endangered species are mentioned in the pipeline planning regulation.[C1] Location restrictions are provided (for example, pits shall not be located within 100 feet of a stream, body of water or wetland, or within 200 feet of a water supply). In addition, wastes from below the casing seat (potentially contaminated with oi and gas fluids) may not be disposed or land applied within 200 feet of an existing building.
Tank Requirements	Regulations for tanks refer to requirements under 40 CFR Part 112. Signs are required at tank batteries, and at least 2 feet of freeboard is necessary for all open tanks or storage structures. While specific construction materials are not specified, the container must be impermeable to contain the regulated substances which are used or produced during drilling, altering, completing, recompleting, servicing and plugging the well. Modular large volume tanks are addressed in the regulations, and those that exceed 20,000-gallon capacity need prior Department approval. A permit is required for removal of tank bottoms. Tank monitoring and netting requirements are not specifically addressed in the regulations. Open top structures are not allowed for storage of produced fluids (brine and hydrocarbons). Because the tank rules reference 40 CFR Part 112, federal requirements for construction and operation may apply.
Pit Construction and Operation Requirements	Pit contents recognized in the regulations include a wide range of wastes generated from drilling, altering, completing, recompleting, servicing and plugging the well including brines, drill cuttings, drilling muds, oils, stimulation fluids, well treatment and servicing fluids, plugging and drilling fluids. Pits require a permit and may not be used for temporary storage. A distinction is made between (1) pits used for uncontaminated drill cuttings from above the casing seat, tophole water (generated from drilling the shallow portion of the hole) and fresh water and (2) pits used to contain drill cuttings from below the casing seat, pollutional substances, wastes or fluids other than tophole water, fresh water and uncontaminated drill cuttings. Pits for contaminated drill cuttings or fluids other than tophole or fresh water have more stringent requirements, such as a synthetic liner or an alternative material (if approved by the Department) and the bottom of the pit shall be at least 20 inches above seasonal high groundwater table.

C1) § 78a.68. Oil and gas gathering pipelines also includes associated facilities which may consist of pigging stations, drip pits and compressor stations which may handle or store exempt E&P wastes. The regulation requires flagging of endangered species habitat prior to land clearing.

Table C-2. Summary of Regulations for E&P Wastes in Pennsylvania

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Fencing is required for well development impoundments only and not pits specifically, although a well development impoundment is functionally equivalent to a pit. Berm requirements are specified for well development impoundments at unconventional wells and produced fluids containment at conventional wells. Regulations also address signage, inspections, temporary pit requirements, and run-on/run-off controls. Groundwater monitoring does not appear to be required for wells or specific waste management units. However, the regulations imply that water quality data from preconstruction monitoring at centralized impoundments is required. State guidance notes that under PA Act 13 (2012 improvements to oil and gas laws) there is a presumption of liability for contamination of private water supply wells within 2500 feet of oil and gas wells. While the regulations have no requirement for pre-drill sampling, they put the onus on oil and gas industry for groundwater monitoring at nearby water supplies. Onsite processing of wastes at noncommercial fluid recycling pits is allowed for beneficial use only. Centralized pits at unconventional wells require a permit. Regulations do not address leak detection or monitoring or netting of pits.
Pit Closure Requirements	Conventional well regulations allow closure of lined pits in place and specify liquids must be removed prior to backfilling of the pit. A permit may be required. Remaining contaminated drill cuttings (defined as residual waste) must be encapsulated in the liner and folded over (or an additional liner added). Regulations also require covering the waste prior to backfilling with at least 18 inches of soil. Cuttings from unconventional wells cannot be disposed in pits without approval of the director and in compliance with regulations for management of residual wastes. Pits containing production fluids must be closed within 9 months after completion of drilling. Pits used during servicing, plugging and recompleting a well shall be closed within 90 days of construction. Regulations state that inspections of wells with onsite brine disposal or residual waste are intended to be inspected at least once per year. Bonds are required for wells, but there are no financial security requirements for pits or other waste management units.
Spill Notification	The owner/operator shall notify the appropriate regional office of the Department as soon as practicable (but no later than 2 hours) after detecting or discovering a reportable release of brine on or into the ground at the well site. A reportable release of brine is defined as “spilling, leaking, emitting, discharging, escaping or disposing of one of the following: (i) More than 5 gallons of brine within a 24-hour period on or into the ground at the well site where the total dissolved solids concentration of the brine is equal or greater than 10,000 mg/l. (ii) More than 15 gallons of brine within a 24-hour period on or into the ground at the well site where the total dissolved solids concentration of the brine is less than 10,000 mg/l.” Unconventional wells: Notification is required as soon as practicable but no later than 2 hours after discovering the following spills/releases at unconventional well sites: (1) spills or releases of a regulated substance causing or threatening pollutions of the Commonwealth or (2) spills or releases of 5 gallons or more of a regulated substance over a 24-hour period that is not completely contained by secondary containment. The operator or other responsible party shall take necessary interim corrective actions, identify and sample water supplies that have been polluted or threatened. Temporary emergency storage or transportation methods may be approved by the Department.

Table C-2. Summary of Regulations for E&P Wastes in Pennsylvania

Topic Area	Summary
Corrective Action	"Upon the occurrence of any release, the owner or operator shall take necessary corrective actions to: (1) Prevent the substance from reaching the waters of this Commonwealth. (2) Recover or remove the substance which was released. (3) Dispose of the substance in accordance with this subchapter or as approved by the Department." (78.66 - https://www.pacode.com/secure/data/025/chapter78/025_0078.pdf) Unconventional wells: "Remediation of an area polluted by a spill or release is required. The operator or other responsible party shall remediate a release in accordance with the following: (1) Spills or releases to the ground of less than 42 gallons at a well site that do not pollute or threaten to pollute waters of the Commonwealth may be remediated by removing the soil visibly impacted by the spill or release and properly managing the impacted soil in accordance with the Department's waste management regulations. The operator or responsible party shall notify the Department of its intent to remediate a spill or release in accordance with this paragraph at the time the report of the spill or release is made. (2) For spills or releases to the ground of greater than or equal to 42 gallons or that pollute or threaten to pollute waters of the Commonwealth, the operator or other responsible person must demonstrate attainment of one or more of the standards established by Act 2 and Chapter 250 (relating to administration of Land Recycling Program)." (78a.66 - https://www.pacode.com/secure/data/025/chapter78a/025_0078a.pdf)
Off-site Landfills	E&P waste disposal is allowed at municipal solid waste landfills that are permitted to accept the waste. Testing of waste and its use as daily cover are not specifically addressed in the regulations.
Land Application	Drill cuttings may be land applied, however, specifications vary depending on whether the materials originate from above or below the casing seat, and a permit is required. Requirements for land application are detailed and address contaminants, distance from sensitive receptors, soil thickness, percolation controls (frozen ground and free liquid content), loading and application rate, and revegetation requirements. Tophole water or water in a pit as a result of precipitation may not be land applied unless specific water quality requirements are met.
Beneficial Use	Regulations state that production brines from unconventional wells may not be used for dust suppression, road stabilization, pre-wetting, anti-icing and de-icing. Conventional well regulations are moot on the application of brines to roads (roadspreading) but a 2011 PA DEP fact sheet states "DEP considers roadspreading of brine for dust control and road stabilization to be a beneficial use of the brine." And further explains that brines from shale gas formations are not allowed to be used. The fact sheet outlines seven components of a plan that must be addressed prior to receiving a permit for beneficial use. Road spreading is strictly controlled and subject to 14 operating requirements relating to rate and frequency, sources of brine, chemical composition and presence of contaminants, proximity to water sources and sensitive receptors, spreading equipment, road conditions and monthly reporting.
Waste Minimization/ Management	Regulations do not specify closed loop drilling, but pits are not allowed for unconventional well drilling, therefore it assumed that closed loop or pitiless drilling is required. Produced water recycling is not required.
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities for water or cuttings are not specifically addressed in these regulations.
NORM and TENORM	State regulations do not address NORM/TENORM. Radiation testing is required for disposal at off-site municipal landfills but not for NORM/TENORM specifically.

C.3. Alaska

Alaska accounted for approximately 8.4% of the nation's oil and gas production in 2016, all from conventional resources, according to the U.S. Energy Information Agency. The Alaska Oil and Gas Conservation Commission within the Department of Administration regulates oil and gas production and facilities. Solid and hazardous waste are regulated by the Alaska Department of Environmental Conservation, Division of Environmental Health. NORM/TENORM is not specifically addressed in state oil and gas regulations. Many oil and gas and solid waste regulations were updated in 2017, in particular regulations regarding drilling waste disposal. **Table C-3** provides a summary of the regulations identified for E&P wastes in Alaska.

Table C-3. Summary of Regulations for E&P Wastes in Alaska

Topic Area	Summary
Definitions	E&P regulations contain 77 definitions, but few are related to the waste management processes. Pits are not included in the definitions and only reserve pits are mentioned by name/use in these regulations.
Waste Unit Location Requirements	There are no specific siting or location requirements for waste management facilities associated with drilling, completion and production facilities. Solid waste regulations related to siting and locations are dispersed throughout the rules for drilling waste landfills and include general operating requirements to not impact surface water or groundwater. Endangered species are not specifically addressed in these regulations. The only setback specified is for a new landfill or expansion of an existing landfill that may not be constructed within 500 feet of a drinking water supply well.
Tank Requirements	Regulations refer to API standards for construction, including steel and fiberglass. Tank monitoring requires an external gage or catchment/sump. No other tank requirements are included in these regulations; modular large volume tanks, netting, tank monitoring and tank bottom removal are not specifically addressed.
Pit Construction and Operation Requirements	All drilling pits (including completion and production pits) are considered drilling waste temporary storage facilities and are included under the solid waste regulations. Permits are not required for pits, but a drilling waste storage plan is necessary as part of the well permitting process, and requires information on the location, construction specifications operational practices, and ultimate disposal location of the wastes. Reserve pits for the confinement of drilling fluids and cuttings are the only type of pit mentioned by name/use. Reserve pits have few requirements other than to be properly sized and impervious. Liners for temporary pits are required and must be made of flexible geomembrane (30 or 60 mils thick) that is compatible with petroleum. Precipitation should be included in the design to ensure that a minimum freeboard of 2 feet is maintained, and confinement dikes should be avoided or kept to a minimum; pit construction must ensure integrity. Run-on/run-off control measures are not specified for pits but indicate that runoff from landfills should not be polluted run-off water. Signs are required for wells and drill waste landfills but not pits specifically. Pit requirements are not provided for leak detection/monitoring, fencing, netting, depth to groundwater, groundwater monitoring, inspection, non-commercial fluid recycling pits or centralized pits.

Table C-3. Summary of Regulations for E&P Wastes in Alaska

Topic Area	Summary
Pit Closure Requirements	Pit closure consists of a general requirement that upon completion the operator shall proceed with diligence to leave the reserve pit in a condition that does not constitute a hazard to freshwater. A visual site inspection must be conducted to verify that all drilling waste has been removed. Financial security for pits is included in the general well bonding.
Spill Notification	Spill notification is not specifically addressed in the state regulations.
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	Drilling waste monofills are specified in the solid waste regulations. General requirements allow for only RCRA-exempt wastes (Footnote: the citation date "40 C.F.R. 261.4(b)(5), revised as of July l, 1998" appears to be incorrect). Regulations specify design standards including liners, freeboard, protection of surface water and groundwater, and maintain integrity. Visual and groundwater monitoring is required. Drilling waste landfills in permafrost areas must be designed and monitored to protect the permafrost. Closure of the landfill requires removal of liquids, capping and post closure care requirements (deed notice and visual monitoring for 5 years). Testing and use of waste as a daily cover in municipal solid waste landfills are not specifically addressed.
Land Application	Land application is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use of drill cuttings may be allowed by special request/approval.
Waste Minimization/ Management	Waste minimization and management activities, such as closed loop drilling and produced water recycling, are not specifically addressed in these regulations.
Commercial recycling and reclamation facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in the state regulations.
NORM and TENORM	NORM and TENORM are not specifically addressed in the state regulations.

C.4. Oklahoma

In 2016, Oklahoma accounted for approximately 7.3% of the nation's oil and gas production according to the U.S. Energy Information Agency. Oil and gas production come from conventional resources (shallow vertical wells) that have been producing since the early 1900's and several recent unconventional resources play across the state.[C2] In 2016, about 20% of the completed wells were from conventional reservoirs. The Oil and Gas Division within the Oklahoma Corporation Commission regulates oil and natural gas production in the state. The Department of Environmental Quality, Land Protection Division is responsible for management of solid waste. NORM/TENORM is not specifically addressed in state oil and gas regulations.

C2) A play is an area in which hydrocarbon accumulations or prospects of a given geologic type occur. A play may comprise many different fields or may be a continuous accumulation of oil and gas across a large area. Examples: Marcellus, Utica, Mississippi Lime, Eagle ford and others.

Oil and Gas Conservation regulations (Title 165, Chapter 10) include 19 chapters and are regularly updated. Sections of the Drilling regulations (Chapter 3) Pollution Abatement regulations (Chapter 7), Commercial Recycling (Chapter 8) and Commercial Disposal (Chapter 9) regulations have been updated in 2013, 2015 and 2017. Regulations provide specifications and requirements, and also allow the OCD to approve alternative approaches by operators. **Table C-4** provides a summary of the regulations identified for E&P wastes in Oklahoma.

Table C-4. Summary of Regulations for E&P Wastes in Oklahoma

Topic Area	Summary
Definitions	Approximately 130 definitions are provided in the general provisions for oil and gas operations (Title 165, Chapter 10). Multiple pit types are defined, including commercial pits, completion/fracture/workover pits, emergency pits, noncommercial pits, off-site reserve pits, recycling/reuse pits, remediation pits and reserve/circulation pits. Other terms including "truck wash pit" and "deleterious substances" are defined.[C3] Land farming is referred to as soil farming in the regulations.
Waste Unit Location Requirements	Regulations pertaining to floodplains, surface water and groundwater are dispersed throughout the drilling and pollution abatement sections, while regulations for endangered species are overarching and only included as notices to operators that they must comply with federal statutes, such as the Bald Eagle Protection Act and the Migratory Bird Treaty Act. Siting requirements are provided for noncommercial pits, commercial pits, and commercial facilities, including landfarming and recycling facilities. Requirements vary from general (pits and facilities must be constructed such that contents will not be harmful to groundwater, surface water, soils, plants or animals) to specific (for example, noncommercial pits, commercial pits, and commercial landfarming or recycling facilities may not be constructed within a 100-year floodplain). Residential setback is not specified in these regulations. Minimum depth to groundwater requirements are 25 feet for pits and other waste facilities.
Tank Requirements	General requirements are provided for tanks. Examples include "protection of migratory birds" for open tanks, and they should be "constructed and maintained so as to prevent pollution." Detailed specifications are not provided. Crude oil tanks (which may include tank bottoms) also fall under general requirements such as "Oil storage tanks shall be constructed so as to prevent leakage. Dikes or retaining walls, where necessary, shall be constructed, based on tank capacity and throughput, so as to prevent oil or deleterious substances from causing pollution and to ensure public safety." While tank bottom removal permits are not required for tanks managed by operators, they are required for commercial tank bottom reclamation facilities. Modular large volume tanks, tank berms and containment, and monitoring and are not specifically addressed in the regulations.

C3) Deleterious substance is a key waste term in the Oklahoma regulations covering a wide range of materials and wastes. It includes any chemical, salt water, oil field brine, waste oil, waste emulsified oil, basic sediment, mud, or injurious substance produced or used in the drilling, development, production, transportation, refining, and processing of oil, gas and/or brine mining.

Table C-4. Summary of Regulations for E&P Wastes in Oklahoma

Topic Area	Summary
Pit Construction and Operation Requirements	Construction and operation requirements are provided for noncommercial pits, which include completion, fracture, and workover pits, emergency pits, recycling/reuse pits, spill containment pit, remediation pits and reserve/circulation pits. Permits are required for such pits. Liner requirements vary for noncommercial pits, including reserve/circulation and/or completion/fracture/workover pits. The requirements are determined by the Commission's Technical Services Department and depend upon soil and fluid characteristics for each well site. The site will be classified to require one of five categories of containment (liner systems) ranging from unlined to geomembrane liners. Details for each category is provided in the regulations. In addition, emergency pits are not required to be lined, and basic sediment pits must have a geomembrane liner. Fencing is required for commercial pits and noncommercial brine disposal and flowback water pits but are not required for reserve and circulation pits. Requirements for netting refer to federal statutes. Freeboard requirements range from 6 inches to 3 feet depending on the pit construction and contents, and pits constructed to not receive runoff water. Requirements for minimum depth to groundwater, berm construction, and signage are also provided. Offsite reserve pits and recycling require signs, but pits associated with well sites only require general lease signs. Flowback water pits with capacity of 50,000 bbl. (either onsite or offsite) require signage. Groundwater monitoring is necessary for brine disposal well pits and flowback pits with capacities greater than 50,000 barrels. Inspections are only specified for flowback water pits. OCD is required to inspect all reserve and circulation pits in the special rule areas of Atoka, Pittsburg and Coal counties Discharge permits are required for produced water and hydrostatic test/storm water with elevated constituents. Saltwater disposal pits and flowback pits are defined as temporary storage and require permits. Non-commercial fluid recycling pits and centralized pits (only for recycling and reuse of drilling mud) are also addressed in the regulations.
Pit Closure Requirements	Liquids removal is required prior to pit closure, and multiple options for solids are allowed including on site burial with or without stabilization and offsite disposal. Closure in place requires minimum of three feet of soil cover and erosion control. The closure schedule is provided in the regulations and depends upon the pit category or type/contents. Most pits, including all reserve/circulation and flowback water pits must be closed within three to 12 months, but flare and spill pits must be closed within 30 days, and basic sediment pits must be closed within 60 days. Inspection, sampling and financial security are all required for closure of pits.
Spill Notification	Nonpermitted discharges require verbal reporting within 24 hours of discovery of (i) Any non-permitted discharge of deleterious substances of ten barrels or more (single event) to the surface; or (ii) Any discharge of a deleterious substance, regardless of quantity, to the waters of the State. A written report shall be filed within 10 business days.
Corrective Action	The Pollution Abatement regulations refer to cleanup practices and requirements addressed in the general practices appearing in the Oil and Gas Conservation Division's Guardian Guidance document. The guidance is a step by step methodology containing numerical and risk based cleanup approaches.

Table C-4. Summary of Regulations for E&P Wastes in Oklahoma

Topic Area	Summary
Off-site Landfills	Disposal of E&P waste at offsite landfills is not specified in the regulations but rather based on Department of Environmental Quality approval or landfill permit requirements, and testing is required prior to disposal. Use of waste as daily cover is not specifically addressed in the regulations.
Land Application	Water-based fluids and/or drill cutting from earthen pits and tanks may be land applied with a permit. Land restrictions (such as a maximum slope of 8% and minimum depth to bedrock of 20 inches) are provided in the extensive set of regulations. Sampling requirements and limitations/conditions for application are also included. Details and conditions for commercial soil farming are also included.
Beneficial Use	Beneficial use of brine (reuse and recycling) is allowed but details are not included in regulations. Roadspreading is not allowed. However, the regulations allow waste oil, residue and crude oil contaminated soil to be applied to lease roads and county roads with a permit. According to the table of allowable uses, drill cuttings from freshwater and oil-based muds can be applied to lease roads also.
Waste Minimization/ Management	Waste minimization practices, such as closed loop drilling and recycling of produced water, are not specifically addressed in the regulations.
Commercial Recycling and Reclamation Facilities	Subchapter 9 of Title 165, Chapter 10 addresses commercial disposal facilities, including pits, soil farming, disposal well surface facilities, and recycling facilities. Detailed requirements, including permitting, construction, financial security, and sampling/monitoring are provided for each commercial facility type.
NORM and TENORM	NORM and TENORM are not specifically addressed in state regulations.

C.5. North Dakota

In 2016, North Dakota accounted for approximately 6% of the U.S. oil and gas production as indicated by U.S. Energy Information Agency data. E&P wastes generated in North Dakota are regulated by the Industrial Commission of North Dakota, Division of Oil and Gas. Off-site waste disposal and TENORM are regulated under the North Dakota Department of Health, Solid Waste Management and Land Protection. Oil and gas regulations are amended frequently, including several updates in 2012, 2014, and 2016, which addressed fencing, drilling pits and reserve pits, in addition to other topics. Updated solid waste TENORM rules became effective in 2015. **Table C-5** provides a summary of the regulations identified for E&P wastes in North Dakota.

Table C-5. Summary of Regulations for E&P Wastes in North Dakota

Topic Area	Summary
Definitions	The General Oil and Gas Rules and Regulations (Chapter 43-02-03) provide 52 general definitions including "occupied dwelling" (lived in by a person at least six months in a calendar year). The term "saltwater handling facility" is a broad definition that appears to include any container or site used for handling storage or disposal throughout the drilling, completion and production phases. Definitions of pit types defined in the regulations include reserve pit, earthen pits/open receptacles, and drilling pits.

Table C-5. Summary of Regulations for E&P Wastes in North Dakota

Topic Area	Summary
Waste Unit Location Requirements	General location standards are provided for solid waste facilities, not E&P waste facilities specifically. For example, no solid waste management facility may be located in areas which result in impacts to human health or environmental resources or in an area which is unsuitable because of reasons of topography, geology, hydrology, or soils. Solid waste regulations contain more specific requirements; for example, solid waste facilities are not allowed within a one hundred-year floodplain or in areas designated as critical habitats for endangered or threatened species of plant, fish, or wildlife. Oil and gas regulations provide general requirements for siting. Drilling pits shall not be located in, or hazardously near, bodies of water. Saltwater handling facilities and treating plants shall be sited in such a fashion that they are not located in a geologically or hydrologically sensitive area. There are no specific setback requirements for E&P waste management facilities.
Tank Requirements	Produced water tanks and saltwater handling facilities require dikes when deemed necessary by the director. Dikes must be constructed of sufficiently impermeable material to provide emergency containment. Tank monitoring and netting for open tanks are not specifically addressed. The director may permit portable-collapsible receptacles used solely for storage of fluids used in completion and well servicing operations, although no flowback fluids may be allowed.
Pit Construction and Operation Requirements	Regulations in North Dakota cover and require permits for the following pit types: reserve pit, earthen pit/open receptacle, and drilling pits. Unlined earthen pits for saltwater, drilling mud, crude oil, waste oil, or other wastes are prohibited, except in an emergency and upon approval by the director. The director may permit pits or receptacles used solely for the purpose of flaring casinghead gas. Pits for treatment plants and saltwater facilities are prohibited unless authorized by an appropriate regulatory agency. Regulations allow for less stringent pit and disposal requirements for shallow wells using freshwater muds. Limited details are provided for pit construction and operation. Liners are mentioned but no details are included (for example, "A *lined* earthen pit or open receptacle may be temporarily used to retain oil, water, cement, solids, or fluids generated in well plugging operations…Freshwater pits shall be *lined* and no pit constructed for this purpose shall be wholly or partially constructed in fill dirt unless approved by the director"). Fencing is required for open pits and ponds that contain saltwater or oil and is not required for drilling or reserve pits used solely for drilling, completing, recompleting or plugging except after 90 days or unless indicated by the director. All pits and ponds that contain oil must be fenced, screened and netted. Berm specifications are general for drilling pits ("shall be diked in a manner to prevent surface water from running into the pit") while berms for saltwater handling facilities are more specific (for example, height requirements and must be constructed of "sufficiently impermeable material"). At saltwater handling facilities and treating plants, waste, recovered solids, and fluids must be stored and handled in such a manner to prevent runoff or migration offsite. Signage is required for freshwater pits, as well as portable-collapsible receptacles. Drilling pits require inspection by an authorized representative of the director prior to lining and use. Inspection was not noted for other types of pits. Monitoring plans and leak detection, which may include groundwater monitoring, are necessary for all buried and partially buried structures at treatment plant facilities.

Table C-5. Summary of Regulations for E&P Wastes in North Dakota

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Regulated pits may be used temporarily to (1) retain oil, water, cement, solids or fluids generated during well plugging operations containment, or (2) contain incidental fluids such as trench water and rig wash. Flare pits are considered temporary. Noncommercial fluid recycling pits are not specifically prohibited or allowed, however saltwater handling and disposal operations or fluid and tank bottom treatment at the well site which typically recover skim oil from their operations, is permitted. Central production facilities and centralized tank batteries are discussed but centralized pits are not specifically addressed. Freeboard requirements, minimum depth to groundwater, and discharge permits are not specifically addressed in the regulations.
Pit Closure Requirements	Liquids removal is required for closure of drilling, reserve and temporary pits. The contents of an earthen pit or receptacle must be removed within seventy-two hours after operations have ceased and must be disposed of at an authorized facility. Drilling waste in reserve and drilling pits should be encapsulated in the pit and covered with at least four feet [1.22 meters] of backfill and topsoil and surface sloped, when practicable, to promote surface drainage away from the reclaimed pit area. Pits shall be reclaimed within 30 days after operations have ceased (earthen pit) or within 30 days after the drilling of a well or expiration of a drilling permit (drilling pit). Reserve pits shall be closed within a reasonable timeframe but not more than one year after the completion of a shallow well, or prior to drilling below the surface casing shoe on any other well. Prior to reclaiming a drilling pit, the operator or the operator's agent shall obtain verbal approval from the director of a pit reclamation plan. Financial security for pits is not required but is included as a part of the overall well permit bond.
Spill Notification	The operators or responsible parties shall verbally notify the director immediately and follow up utilizing the online initial notification report within twenty-four hours after discovery of any fire, leak, spill, blowout, or release of fluid. The commission, however, may impose more stringent spill reporting requirements if warranted by proximity to sensitive areas, past spill performance, or careless operating practices as determined by the director.
Corrective Action	For spill cleanup, discharged fluids must be properly removed and may not be allowed to remain standing within or outside of diked areas. Operators and responsible parties must respond with appropriate resources to contain and clean up spills.
Off-site Landfills	North Dakota Administrative Code Section 43-02-03-19.2 states in part that all waste material associated with exploration or production of oil and gas must be properly disposed of in an authorized facility in accord with all applicable local, state, and federal laws and regulations. This includes filter socks and other filter media but does not require the offsite disposal of drilling mud from shallow wells or drill cuttings associated with the drilling of a well. Effective June 1, 2014, a container must be maintained on each well drilled in North Dakota to store filters until they can be properly disposed of in an authorized facility. Testing of waste prior to disposal and use of E&P waste as daily cover are not specifically addressed in the regulations.
Land Application	Land application is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in the state regulations.

Table C-5. Summary of Regulations for E&P Wastes in North Dakota

Topic Area	Summary
Commercial Recycling and Reclamation Facilities	Saltwater handling facilities and treating plants are regulated, and a bond is required for these facilities. The operator of a saltwater handling facility [or treating plant] shall provide continuing surveillance and conduct such monitoring and sampling as the commission may require. An offsite reclamation manifest is also required. "'Treating plant' means any plant permanently constructed or portable used for the purpose of wholly or partially reclaiming, treating, processing, or recycling tank bottoms, waste oils, drilling mud, waste from drilling operations, produced water, and other wastes related to crude oil and natural gas exploration and production. This is not to be construed as to include saltwater handling and disposal operations which typically recover skim oil from their operations, treating mud or cuttings at a well site during drilling operations, or treating flowback water during completion operations at a well site." "'Saltwater handling facility' means and includes any container and site used for the handling, storage, disposal of substances obtained, or used, in connection with oil and gas exploration, development, and production and can be a stand-alone site or an appurtenance to a well or treating plant."
NORM and TENORM	Disposal of TENORM is allowed at a licensed facility, and storage requirements are provided. Limitations include (1) TENORM waste up to, but not exceeding 50.0 picocuries per gram of Radium-226 plus Radium-228, and (2) equipment contaminated with TENORM which does not exceed a maximum exposure level of one hundred microroentgen per hour, including background radiation. Landfill requirements for TENORM disposal include a composite liner (at least three feet [91.4 centimeters] of recompacted clay with a hydraulic conductivity not to exceed 1 x 10^{-7} centimeters per second overlain with at least a sixty mil flexible membrane liner), and at least one-foot of non-TENORM waste or daily cover material by the end of each operating day (or once every 24-hour period for continuous operations). TENORM waste must be buried at least 10 feet below the surface of the final cover. Additional cover thickness may be required depending on the slope of the landfill. The leachate collection system and groundwater monitoring network shall be analyzed for background concentration of radionuclide parameters prior to receipt of any TENORM waste. Leachate shall be analyzed for radionuclides at the same frequency as groundwater samples are collected. If radionuclides are detected in leachate at a concentration greater than the concentrations listed below, then the groundwater monitoring network must begin analysis for radionuclide parameters: - Radon: 4,000 picocuries per liter (pCi/L) - Combined Radium-226 and Radium-228: 5 pCi/L - Alpha particle activity (excluding radon and uranium): 15 pCi/L - Uranium: 30 micrograms per liter (ug/L).

C.6. Colorado

According to data from the U.S. Energy Information Agency, in 2016, Colorado accounted for 5.1% of the U.S. oil and gas production from conventional and unconventional resources. Oil and gas wastes in Colorado is regulated by the Oil and Gas Conservation Commission under the Department of Natural Resources. Off-site waste disposal and TENORM are regulated by the Colorado Department of Public Health and Environment. Numerous sections of the Colorado oil and gas regulations were revised in

2015 to address practices in unconventional resource exploration and production. Additional updates were made in 2016. **Table C-6** provides a summary of the regulations identified for E&P wastes in Colorado.

Table C-6. Summary of Regulations for E&P Wastes in Colorado

Topic Area	Summary
Definitions	Section 100 of the Colorado Oil and Gas Code provides over 180 definitions including definitions for 15 pit types: drilling pits (includes ancillary pits, completion pits, flowback pits, and reserve pits), production pits (includes skimming/settling pits, produced water pits, percolation pits and evaporation pits) special purpose pits (includes blowdown, flare, emergency, basic sediment/tank bottom, workover and plugging pits) and reserve pits. The definition of exploration and production waste cites the RCRA exemption and provides additional clarification that wastes derived from gas plants along feeder lines, regardless of change in gas custody, are included in the definition. The regulations define a designated setback zone which incorporates definitions for two different setback zones (exclusion and buffer), and urban mitigation areas where additional regulations may apply.
Waste Unit Location Requirements	Colorado setback requirements for well and production facilities vary depending on activity and structure types. For example, the setback is 350 feet for designated outside activity areas and 1,000 feet for high occupancy building units. These requirements may be less restrictive with a mitigation plan. Production pits, special purpose pits (other than emergency pits), and flowback pits containing E&P waste shall not be allowed within a defined Floodplain, unless approved by the director. In addition, the operator must determine whether the proposed oil and gas location falls within Sensitive Wildlife Habitat or a Restricted Surface Occupancy area (definitions provided in regulations). A consultation with Colorado Parks and Wildlife is then required. Minimum depth to groundwater for pits is not specified.
Tank Requirements	Tank construction and operation regulations provide general requirements. For example, buried or partially buried tanks, vessels, or structures used for storage of E&P waste shall be properly designed, constructed, installed, and operated in a manner to contain materials safely. A synthetic or engineered liner shall be placed directly beneath. Such vessels shall be tested for leaks after installation and maintained, repaired, or replaced to prevent spills or releases of waste. There are special requirements for setback locations. Tank berms and containment structures must be sufficiently impervious and are required for all tanks containing oil, condensate, or produced water with greater than 3,500 milligrams per liter (mg/l) total dissolved solids (TDS). Recent regulations specify that containment berms around all tanks must be constructed of steel rings or another engineered technology. Requirements are not provided for modular large volume tanks or netting of open tanks. Tank bottoms may be addressed by disposal at a commercial solid waste disposal facility, treatment at a centralized E&P waste management facility, injection into a permitted Class II injection well, or by an alternate method approved by the director.
Pit Construction and Operation Requirements	Permits are required for pits covered by these regulations: drilling pits, ancillary pits, completion pits, flowback pits, reserve pits, production pits, skimming/settling pits, produced water pits, percolation pits and evaporation pits.

Table C-6. Summary of Regulations for E&P Wastes in Colorado

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Pits are not allowed within the Buffer Zone Setback (1,000 feet), except fresh water storage pits, reserve pits to drill surface casing, and emergency pits. In addition, unlined pits cannot be constructed on fill material or in areas where pathways for communication with ground water or surface water are likely to exist. Liners are required for certain pit types or waste characteristics (details are provided in the regulations). In Sensitive Areas, the director may require a leak detection system for the pit or other equivalent protective measures, that may include increased record-keeping requirements, monitoring systems, and underlying gravel fill sumps and lateral systems. In making such determination, the director shall consider the surface and subsurface geology, the use and quality of potentially-affected ground water, the quality of the produced water, the hydraulic conductivity of the surrounding soils, the depth to ground water, the distance to surface water and water wells, and the type of liner. In addition, pit level indicators shall be used within Designated Setback Locations. Pits must be constructed, monitored, and operated to provide for a minimum of two (2) feet of freeboard at all times. Netting and fencing requirements appear to be a site specific decision by the operator (and approved by the director), as follows: appropriate netting or fencing shall be used where necessary to protect public health, safety and welfare or to prevent significant adverse environmental impacts resulting from access to a pit by wildlife, migratory birds, domestic animals, or members of the general public." Well sites constructed within Designated Setback Locations must be adequately fenced to restrict access by unauthorized persons. Baseline groundwater sampling is required for new wells (not specific waste units), and signage is required for wells, batteries, centralized E&P waste management facilities and tanks, but neither is indicated for tanks specifically. Discharge permits are required for produced water discharging into Colorado state waters. Produced water, emergency and flare pits are identified as temporary, but requirements are not provided. Non-commercial fluid recycling pits are addressed as multi-well pits. Permitted centralized pits are allowed for the treatment, disposal, recycling or beneficial reuse of E&P waste. This rule applies only to non-commercial facilities. Centralized facilities may include components such as land treatment or land application sites, pits, and recycling equipment. Requirements are not specified for minimum depth to groundwater, berm construction, run-on and run-off controls, or inspections.
Pit Closure Requirements	Removal of liquids and solids is required prior to pit closure. While a specific schedule is not provided for pits, general reclamation for wells is within 3 months on crop land and 12 months on non-crop land. Inspection is required for general site reclamation (not pits specifically). Sampling is necessary to ensure that remaining soil and groundwater concentrations meet specified values (found in Table 910-1). Financial security for pits is not required separately but is included as a part of the overall well permit bond.
Spill Notification	Notification of spills is required within 24 hours if certain criteria are met.
Corrective Action	A Site Investigation and Remediation Workplan (Form 27) may be required when threatened or actual significant adverse environmental impacts on any air, water, soil or other environmental resource from a spill/release exist or when necessary to ensure compliance with the concentration levels in Table 910-1 with consideration to Colorado Water Quality Control Commission (WQCC) ground water standards and classifications. Such spills/releases shall be remediated in accordance with oil and gas regulations.

Table C-6. Summary of Regulations for E&P Wastes in Colorado

Topic Area	Summary
Off-site Landfills	Waste disposal at off-site facilities is allowed for produced water (permitted commercial facilities) and drilling fluids and oily waste (commercial solid waste facilities). Other waste such as workover fluids, tank bottoms, pigging wastes from gathering and flow lines, and natural gas gathering, processing, and storage wastes may be addressed by disposal at a commercial solid waste disposal facility, treatment at a centralized E&P waste management facility, injection into a permitted Class II injection well, or by an alternate method approved by the director.
Land Application	Land application of some E&P waste is allowed in Colorado. Water/bentonite-based muds do not require a permit and may be used for lease road and site construction (other uses require approval), or land treatment/application at a centralized E&P waste management facility. Water-based bentonitic drilling fluids may be applied at a centralized E&P waste management facility at an average thickness of no more than three (3) inches prior to incorporation. The drilling fluids must be applied to prevent ponding or erosion and incorporated as a beneficial amendment into the native soils within ten (10) days of application and resulting concentrations shall not exceed those in Table 910-1. Director approval is not required when such drilling fluids are used a soil amendment. Oily waste includes those materials containing crude oil, condensate or other E&P waste, such as soil, frac sand, drilling fluids, and pit sludge that contain hydrocarbons. Land treatment of oily waste is allowed onsite or at centralized E&P waste management permitted facilities. Requirements include removal of free oil from the oily waste prior to land treatment, no pooling, ponding, or runoff, and no contamination of storm water runoff, ground water, or surface water. Treatment by disking, tilling, aerating, or addition of nutrients, microbes, water or other amendments, is required to enhance biodegradation. Land-treated oily waste incorporated in place or beneficially reused must be in compliance with the concentrations in Table 910-1.
Beneficial Use	Beneficial use of E&P waste in Colorado includes spreading produced water (with less than 3,500 mg/L TDS) on lease roads outside sensitive areas, when authorized by the surface owner and in accordance with an approved waste management plan (per Rule 907.a(3)). Such road spreading shall not impact waters of the state, shall not result in pooling or runoff, and the adjacent soils shall meet the concentration levels in Table 910-1. Use of flowback fluids is not allowed for dust suppression. In addition, to encourage and promote waste minimization, operators may propose plans for managing E&P waste through beneficial use, reuse, and recycling by submitting a written management plan to the director for approval on a Sundry Notice. Such plans shall describe, at a minimum, the type(s) of waste, the proposed use of the waste, method of waste treatment, product quality assurance, and shall include a copy of any certification or authorization that may be required by other laws and regulations. The director may require additional information.
Waste Minimization/ Management	Closed loop drilling systems are required within the Buffer Zone Setback. Waste minimization is considered a best management practice and encouraged, as noted above.

Table C-6. Summary of Regulations for E&P Wastes in Colorado

Topic Area	Summary
Commercial Recycling and Reclamation Facilities	Produced water may be disposed at permitted commercial facilities. No person shall accept water produced from oil and gas operations, or other oil field waste for disposal in a commercial disposal facility, without first obtaining a Certificate of Designation from the County in which such facility is located, in accordance with the regulations pertaining to solid waste disposal sites and facilities as promulgated by the Colorado Department of Public Health and Environment. Financial security, offsite manifests and monitoring/testing during commercial recycling operation are not specifically addressed in these regulations.
NORM and TENORM	The Colorado Department of Public Health and Environment has authority under numerous Colorado statutes and regulations that are relevant to the control and disposition of TENORM. Interim Policy and Guidance issued in 2007 clearly describes disposal options and locations for oil and gas-related TENORM. Testing is required for each shipment prior to transport. TENORM disposal is allowed, and limitations vary with the type of facility. One hazardous waste landfill in Colorado can accept up to 400 pCi/g Ra-226 and 2,000 pCi/g total activity, with a constraint on source material limits for uranium and thorium. Three similar facilities exist in other states. Municipal solid waste landfill limitations include 3 pCi radon, 30 pCi uranium, and 3 pCi thorium. Action/Management Plans and storage requirements are not specifically addressed in the interim policy.

C.7. Wyoming

In 2016, Wyoming accounted for approximately 4.9% of the nation's oil and gas production according to the U.S. Energy Information Agency. E&P wastes generated in Wyoming are regulated by the Wyoming Oil and Gas Conservation Commission. Regulations regarding wastes disposed offsite are not specifically addressed in the regulations. NORM and TENORM wastes are regulated under the Wyoming Department of Environmental Quality Solid and Hazardous Waste Division. Several areas of the regulations, including new groundwater monitoring requirements, were updated in 2015 and 2016. **Table C-7** provides a summary of the regulations identified for E&P wastes in Wyoming.

Table C-7. Summary of Regulations for E&P Wastes in Wyoming

Topic Area	Summary
Definitions	The following pits are subject to this regulation: (i) Reserve pits on the drilling location; (ii) Reserve pits off the location within a lease, unit or communitized area permitted by Owner or unit Operator drilling the well; (iii) Produced water retention pits, skim pits, and emergency production pits including the following: (A) Pits associated with approved disposal wells which act as fluid storage, filtering or settling ponds prior to underground disposal in a Class II well; (B) Pits constructed for disposal of produced fluids in connection with oil and gas exploration and production used as part of the filtering and/or settling process upstream of a National Pollutant Discharge Elimination System (NPDES) discharge point;

Table C-7. Summary of Regulations for E&P Wastes in Wyoming

Topic Area	Summary
Definitions (cont.)	(C) Pits constructed in association with heater treaters or other dehydration equipment used in production, such as free water knockouts, or first, second and third stage separators; (D) Pits constructed for blowdown or gas flaring purposes. (iv) Pits constructed for the storage and treatment of heavy sludges, oils, or basic sediment and water (BS&W) in connection with production operations; (v) Temporary pits constructed during well workovers, including spent acid and frac fluid pits; (vi) Permanent or temporary emergency use pits; (vii) Miscellaneous pits associated with oil and gas production not listed above.
Waste Unit Location Requirements	Wyoming residential setback requirements for wells and production facilities address occupied structures (residential, school, business, and hospital use). Pits are prohibited "in drainages, or in the floodplain of a flowing or intermittent stream, or in an area where there is standing water during any portion of the year" and unlined pits are prohibited in fill material. Critical areas for pit placement are also defined and include criteria for distances to water supplies and wetlands, residences and other structures, groundwater depth, total dissolved solids content and soil type. While pits are not prohibited in critical areas, they may require additional protection. In addition, the Wyoming Environmental Quality Act restricts any commercial oil field waste disposal facility from being constructed or operated within one mile of any occupied dwelling or any public or private school, without approval. Endangered species are not specifically addressed in the regulations; however the regulations do indicate the Commission shall adopt policies and practices that may be required in compliance with the Greater Sage-Grouse Core Protection Area.
Tank Requirements	Rules include general performance requirements of tanks ("maintain tanks in a work-like manner which will preclude seepage from their confines and provide for all applicable safety measures"). The use of crude oil tanks without tops is strictly prohibited. There are no specific requirements in the oil and gas regulations for berm and containment materials for tanks, or for protective netting and tank monitoring. However, "If an SPCC Plan is applicable, any oil spilled within the SPCC containment berms at a tank battery shall be promptly removed and any containment devices installed to contain drips and spills during hose hookup shall be emptied and/or cleaned as necessary to prevent access by wildlife, domestic animals, or migratory birds." A permit is not required for tank bottom removal, but disposal of produced water, tank bottoms and other miscellaneous solid waste should be in a manner which is in compliance with the Commission's rules or other state, federal, or local regulations. Modular large volume tanks are not specifically addressed in the regulations.
Pit Construction and Operation Requirements	WOGCC rules cover construction and operation of various pit types, including reserve pits, produced water pits, skim pits, emergency pits, temporary pits and miscellaneous pits. Emergency pits are defined as temporary pits. Pits in critical areas with groundwater less than 20 feet are prohibited, and unlined pits shall not be constructed in fill. Reserve pits cannot be used as production pits; hazardous waste pits are prohibited.

Table C-7. Summary of Regulations for E&P Wastes in Wyoming

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Liners are required for pits constructed in fill or those retaining oil base drilling muds, high density brines, and/or completion or treating fluids, or if the produced water has a total dissolved solids concentration greater than 10,000 mg/L. Details for liners and slopes (3:1) are provided, while general guidelines are included for freeboard (Liquids must be kept at a level that takes into account extreme precipitation events and prevents overtopping and unpermitted discharges.) Specifications for other elements of pit construction and operation including run-on/run-off controls and berm construction are not included in these rules. Fencing is required for all pits and netting is necessary when timely removal of fluid is not possible. Signage is required for each pit, unless in close proximity to marked wells. Discharge permits are required to discharge stormwater that has come in contact with any overburden, raw material, intermediate products, finished products, byproducts or waste products located on the site. Storm water discharges associated with small construction activity require permit authorization as of March 10, 2005. A groundwater baseline sampling, analysis and monitoring plan for the site (not specific to pits) is required as part of the application to drill or deepen a well. "Monitoring systems may be required for pits constructed in sensitive areas [as specified in the permit]. Such pits must be operated in a manner that avoids damage to liner integrity. Periodic inspections, weekly at a minimum, of pits must be made by the Owner or Operator and documentation of such inspections may be required to be submitted to the Supervisor at his request… The Supervisor is also authorized to require the testing necessary for the regulation of oil field pits and wastes." Permits for noncommercial centralized pits may be more stringent than for individual pits; they are issued for a five-year term and may be renewed at the discretion of the Supervisor. Noncommercial fluid recycling pits are not specifically addressed in these regulations.
Pit Closure Requirements	Pit closure may include evaporation and subsequent burial of solids depending on the fluids, type of pit and solids content. Burial methods cannot compromise the integrity of the liner without written approval by the Supervisor. One-time landspreading of reserve pit fluids on the drilling pad may be approved. Trenching or squeezing of pits is expressly prohibited. Notice (24 hours) is required prior to pit closure to allow the Commission staff to witness closure operations. Commercial treatment of pits may be approved. Pit reclamation should be completed in a timely manner as climatic conditions allow. Production and reserve pits should be reclaimed after they have dried sufficiently following removal of any oil, sheens or other hydrocarbons, and no later than one year after the date of last use, unless a variance is granted. High salt content materials must be removed prior to pit closure. Inspections may be required (at the Commission's option), and sampling is determined by the Supervisor based upon site-specific conditions. All disturbed areas on state lands will be reseeded. A Sundry Notice shall be submitted upon completion of pit closure. Pit bonds may be required. Pits used solely for the retention of water produced in association with the recovery of coalbed methane gas in the Powder River Basin may be left open with approval.
Spill Notification	Oil and gas rules indicate that uncontained spills or unauthorized releases of produced fluids, drilling muds, produced water, hydrocarbons, or chemicals which enter, or threaten to enter, waters of the state must be verbally reported to the Commission no later than the next business day following discovery of the incident. The Owner or Operator shall file a written report within 15 working days. Notification for contained spills depends upon the volume of the spill.

Table C-7. Summary of Regulations for E&P Wastes in Wyoming

Topic Area	Summary
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	Regulations for offsite disposal are unclear. Testing of the waste is determined by the Supervisor based upon site-specific conditions. Regulations do not address drill cuttings as daily cover in landfill.
Land Application **Beneficial Use**	Regulations related to land application and beneficial use are intertwined in the regulations and may be somewhat confusing. Landfarming and landspreading must be approved by the Department of Environmental Quality, whereas jurisdiction over roadspreading or road application is shared by DEQ and the Commission. The Commission is the agency responsible for permitting road applications of E&P wastes in drilling fluids, produced water and produced water-contaminated soils, waste crude oil, sludges, and oil-contaminated soils inside the boundaries of a lease, unit, or communitized area. Landfarming, landspreading, and roadspreading shall be protective of human health and the environment and shall be performed in compliance with all other applicable State and Federal regulations and requirements." Testing and analysis are required on permit applications for road application of wastes.
Waste Minimization/ Management	Depending upon location of pit, the Commission may make modifications as necessary to provide additional protection from site activities, which may include running a closed drilling system. In areas where groundwater is less than 20 feet below the surface, a closed system must be utilized for well drilling operations. "The Commission encourages the recycling of drilling fluids and by administrative action approves the transfer of drilling fluids intended for recycling. When removed as a product for use in a drilling operation on another lease, drilling fluid is not classified as a waste. If federal leases are involved, the Owner or Operator must obtain the approval of the Bureau of Land Management (BLM). The Supervisor requires the following information be included on the Form 14B or on a Sundry Notice (Form 4) estimated volume, estimated date of transfer, mud recap, analyses which include at a minimum, pH, chlorides, and oil and grease. To protect shallow groundwater, drilling muds with chlorides testing in excess of 3,000 parts per million or those containing hydrocarbons cannot be used in drilling operations until after the surface casing has been set."
Commercial Recycling and Reclamation Facilities	Regulations do not address commercial recycling or reclamation facilities.
NORM and TENORM	The Wyoming Department of Environmental Quality, Solid and Hazardous Waste Division (SHWD) provides guidelines regarding NORM, which is considered a solid waste, and states the regulation of NORM is supported by existing statutes and regulations. Solid waste disposal is allowed up to 50 pCi/g of radium-226 but the volume accepted depends on the concentration. Up to 20 cubic yards of waste containing NORM between background (or 8pCi/g) and 30 pCi/g of radium-226 may be disposed in a state-permitted solid waste disposal facility with approval from the landfill operator, and may be stored for up to one year without prior written authorization from SHWD. Up to 10 cubic yards with NORM between 30 and 50 pCi/g may be disposed in a state-permitted solid waste disposal facility with approval from the landfill operator and a minimum 4-feet of approved cover material. Such waste may be stored for a period not to exceed 180 days without prior written authorization from SHWD. NORM/TENORM wastes exceeding 50 pCi/g of radium-226 cannot be disposed in conventional solid waste facilities in Wyoming and must be disposed at facilities outside of Wyoming that accept such low-level radioactive waste. Oil and gas regulations do not address NORM/TENORM.

C.8. New Mexico

In 2016, New Mexico accounted for approximately 4.6% of the nation's oil and gas production according to the U.S. Energy Information Agency. Oil and gas are produced from both conventional and unconventional resources, and the state also has coal bed methane production. The New Mexico Oil Conservation Division (OCD) within the Department of Energy, Minerals and Natural Resources regulates oil and natural gas production. The Environmental Improvement Board is responsible for the promulgation of rules and standards in many areas including food protection, air, radiation, waste, drinking water and others. NORM related to oil and natural gas production is regulated by both the New Mexico Oil Conservation Division and the Environmental Improvement Board.

OCD has promulgated a set of 15 rules (chapters) which include extensive requirements for waste management. Title 19, Chapter 15, Part 17 (Pits, Closed-Loop Systems, Below-Grade Tanks and Sumps) was updated in June 2013. Most sections in Part 2 (General Provisions for Oil and Gas Operations) were updated in December 2008 but a few were amended several times since then including the latest in June 2018. The waste management practices (produced water, drilling fluids, liquid wastes, and surface waste management facilities were updated in 2015 and 2016. **Table C-8** provides a summary of the regulations identified for E&P wastes in New Mexico.

Table C-8. Summary of Regulations for E&P Wastes in New Mexico

Topic Area	Summary
Definitions	Approximately 180 definitions are provided in the general provisions for oil and gas operations (Title 19, Chapter 15, Part 2). Twenty additional definitions are provided in Part 17 (Pits, Closed-Loop Systems, Below-Grade Tanks and Sumps), which include four types of pits: emergency pit, multi-well fluid management pit, permanent pit and temporary pit. Additional definitions are included in other sections of the regulations. The definitions of pits are comprehensive and sometimes include regulations on their use. For example, the definition of multi-well fluid management pit notes that it can not be used for disposal of drilling, completion or other waste, and any additional of wells for the pit use must go to a hearing.
Waste Unit Location Requirements	Detailed siting requirements are provided for temporary pits (containing low chloride fluids or not low chloride fluids), permanent pit or multi-well fluid management pits, material excavated during pit construction and below-grade tanks. For example, setbacks for various pits range from 300 to 1,000 feet from residential buildings and 100 to 500 feet from a wetland. Minimum depth to groundwater ranges from 25 to 50 feet below the bottom of the pit/tank depending on the type. Emergency pits are exempt from such location restrictions. Siting requirements are comprehensive and include criteria such as streams, playas, sinkholes, unstable areas, municipal boundaries (not allowed within municipal boundaries), wells, wetlands, mines, and floodplains. Endangered species are not specifically addressed in the siting and location requirements.

Table C-8. Summary of Regulations for E&P Wastes in New Mexico

Topic Area	Summary
Tank Requirements	Tank requirements for below-grade tanks are included in the pit requirements and be “constructed of materials resistant to the below-grade tank’s particular contents and resistant to damage from sunlight.” Above ground open-top tanks require screen, nets or be otherwise rendered non-hazardous to wildlife, including migratory birds. Where netting or screening is not feasible, the operator shall on a monthly basis inspect for, and within 30 days of discovery, report discovery of dead migratory birds or other wildlife to the appropriate wildlife agency and to the appropriate division district office in order to facilitate assessment and implementation of measures to prevent incidents from reoccurring. Berms (fire walls) are not required unless tanks are within the city limit or 1000 feet from a residence. Oil and gas regulations include limited requirements for construction or operation of above ground tanks, but the Petroleum Storage Tank division regulates crude oil tanks and has extensive regulations for construction and operation. Modular large volume tanks, tank monitoring and tank bottom removal are not specifically addressed in the oil and gas regulations.
Pit Construction and Operation Requirements	Extensive construction and operation requirements are provided for temporary pits, permanent pits and multi-well pits. Permits are required for such pits, and unlined pits are prohibited. The application requirements for pit permits differs for each type of pit and require information on the design, operating, maintenance and closure. Permanent pit design must be signed by a registered engineer. Liner requirements vary by pit type and range from single geomembrane liner (temporary) to primary and secondary liners with a leak detection system (permanent and multi-well). Additional construction details including pit slope, liner installation and performance criteria are provided in the regulations. Signs, fencing and netting are required. A separate pit sign is only required if the pit is not associated with a well site where a sign is already posted. OCD must be given the opportunity to inspect the pit prior to liner installation. Minimum depth to groundwater ranges from 25 to 50 feet depending on pit type. A freeboard of 3 feet is required for permanent pits, and the volume of a temporary pit can not exceed 10-acre feet including freeboard. Specifications for berms, ditches and other diversions are not provided but should be constructed to prevent run-on of surface water. The pit application package requires a hydrologic analysis of the proposed pit location and detailed design and operation information. An approved discharge plan is required for some discharges, and a permit is required for the discharge of hydrostatic test water. Groundwater monitoring of the pit or well site is not required but inspections are mandated and operators must inspect pits on daily or weekly basis, depending on pit use, as specified in the regulations. Noncommercial fluid recycling pits are specifically addressed in the regulations and have an extensive set of design requirements and operational requirements. No permit is required for recycling facilities if the water is used for drilling, completion, producing, secondary recovery, pressure maintenance or plugging of wells. Evaporation, storage, treatment and skimmer ponds are addressed in a separate set of regulations and include detailed technical requirements for design and operation.

Table C-8. Summary of Regulations for E&P Wastes in New Mexico

Topic Area	Summary
Pit Closure Requirements	Pit closure requirements are well defined in the OCD regulations. A closure plan describing the closure method and procedures is required for all pit types as part of the pit permit application process. Requirements for pit closure are provided based on the final disposal location of the waste (off-site disposal or buried in place). Liquids removal is required prior to pit closure, and solids removal is necessary for off-site disposal. Burial in place is allowed but testing of waste and oils is required. Waste stabilization and a covering by a liner may be required. A closure schedule and sampling requirements (number of samples, analytes and methods) are included in the regulations. Financial security is required for the general well permit, not pits specifically. Inspections of pit closure are not required, but the OCD must be notified prior to pit closure.
Spill Notification	Release notification is discussed "To require persons who operate or control the release or the location of the release to report the unauthorized release of oil, gases, produced water, condensate or oil field waste including regulated NORM, or other oil field related chemicals, contaminants or mixtures of those chemicals or contaminants that occur during drilling, producing, storing, disposing, injecting, transporting, servicing or processing and to establish reporting procedures." Notification for a major release includes immediate verbal notification (within 24 hours) and follow-up written notification within 15 days; minor release requires only written notification (within 15 days). A major release includes (1) an unauthorized release of a volume, excluding gases, in excess of 25 barrels; (2) an unauthorized release of a volume that: (a) results in a fire; (b) will reach a watercourse; (c) may with reasonable probability endanger public health; or (d) results in substantial damage to property or the environment; (3) an unauthorized release of gases in excess of 500 MCF; or (4) a release of a volume that may with reasonable probability be detrimental to water or exceed the standards in Subsections A and B or C of 19.15.30.9 NMAC. Minor release means an unauthorized release of a volume, greater than five barrels but not more than 25 barrels; or greater than 50 MCF but less than 500 MCF of gases.
Corrective Action	Corrective action is specified as "The responsible person shall complete division-approved corrective action for releases that endanger public health or the environment. The responsible person shall address releases in accordance with a remediation plan submitted to and approved by the division or with an abatement plan submitted in accordance with 19.15.30 NMAC." Title 19, Chapter 15, Part 30 (Remediation) has the following objective: "To abate pollution of subsurface water so that ground water of the state that has a background concentration of 10,000 mg/l or less TDS is either remediated or protected for use as domestic, industrial and agricultural water supply, and to remediate or protect those segments of surface waters that are gaining because of subsurface-water inflow for uses designated in the water quality standards for interstate and intrastate surface waters in New Mexico, 20.6.4 NMAC; and abate surface-water pollution so that surface waters of the state are remediated or protected for designated or attainable uses as defined in the water quality standards for interstate and intrastate surface waters in New Mexico, 20.6.4 NMAC."

Table C-8. Summary of Regulations for E&P Wastes in New Mexico

Topic Area	Summary
Off-site Landfills	Disposal of E&P waste is allowed at commercial and non-commercial (operator owned) solid waste facilities as specified in the regulations. Regulations contain an extensive set of requirements for construction, operation, closure and post closure of surface waste management facilities (centralized facilities, landfills, small landfarms, large landfarms, evaporation ponds, treatment ponds and skimmer ponds. Signs are required for all subsurface facilities (landfills and landfarms) and permits are required for all facilities except small landfarms (less than 2 acres and 2000 cubic yards of waste). Testing is required prior to disposal. In addition, produced water may be processed at "recycling facilities such as skimmer and evaporate ponds. Permitted solid waste facilities require financial security. Solid waste guidance allow use of treated petroleum contaminated waste as an alternative daily cover if it meets soil quality criteria for the facility.
Land Application	E&P waste consisting of soil and drill cuttings predominately contaminated by petroleum hydrocarbons may be landfarmed. Specifications and conditions for landfarming are included in the regulations (for example, the waste must be sufficiently free of liquid content to pass the paint filter test and background testing is required prior to land application). A land farm permit is required for large landfarms and Form C-137 is required for small landfarm.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Closed loop drilling and recycling of produced water are considered best management practices but are not required.
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities are addressed in these regulations, including monitoring/testing during operation and financial security/closure. An offsite reclamation manifest is not required.
NORM and TENORM	NORM is defined in the environmental regulations and also addressed in a separate section of the oil and gas regulations. Under the oil and gas regulations, NORM with less than 30 pCi/g Ra 226 or 150 pCi/g of any other radionuclide is exempt from disposal regulation. Disposal limitations and conditions are based on the general permit conditions provided in the regulations, and may be allowed at commercial or centralized surface waste management facilities, plugged and abandoned wells and injection wells. Regulations specifically allow NORM to be disposed at or near the surface at the site of generation. An action plan/management plan is required, and testing is required prior to disposal. Storage requirements for regulated NORM are provided in the regulations.

C.9. Louisiana

In 2016, Louisiana accounted for approximately 4.4% of the nation's oil and gas production, according to the U.S. Energy Information Agency. Louisiana has long history of producing oil and gas from conventional reservoirs but has recently increased unconventional production from the Haynesville and Tuscaloosa Marine Shale. Less than 10% of Louisiana's oil and gas production is from offshore, state-controlled lands. The Department of Natural Resources has three offices that oversee oil and gas resources in Louisiana: The Office of Conservation, the Office of Mineral Resources and the Office of Coastal Management. The Geological Oil and Gas Division within the Office of Conservation regulates oil and gas production activities. The Louisiana Department of Environmental Quality, Office of Environmental Compliance, Division of Emergency and Radiological Services regulates NORM in the state.

Oil and gas regulations included in Title 43 Natural Resources, Part XIX Office of Conservation are current as of March 2017, but the regains did not specify when the sections were last updated. NORM regulations contained in Title 33 Environmental Quality, Part XV Radiation Protection are dated October 2014. A new rule regarding hydraulic fracturing in the Haynesville Shale became effective in 2011.. **Table C-9** provides a summary of the regulations identified for E&P wastes in Louisiana.

Table C-9. Summary of Regulations for E&P Wastes in Louisiana

Topic Area	Summary
Definitions	Approximately 50 definitions are provided for the storage, treatment and disposal of E&P waste in the Definitions section of Chapters 3 (on-site) and 5 (off-site) of Title 43. In Chapter 3 (on-site), a pit is defined as "for purposes of this Chapter, a natural topographic depression or man-made excavation used to hold produced water or other exploration and production waste, hydrocarbon storage brine, or mining water. The term does not include lined sumps less than 660 gallons or containment dikes, ring levees or firewalls constructed around oil and gas facilities." A slightly different version is presented in Chapter 5 (off-site) where a pit is defined as "an earthen surface impoundment constructed to retain E&P Waste, often referred to as a pond or lagoon. The term does not include lined sumps less than 660 gallons." Production Pits are defined as either earthen or lined storage pits for collecting E&P Waste sediment periodically cleaned from tanks and other producing facilities, for storage of produced water or other exploration and production wastes produced from the operation of oil and gas facilities, or used in conjunction with hydrocarbon storage and solution mining operations, and include the following types: 1. *Burn Pits*—earthen pits intended for use as a place to temporarily store and periodically burn exploration and production waste (excluding produced water) collected from tanks and facilities. 2. *Compressor Station Pits*—lined or earthen pits intended for temporary storage or disposal of fresh water condensed from natural gas at a gas pipeline drip or gas compressor station. 3. *Natural Gas Processing Plant Pits*—lined or earthen pits used for the storage of process waters or stormwater runoff. No produced water may be stored in a natural gas processing plant pit. 4. *Produced Water Pits*—lined or earthen pit used for storing produced water and other exploration and production wastes, hydrocarbon storage brine, or mining water. 5. *Washout Pits*—lined earthen pits used to collect wash water generated by the cleaning of vacuum truck tanks and other vessels and equipment only used to transport exploration and production waste. Any materials other than E&P Waste are prohibited from being placed in such pits. 6. *Well Test Pits*—small earthen pits intended for use to periodically test or clean up a well. 7. *Emergency Pits*—lined or earthen pits used to periodically collect produced water and other E&P Waste fluids only during emergency incidents, rupture or failure of other facilities.

Table C-9. Summary of Regulations for E&P Wastes in Louisiana

Topic Area	Summary
Definitions (Cont.)	8. *Onshore Terminal Pits*—lined or earthen pits located in the coastal area used for storing produced water at terminals that receive crude oil and entrained water by pipeline from offshore oil and gas production facilities. 9. *Salt Dome Cavern Pits*—lined or earthen pits located in the coastal area associated with the storage of petroleum products and petroleum in salt dome caverns. Reserve pits are also defined as "temporary earthen pits used to store only those materials used or generated in drilling and workover operations."
Waste Unit Location Requirements	Production pits, may not be constructed in certain flood hazard boundary areas unless such pits have levees which have been built at least 1 foot above the 100-year flood level and able to withstand the predicted velocity of the 100-year flood. Location, construction and use of such pits is discouraged. These levee height requirements do not apply to production pits less than 10'x10'x4' deep, contain only brine and produce less than or equal to one barrel of saltwater per day. On-site burn pits and well test pits shall not be located less than 100 feet from a well location, tank battery, separator, heater-treater, or any and all other equipment that may present a fire hazard. Unlined pits and burial cells shall not be deeper than five feet above the high seasonal water table. Contamination of a groundwater aquifer or a USDW with E&P waste is strictly prohibited. In addition, the injection of E&P Waste into a groundwater aquifer or a USDW is strictly prohibited. Commercial solid waste facilities and transfer stations may not be within 1/4 mile of a public water supply well or within 1,000 feet of a private water supply well for facilities permitted after January 1, 2002. Commercial facilities and transfer stations may not be located in any area: where such area, or any portion thereof, has been designated as wetlands by the U.S. Corps of Engineers during, or prior to, initial facility application review, unless the applicable wetland and DNR Coastal Management Division coastal use permits are obtained. Specifications for flood areas discussed above also apply to these facilities. Commercial facilities and transfer stations may not be within 500 feet of a residential, commercial, or public building, church, school or hospital. Additional setbacks are necessary when the perimeter of Type A land treatment units are within the restricted residential area for storage tank sludges and gas [plant wastes waste types 6 and 12 (depending on concentration of total benzene). *[Type A Facility—a commercial E&P Waste disposal facility within the state that utilizes technologies appropriate for the receipt, storage, treatment, or disposal of E&P Waste solids and fluids (liquids) for a fee or other consideration. Type B Facility—a commercial E&P Waste disposal facility within the state that utilizes underground injection technology for the receipt, storage, treatment, and disposal of only saltwater or other E&P Waste fluids (liquids) for a fee or other consideration.]* Transfer stations are exempt from the location requirement of 500 feet from a commercial building. Location restrictions for land treatment units are discussed in that section below. Endangered species are not specifically addressed in the oil and gas regulations.

Table C-9. Summary of Regulations for E&P Wastes in Louisiana

Topic Area	Summary
Tank Requirements	Commercial facilities and transfer stations shall be operated in compliance with, but not limited to, the following: 1. The area within the confines of tank retaining walls (levees) shall be kept free of debris, trash, and accumulations of oil or other materials which may constitute a fire hazard. Portable gasoline powered engines and pumps must be supervised at all times of operation and stored at least 50' from tank battery firewalls when not in use. Vent lines must be installed on all E&P Waste storage tanks and must extend outside of tank battery firewalls. 2. The area within the confines of tank retaining walls (levees) must be kept free of accumulations of E&P waste fluids and water. Such fluids shall be properly disposed of by injection into a Class II well or discharged in accordance with the conditions of a discharge permit granted by the appropriate state agency. 3. Tank retaining walls shall be kept free of debris, trash, or overgrowth which would constitute a fire hazard or hamper or prevent adequate inspection. 4. Tank retaining walls (levees) must be constructed of soils which are placed and compacted in such a manner as to produce a barrier to horizontal movement of fluids. The levees must be properly tied into the barrier along the bottom and sides of the levees. All levees must be provided with a means to prevent erosion and other degradation. "Each permanent oil tank or battery of tanks that are located within the corporate limits of any city, town or village, or where such tanks are closer than 500 feet to any highway or inhabited dwelling or closer than 1000 feet to any school or church, or where such tanks are so located as to be deemed a hazard by the Commissioner of Conservation, must be surrounded by a dike (or firewall) or retaining wall of at least the capacity of such tank or battery of tanks, with the exception of such areas where such dikes (or firewalls) or retaining walls would be impossible such as in water areas. At the discretion of the Commissioner of Conservation, firewalls of 100% capacity can be required where other conditions or circumstances warrant their construction. 1. In water, swamp or marsh areas, where the building of firewalls is impossible or impracticable, in the future, permanent tanks shall be placed on an impervious platform surrounded by a metal gutter to catch all the oil and other wastes which may cause either a fire-hazard or pollution. A sump shall be provided to catch the run-off from the gutters; however, if the operator or company has devised a plan which serves the same purpose, the District Manager may after being presented with the plan, waive the above requirements. 2. Tanks not falling in the above categories (Paragraphs 1 and 2) must be surrounded by a retaining wall, or must be suitably ditched to a collecting sump, each of sufficient capacity to contain the spillage and prevent pollution of the surrounding areas." Netting, modular large volume tanks, monitoring, construction and tank bottom removal are not specifically addressed in the oil and gas regulations.

Table C-9. Summary of Regulations for E&P Wastes in Louisiana

Topic Area	Summary
Pit Construction and Operation Requirements	The following pit types are defined and separate specifications are provided in the regulations for Produced Water, Onshore Terminal, and Washout Pits; Reserve Pits; Burn Pits; Well Test Pits; Emergency Pits; Natural Gas Processing Plant Pits, Compressor Station Pits, and Salt Dome Cavern Pits. Permits are required for injection wells, and signage is required for the well site; neither are required for pits specifically. Production pits (except as noted below) require a liner with a hydraulic conductivity no greater than 1 x 10-7 cm/sec for 3 continuous feet of clay, which may include the following types of liners: natural liner; soil/mixture liner, recompacted clay liner, manufactured liner or a combination liner. An alternate groundwater aquifer and USDW protection system may be approved by the Office of Conservation. Pits constructed with a manufactured liner must have side slopes of 3:1 and the liner at the top of the pit must be buried in a 1' wide and 1' deep trench. Sufficient excess liner material shall be placed in the pit to prevent tearing when filled with E&P waste. Pits that meet the following criteria are not required to have a liner: production pits located within an 'A' zone (FEMA - One-percent-annual-chance flood event) that are less than or equal to 10' x 10' x 4' deep; contain only produced brine; and is utilized for gas wells producing less than 25 mcf per day and less than or equal to one barrel of saltwater per day (bswpd). Burn pits, compressor station pits, natural gas processing plant pits, well test pits, salt dome cavern pits are exempt from the liner requirements above. Produced water pits, washout pits and onshore terminal pits located in the coastal area shall comply with the above requirements, unless such pit is subject to an approved Louisiana Water Discharge Permit System permit. For Emergency Pits, groundwater aquifer and USDW protection shall be evaluated on a case-by-case basis. Operators who intend to utilize existing or new emergency pits without liners must demonstrate by written application to the Office of Conservation that groundwater aquifer and USDW contamination will not occur; otherwise, emergency pits shall be lined. Applications to demonstrate unlined pits will not contaminate groundwater aquifers and USDW's shall at a minimum address the following: Emergency Incident Rate, soil properties, Groundwater Aquifer Evaluation, and Produced Water Composition (total dissolved solids and oil and grease). All emergency pits required to be lined must conform to hydraulic conductivity requirements (1 x 10-7 cm/sec for 3 continuous feet of clay). No produced water or any other E&P Waste shall be intentionally placed in any emergency pit not meeting the hydraulic conductivity requirements, except in the case of an emergency incident. In emergency situations, notice must be given to the Office of Conservation within 24 hours after discovery of the incident. Produced water and any other E&P Waste must be removed from the pit within seven days following termination of the emergency situation. Levees or walls are necessary to protect pits from surface water flow and serve as secondary containment. Specific requirements for levees are only provided for flood areas (levees must be constructed at least 1 foot above the 100-year flood elevation) and coastal areas (levees must have an elevation of at least 2 feet above mean high tide). A freeboard of 2 feet is required from the top of the pit/levee. Unlined pits shall not be within 5 feet of the seasonal high groundwater table. Minimum depth to groundwater is not specified for other pit types.

Table C-9. Summary of Regulations for E&P Wastes in Louisiana

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Upon a determination by the operator or the Office of Conservation that any pit subject to this rule is likely to contaminate a groundwater aquifer or a USDW, the Office of Conservation shall require the timely submission of a plan for the prevention of such contamination. Such plan may include using an under-built drainage and collection system, monitoring wells, and/or other means that the Office of Conservation may approve to prevent or detect contamination. Any required monitor wells shall be registered with the appropriate state agency. When required, monitoring shall be conducted on a quarterly schedule. A written report summarizing the results of such monitoring shall be submitted to the Office of Conservation within 30 days of the end of each quarter. Except for reserve pits, operators must notify the Office of Conservation of the intent to construct new pits at least 10 days prior to start of construction. Notification shall contain all information requested in §305.D or §303.K.4 as appropriate. The Office of Conservation may inspect any proposed pit site prior to or during construction; however, initial use of the completed pit need not be deferred if no inspection is made. A waste management and operations plan (WMOP) is required for commercial facilities and transfer stations and should include "a plan for routine inspection and maintenance of monitoring equipment (e.g., gauges, monitor wells, etc.) to ensure and demonstrate compliance with permit and regulatory requirements." Reserve pits are defined as "temporary earthen pits used to store only those materials used or generated in drilling and workover operations." Emergency pits are also discussed, which are only to be used during emergencies. Leak detection monitoring, noncommercial fluid recycling pits and centralized pits are not specifically addressed in the regulations. Discharges into man-made or natural drainage or directly into state waters will be allowed only after the necessary discharge permit has been obtained from the appropriate state and/or federal agencies and in accordance with the conditions of such permit. A Louisiana Water Discharge Permit System (LWDPS) permit may be required.
Pit Closure Requirements	A variety of pit closure techniques are allowed: onsite land treatment, burial, solidification, onsite land development, or other techniques approved by the Office of Conservation. Otherwise, all E&P waste must be manifested and transported offsite to a permitted commercial facility unless temporarily used in hydraulic fracture stimulation operations conducted on the Haynesville Shale Zone. Details are provided for each process but specifications about liquids and solids removal is not included specifically. A pit being closed by passive closure (not defined in the regulations) does require inspection by a conservation enforcement officer. Inspections do not appear to be necessary for other pit closure activities. However, documentation of testing and closure activities, including onsite disposal of E&P waste, shall be maintained in operator's files for at least three years after completion of closure activities. Upon notification, the Office of Conservation may require the operator to furnish these data for verification of proper closure of any pit. If proper onsite closure has not been accomplished, the operator will be required to bring the site into compliance with applicable requirements. Sampling is required prior to closure of any pit and for all closure and onsite and offsite disposal techniques excluding subsurface injection of reserve pit fluids. O&G waste must be analyzed for the following: pH, total metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, zinc), oil and grease, soluble salts and cationic distributions, and radioisotopes (for pits located in the coastal area closed after October 20, 1990).

Table C-9. Summary of Regulations for E&P Wastes in Louisiana

Topic Area	Summary
Pit Closure Requirements (Cont.)	Financial security is required for the well site and associated activities. Financial security shall remain in effect until release thereof is granted by the commissioner pursuant to written request by the operator. Such release shall only be granted after plugging and abandonment and associated site restoration is completed and inspection thereof indicates compliance with applicable regulations or upon transfer of such well to an exempt operator. Plugging and abandonment of a well, associated site restoration, and release of financial security constitutes a rebuttable presumption of proper closure but does not relieve the operator from further claim by the commissioner should it be determined that further remedial action is required. Commercial facilities and transfer stations shall maintain a bond or irrevocable letter of credit on file with the Office of Conservation to provide for adequate closure of the facility. A closure schedule was not provided in the regulations.
Spill Notification	A waste management and operations plan (WMOP) is required for commercial facilities and transfer stations and should include "a contingency plan for reporting, responding to and cleaning up spills, leaks, and releases of E&P Wastes or treatment byproducts, including provisions for notifying applicable local, state and federal emergency response authorities and for taking operator-initiated emergency response actions." Any spills that occur during the offsite transportation of E&P waste shall be reported by phone to the Office of Conservation, within 24 hours of the spill and the appropriate state and federal agencies. Information regarding spills at the well site are not provided in these regulations.
Corrective Action	Corrective actions resulting from spills are not specifically addressed in the regulations. If monitoring of a groundwater aquifer or USDW indicates contamination due to a discharge from a pit, the owner or operator shall immediately notify the Office of Conservation. Within 30 days, the operator shall empty the pit of all E&P Waste and submit a remedial plan for prevention of further contamination of any groundwater aquifer or any USDW. Upon approval, the remedial plan shall be implemented by the operator and monthly progress reports, reviewing actions taken under the plan and their results, will be filed with the Office of Conservation until all actions called for in the plan have been satisfactorily completed.
Off-site Landfills	Regulations state “At the option of the generator, E&P waste may be treated and/or disposed at Department of Natural Resources (DNR) permitted commercial facilities and transfer stations under the provisions of this Chapter or Department of Environmental Quality (DEQ) permitted facilities as defined by LAC 33:V and VII which are permitted to receive E&P Waste which are subject to relevant DEQ regulations. If received, stored, treated and/or disposed at a DEQ regulated facility, E&P waste would become the sole regulatory responsibility of DEQ upon receipt.” It is unclear which type of DEQ regulated facility accepts E&P waste. Waste characterization is required prior to offsite storage, treatment or disposal. At a minimum, E&P Waste should be tested for the following constituents: pH, TPH, EC, TCLP benzene, SAR, ESP and the following metals: As, Ba, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, Ag and Zn. E&P waste may be re-used as daily cover at a sanitary landfill if compliance with testing criteria is achieved for moisture content, pH, EC, SAR, ESP, total barium, leachate testing for TPH and chlorides, benzene, metals and NORM. The use of reusable material in a sanitary landfill will require written approval of the Department of Environmental Quality.

Table C-9. Summary of Regulations for E&P Wastes in Louisiana

Topic Area	Summary
Land Application	Land application of E&P waste is permitted both on-site and at off-site commercial facilities. Onsite land treatment allows for pits to be closed by mixing waste with soil from pit levees or wall and adjacent areas, as long as the waste/soil mixture does not exceed a pH of 6-9 and specified criteria for metals. Land treatment in submerged wetland, elevated wetland, and upland areas is permitted if the oil and grease content of the waste/soil mixture after closure is < 1% (dry weight). Additional parameters (EC, SAR and ESP) are provided for elevated freshwater wetland areas where the disposal site is not normally inundated and upland areas. Land treatment at off-site facilities have additional requirements: they shall be isolated from contact with public, private or livestock water supplies, both surface and underground; soil shall contain a slowly permeable horizon at least 12 inches thick containing enough fine grained material within 3 feet of the surface to classify it as fine grained material (CL, OL, MH, CH, or OH under the Unified Soil Classification System) and the seasonal high water table shall remain at least 36 inches below the soil surface. Land treatment cells and associated surface drainage system surfaces shall at no time have an accumulation of oil of more than 1 inch at any surface location, and land treatment cell levels shall be maintained with at least 2 feet of freeboard at all times.[C4] The location restriction for land treatment of E&P wastes is typically 1,000 feet from a residential/public building, church, school or hospital. However, waste types 06 (storage tank sludges) and 12 (gas plant waste solids) have additional limitations depending on their benzene concentrations. For example, waste type 06 with a total benzene concentration greater than 113 mg/kg and waste type 12 less than 3,198 mg/kg total benzene may not be within 2000 feet of such buildings, while waste type 12 with total benzene concentrations greater than 3,198 mg/kg is banned from land treatment.
Beneficial Use	Roadspreading may be conducted using stabilized E&P waste. Reserve pits may be closed by processing the waste material with Department of Environmental Quality approved stabilizing additives and using the mixture onsite to develop lease roads, drilling and production locations, etc. The following conditions must be met for use of waste from reserve pits: pH range of the mixture: 6-12; electrical conductivity (EC) < 8 mmhos/cm; oil and grease content < 1% by weight; total metals content meeting the criteria (see §313.C.2 for limitations), leachate testing for chloride concentration < 500 mg/L; and NORM concentrations do not exceed applicable DEQ criteria or limits. Beneficial use of brine is not specifically mentioned in the regulations. Subsurface disposal of salt water is required and regulated by LAC 43:XIX.401 et seq.
Waste Minimization/ Management	Closed waste storage systems are encouraged but not required. Produced water is not required to be recycled but may be re-used in hydraulic fracturing stimulation activities in the Haynesville Shale. "In order to encourage the conservation and recovery of resources in the oilfield industry, the processing of E&P Waste into reusable materials, in addition to or beyond extraction and separation methods which reclaim raw materials such as crude oil, diesel oil, etc., is recognized as a viable alternative to other methods of disposal."

C4) Freeboard is most commonly applied to liquid controls, but it also can apply to solid wastes. In this case the waste in the land treatment cell must not come within two feet of the top of the berm.

Table C-9. Summary of Regulations for E&P Wastes in Louisiana

Topic Area	Summary
Commercial Recycling and Reclamation Facilities	Off-site treatment, storage and disposal of E&P wastes at commercial facilities and transfer stations is addressed in the regulations. Such activities require approval from the Commissioner and evidence of financial responsibility. A manifest must accompany each shipment, and each load of waste must be sampled (pH, electrical conductivity, chloride (Cl) content and NORM, as required by applicable DEQ regulations and requirements) and results reported on the manifest. An 8-ounce sample (minimum) of each load must be collected and labeled with the date, operator and manifest number, and each sample shall be retained for a period of 30 days.
NORM and TENORM	Louisiana Department of Environmental Quality regulations address NORM waste; oil and gas regulations in the state do not. Definitions in Chapter 14 (Regulation and Licensing of NORM) of Title 33 Environmental Quality, Part XV Radiation Protection, include NORM and TERN (technologically enhanced natural radioactive material). NORM is discussed with regards to E&P waste, while TERN is not mentioned again in the regulations. "A general license is hereby issued to mine, extract, receive, possess, own, use, store, and transfer NORM not exempt in LAC 33:XV.1404 without regard to quantity." Produced waters from crude oil and natural gas production are considered exempt. NORM waste management plan is required to store NORM waste for up to 365 days and should be submitted to the Office of Environmental Compliance for authorization. Storage requirements indicate containers (1) shall be compatible with the NORM waste being stored, (2) shall always be closed and sealed during storage (except when necessary to add or remove waste), and (3) shall not be opened, handled or stored in a matter that may cause them to rupture or leak. Storage of NORM in tanks is allowed but waste piles are prohibited. Inspections of storage areas shall be conducted at least quarterly. Treatment or disposal of NORM waste shall be in accordance with one of the following: 1. by transfer of the wastes to a land disposal facility licensed by the department, the U.S. Nuclear Regulatory Commission, an agreement state, or a licensing state; 2. by alternate methods authorized by the department in writing upon application or upon the department's initiative. The application for alternative methods of disposal shall be submitted to the department for approval; 3. for nonhazardous oilfield waste containing NORM at concentrations not exceeding 30 picocuries per gram of radium-226 or radium-228 by transfer to a nonhazardous oilfield waste commercial facility regulated by the Department of Natural Resources for treatment if the following are met: a. dilution in the end product after treatment does not exceed 5 picocuries per gram above background of radium-226 or radium-228; b. the nonhazardous oilfield waste commercial facility has a program for screening incoming shipments to ensure that the 30 picocuries per gram limit of radium-226 or radium-228 is not exceeded; and c. the Department of Natural Resources (DNR) approves; or 4. for nonhazardous oilfield waste containing concentrations of NORM in excess of the limits in LAC 33:XV.1404.A.1, but not exceeding 200 picocuries per gram of radium-226 or radium-228 and daughter products, by treatment at nonhazardous oilfield waste commercial facilities specifically licensed by the department for such purposes. Regulation of such sites is set forth in a memorandum of understanding between the department and DNR and contained in LAC 33XV.1499 .Appendix C.

C.10. Ohio

According to U.S. Energy Information Agency, in 2016 Ohio accounted for approximately 3.4% of the nation's oil and gas production and includes both conventional and unconventional resources. E&P wastes generated in Ohio are regulated by the Ohio Department of Natural Resources (ODNR), Division of Oil and Gas Resources Management (DOGRM). Wastes disposed offsite fall under the jurisdiction of Ohio Environmental Protection Agency (Ohio EPA) and NORM (cuttings and brine) and TENORM are regulated under both radiation protection and the oil and gas rules. Ohio updated its oil and gas regulations in 2005 to address urban drilling, and again in 2013 for horizontal wells and related waste management issues. **Table C-10** provides a summary of the regulations identified for E&P wastes in Ohio.

Table C-10. Summary of Regulations for E&P Wastes in Ohio

Topic Area	Summary
Definitions	Definitions in the oil and gas regulations cover relatively broad areas (i.e. production operation includes all activities from pad construction to plugging) and do not include definitions for different types of pits. "Urbanized areas" and "horizontal wells" have recently been added to the definitions.
Waste Unit Location Requirements	Ohio setback requirements for wells and tank batteries address inhabited structures (residential business and other uses), various water resources, and streets. The regulations do not address setbacks related to endangered species or wildlife. Pits are not specifically identified in setback requirements however because they are part of the well pad they are covered by well setback rules.
Tank Requirements	Tanks can be used to hold any waste or produced materials. Rules include general performance requirements ("must be constructed and maintained to prevent the escape of waste") but cannot be buried without approval. If approved, buried steel tanks must be steel and catholically protected. There are no specific requirements in the oil and gas regulations for berm and containment materials for tanks, or for protective netting and tank monitoring. Modular large volume tanks are not specifically addressed in the regulations.
Pit Construction and Operation Requirements	DOGRM rules require a waste management plan as part of the well permit application including a description of the pit construction and use. Thus, the rules tend to be general and details are left to the well-specific permits and waste management plans approved by the agency. Rules cover construction and operation of temporary pits (including drilling, completion and production uses) and appear to allow the director discretion in approving and requiring site specific conditions. As of January 2014, pit permits are required. A general requirement for proper construction and safe operation addresses pit management (pits of sufficient size and shape must be constructed adjacent to each drilling well to contain all the drilling muds, cuttings, salt water and oil; no fluid is allowed to overflow). Pits are not allowed as permanent disposal locations for brine or materials coming in contact with refined oil-based substances or other sources of contaminants. Synthetic pit liners are required, but the operator may request a variance. Fencing (urbanized areas and near inhabited structures only) and signage (for the well, not specifically for the pit) are required but specifications for other elements of pit construction and operation including leak detection/monitoring, netting, inspection, freeboard, run-on/run-off controls and berm construction are not included in the rules. Centralized pits are not specifically addressed in the regulations.

Table C-10. Summary of Regulations for E&P Wastes in Ohio

Topic Area	Summary
Pit Closure Requirements	Closure requirements for pits containing fluids from hydraulic fracturing require removal of all materials "upon termination of the fracturing process" and drilling pits in urbanized areas must be closed within thirty days. Inspections and closure sampling are not required by the regulations. Financial security for pits is not required but is included as a part of the overall well permit bond.
Spill Notification	New rules require owners and operators to report releases of oil, condensate, brine, chemical substances and oilfield waste materials that occur above specified thresholds and outside of appropriate containment into the environment.
Corrective Action	Corrective action is not specifically addressed in state regulations.
Off-site Landfills	Drill cuttings that have come into contact with refined oil-based substances or other sources of contamination must be disposed of at a licensed offsite solid waste landfill unless otherwise approved by the Division. Cuttings from air or water-based drilling that have not come into contact with contaminants are not managed as solid waste and may be buried onsite, if in the approved Waste Management Plan. Oil and gas regulations do not require testing of the material for offsite disposal, however disposal facility permits may require testing. Regulations do not address drill cuttings as daily cover in landfill.
Land Application	Regulations give flexibility to include land application in the site-specific waste management plan, but such requests must be approved by the agency.
Beneficial Use	Uncontaminated cuttings may be used offsite for beneficial use but must first obtain approval from Ohio EPA's Division of Materials and Waste Management. Ohio allows county governments to permit the use of brine for road treatment. If the county allows roadspreading certain requirements must be met regarding the distance from vegetation and application methods. Brine from horizontal wells, drilling fluids, and flowback are not allowed to be spread on a road. The brine source must be reported, but fluid testing is not required under the state regulations.
Waste Minimization/ Management	Best management practice documents for well site construction and pre-drilling water sampling are noted in the regulations. Ohio does not have a best management practices manual for E&P waste, however in 2014 ODNR produced a fact sheet summarizing management practices for cuttings from shale wells. Closed loop drilling is not specifically addressed in the regulations, but tanks are allowed for containing drilling fluids.
Commercial Recycling and Reclamation Facilities	Commercial E&P waste recycling or reclamation facilities must have a permit to operate as of January 2014. A detailed description of the process including estimated waste volumes is required in the application.
NORM and TENORM	NORM, including brine and uncontaminated cuttings, are not regulated in Ohio. Drilling-related waste (e.g. tank bottoms, pipe scale, filtrate, recycled cuttings) that is suspected to be TENORM must be tested for radium-226 and radium-228 before leaving the well site; TENORM cannot be disposed of at an oil and gas drill site. Solid waste landfills can only accept TENORM wastes for disposal at concentrations less than 5 pCi/g above natural background ("natural background" is two picocuries per gram or the actual value measured at the site).

C.11. West Virginia

In 2016, West Virginia accounted for approximately 3.1% of the nation's oil and gas production according to the U.S. Energy Information Agency. Most of West Virginia's production is from unconventional resources in the Marcellus Shale, however there is a small amount of shallow oil production and coalbed methane production in the state, and deeper intervals have been explored recently. The Department of Environment Protection regulates oil and natural gas production (Office of Oil and Gas) and solid waste (Solid Waste Management Section). The West Virginia Department of Health and Human Resources regulates TENORM related to oil and natural gas production in the state.

West Virginia Code Title 35 contains the oil and gas rules. Series 8 is a new oil and gas rule that became effective in 2016 for horizontal wells. It is an amendment to the Department of Environmental Protection, Oil and Gas rules. The new rules require the well application to include a water management plan describing the disposal procedures for fracturing and stimulation wastewater, and construction and operation requirements for unconventional wellsite pits and centralized pits. The section also requires water quality testing of wells and springs within 1,500 feet of the well pad. Title 35 Series 2 (1998) implements the solid waste permit by rule requirements for solid waste facilities at E&P sites. **Table C-11** provides a summary of regulations identified for E&P wastes in West Virginia.

Table C-11. Summary of Regulations for E&P Wastes in West Virginia

Topic Area	Summary
Definitions	Approximately 30 definitions are provided in the different parts of oil and gas regulations, including definitions for pits and impoundments. The definitions do not include many technical terms. Pits are any man-made excavation or diked area that contains or is intended to contain an accumulation of process waste fluids, drill cuttings, and/or any other liquid substance that could impact surface water or groundwater, whereas impoundments are man-made excavations or diked areas for the retention of fresh water and into which no wastes of any kind are placed. Definitions do not further divide pit types. Technical specifications are provided in many parts of the rules, but some regulations provide only general requirements or performance-based criteria. For example, tank construction rules note that tanks for storage of oil or other pollutants must be compatible with the material stored and the conditions of storage; and, saltwater disposal facilities should be inspected often.
Waste Unit Location Requirements	Regulations include general requirements for protection of floodplains, groundwater and surface water from wells and production facilities. Endangered species are not specifically addressed in the regulations. Some specifics, however, are provided, such as no oil or gas well shall be drilled nearer than two hundred feet from an existing water well or dwelling without first obtaining the written consent of the owner of such water well or dwelling. Location requirements are also included for centralized pits and impoundments with capacity of more than 5,000 barrels, which specify a minimum depth to groundwater of 20 inches.
Tank Requirements	General tank requirements indicate that berms should be "…sufficiently impervious to contain spilled oil…" For drilling, completion, workover and production operations, secondary containment shall be installed with impermeable basins for tanks used for stored liquids other than freshwater and shall have a capacity of 110% of the largest tank within the battery. Tank monitoring is not required but considered one of several options for spill prevention. Netting for open tanks, modular large volume tanks, construction material and tank bottom removal are not specifically addressed in these regulations.

Table C-11. Summary of Regulations for E&P Wastes in West Virginia

Topic Area	Summary
Pit Construction and Operation Requirements	Regulations refer to pits (with wastewater pits being the only type specified) and centralized pits and impoundments with capacity greater than 5,000 barrels (bbl.). Permits for specific well site work (similar to an Application for Permit to Drill in other states) are required prior to beginning any construction, but pits do not require a special permit. Authorization and approval from the agency is required for centralized impoundments with a capacity of greater than 5,000 bbl. A synthetic liner is required unless an exception is deemed appropriate based on soil analyses. Requirements include fencing, a freeboard of 2 feet, berm specifications, run-on/run-off controls, groundwater monitoring, signage and inspections. Additional requirements for centralized pits include geotechnical analysis, water quality testing, leak detection and monitoring and a minimum depth to groundwater of 20 inches. Discharge of produced water from coalbed methane wells is included in the General Water Pollution Control Permit and includes many conditions for water quality limits and testing. Discharges are not allowed from conventional or horizontal wells without a permit. Fencing is required for pits with capacity greater than 5,000 bbl., but regulations do not address netting for pits. West Virginia does not have regulations for noncommercial fluid recycling pits.
Pit Closure Requirements	Regulations specify liquids removal prior to closure of pits and impoundments and a closure schedule. In addition, inspection and sampling are required. Financial security is included in the well bonding requirement and no special financial security is required for pits or other waste management units.
Spill Notification	Spill notification is required when a facility discharges (1) more than 1,000 gallons into the water of the state in a reportable discharge or (2) oil or other pollutants into the waters of the state in two reported discharges within any twelve-month period. The oil and gas chief is responsible for reviewing the information and issuing an order to require any corrective action deemed necessary to protect against future spills and forward such recommendations to the Regional Administrator for the EPA.
Corrective Action	Corrective action is not specifically addressed in state regulations.
Off-site Landfills	Disposal of E&P waste is allowed in properly permitted municipal solid waste facilities. A July 2015 WVDEP report on drill cuttings in solid waste facilities identified six solid waste landfills currently accepting drill cuttings (WVDEP, 2015). Collected leachate from these facilities is either processed on-site and discharged to a stream or sent to a Publicly Owned Treatment Works (POTW) facility for processing and discharge to a receiving stream. The report also noted that some landfills mix drill cutting materials with municipal solid waste, and others utilize separate dedicated drill cutting material disposal cells. On-site disposal of drill cutting materials is allowed under state regulations, but the 2015 report indicated operators are not utilizing this option. Testing of waste and its use as daily cover are not specifically addressed in the regulations.
Land Application	Under the General Discharge Permit (GP-WV-1-88) fresh water from centralized or specific well pits may be discharged in accordance with the permit conditions. Prior to discharge the water must be sampled, and it must be sprayed or irrigated so that the vegetation and ground can absorb the discharge without runoff.

Table C-11. Summary of Regulations for E&P Wastes in West Virginia

Topic Area	Summary
Beneficial Use	Beneficial use of natural gas well brine is not included in oil and gas regulations but is permitted by the West Virginia Division of Highways for roadway prewetting, anti-icing and de-icing. The approved use is limited to the wintertime application of natural gas well brines in order to minimize the formation of bonded snow and ice to roadway surfaces by utilizing the melting capabilities of salt brine. Specifications and limitations are provided in a memorandum dated 12/22/11. The use of hydraulic fracturing return fluids associated with horizontal or vertical gas wells is not allowable under this memorandum.
Waste Minimization/ Management	Waste minimization activities, such as closed loop drilling and recycling of produced water, are not required.
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in these regulations.
NORM and TENORM	TENORM is defined and addressed in state health regulations, not oil and gas regulations. Landfill screening is conducted prior to acceptance of all wastes, and storage requires an annual registration form. TENORM disposal is allowed at a disposal facility with state or NRC registration or as approved by Department of Health and Human Resources. TENORM waste is exempt if less than 5 pCi/g.

C.12. California

In 2016, California accounted for approximately 2.8% of the nation's oil and gas production, according to the U.S. Energy Information Agency data. Much of California's current production is from older, shallow conventional wells, and about 15% is from offshore state lands. High volume hydraulic fracturing is not common in California at this time.

E&P waste regulations in California are dispersed among many different agencies making it challenging to develop a comprehensive review of statewide regulatory programs. The California Department of Conservation, Division of Oil, Gas and Geothermal Resources (DOGGR) regulates oil and natural gas production in the state. The California Environmental Protection Agency has several departments, such as the Department of Toxic Substances Control (DTSC), the State Water Resources Control Board (and the associated Regional Water Quality Control Boards [RWQCB]), and California Integrated Waste Management Board, all of which may be involved in the permitting process for oil and gas activities, with DTSC having the primary responsibility for oil and gas solid wastes managed in pits and RWQCB managing discharges from waste units. NORM/TENORM is not specifically addressed in state oil and gas regulations.

DOGGR statutes and regulations are current as of February 1, 2019 with various effective dates for each section. Revision dates were not provided in the regulations, but the enacting statutes appear to include several revisions since 2006. Regulations regarding well stimulation treatment (acidizing and hydraulic fracturing) were added in 2015. Solid waste regulations also have varying dates of revision, including many original regulations from 1997.

A Notice of Intention is required to drill for an oil, gas, or geothermal well, and the decision-making body is the State Oil and Gas Supervisor or his or her representative. A consolidated permit incorporating the environmental permits granted by environmental agencies for a project may be issued as a single permit document by the consolidated permit agency.

Unlike all the other states, California does not automatically exempt E&P wastes from RCRA subtitle C. DTSC describes the regulatory status of E&P wastes as follows: "In general, E&P wastes that exhibit hazardous waste characteristics are subject to regulation as hazardous waste under the statutory authority of DTSC, except in those cases where the wastes are hazardous solely because they exhibit the federal characteristic of toxicity" (CalEPA, 2002). **Table C-12** provides a summary of the regulations identified for E&P wastes in California.

Table C-12. Summary of Regulations for E&P Wastes in California

Topic Area	Summary
Definitions	Approximately 50 definitions are provided in the oil and gas regulations Nearly half of the definitions are included in the Well Stimulation Treatment Regulations section from 2015. Solid waste regulations include over 230 definitions. "Sump" is defined as "an open pit or excavation serving as a receptacle for collecting and/or storing fluids such as mud, hydrocarbons, or waste waters attendant to oil or gas field drilling or producing operations." Three types of sumps (pits) are defined: (1) "Drilling Sump" means a sump used in conjunction with well drilling operations. (2) "Evaporation sump" means a sump containing fresh or saline water which can properly be used to store such waters for evaporation. (3) "Operations sump" means a sump used in conjunction with an abandonment or rework operation.
Waste Unit Location Requirements	Specific setback values are not provided in the oil and gas regulations. Setbacks provided in the solid waste regulations for waste management units include distances from airports, ground rupture and rapid geologic change but not residential areas. Location restrictions for sumps indicate that the "collection of waste water or oil shall not be permitted in natural drainage channels. Contingency catch basins may be permitted, but they shall be evacuated and cleaned after any spill. Unlined evaporation sumps, if they contain harmful waters, shall not be located where they may be in communication with freshwater-bearing aquifers." Regulations contain a general prohibition on pollution. "Oilfield wastes, including but not limited to oil, water, chemicals, mud, and cement, shall be disposed of in such a manner as not to cause damage to life, health, property, freshwater aquifers or surface waters, or natural resources, or be a menace to public safety." Disposal sites for oilfield wastes must conform to State Water Resources Control Board and appropriate California Regional Water Quality Control Board regulations. A minimum depth to groundwater is 5 feet for waste management units (including surface impoundments) but not oil and gas sumps specifically. Endangered species are not specifically addressed.

Table C-12. Summary of Regulations for E&P Wastes in California

Topic Area	Summary
Tank Requirements	Regulations state that secondary containment at production facilities be capable of containing the equivalent volume of the largest single piece of equipment within the secondary containment and confine that liquid for a minimum of 72 hours. Tank construction requirements at production facilities are not specified but regulations infer tanks are constructed of metal, based on the associated corrosion control requirements. Regulations allow for non-metal tanks, but they are not subject to the testing and construction requirements for steel tanks. Steel tanks must be inspected for corrosion at least once a month and the minimum thickness for a tank shell/wall must be 0.06 inch with a minimum bottom plate thickness ranging from 0.05 to 0.1 inch. Construction requirements include impermeable base and if replaced, it must have a leak detection system that will either: (1) Channel any leak beneath the tank to a location where it can be readily observed from the outside perimeter of the tank, or (2) Accurately detect any tank bottom leak through the use of sensors. The Supervisor may require a tank bottom leak detection system for any tank with a foundation that does not have an impermeable barrier Netting, monitoring and modular large volume tanks are not specifically addressed.
Pit Construction and Operation Requirements	As mentioned above, pits are referred to as “sumps” in California. Three sump types are defined in the oil and gas regulations: drilling sump, evaporation sump and operations sump. The permit request form is entitled “Notice of Intention” and is required for the well, not sumps specifically. The following prohibitions were noted in the oil and gas regulations with regards to waste disposal which may apply to sumps (pits): • Open unlined channels and ditches shall not be used to transport waste water which is harmful to underlying freshwater deposits. Oil or water containing oil shall not be transported in open unlined channels or ditches unless provisions are made so that they are not a hazard as determined by the Supervisor. • Dumping harmful chemicals where subsequent meteoric waters might wash significant quantities into freshwaters shall be prohibited. Drilling mud shall not be permanently disposed of into open pits. Cement slurry or dry cement shall not be disposed of on the surface. Sumps must be enclosed according to different specifications based upon their location (urban vs. non-urban). Specific details are provided for chain link fences, wire fences and gates. Additional fencing materials may be used if approved by the Supervisor. Sumps, except operations or drilling sumps, which contain oil or a mixture of oil and water shall be screened (netting) to the following specifications: screens should not be greater than 2-inch nominal mesh, be of sufficient strength to restrain entry of wildlife and be supported to prevent contact with the sump fluid. Produced water ponds are regulated by the RWQCB and may be lined or unlined or used as evaporation or percolation pits if approved by the RWQCB. Signage is required for the well site, not pits specifically. Requirements for liners, leak detection monitoring, minimum depth to groundwater, run-off/run-on controls, and groundwater monitoring were not found for sumps but were found for waste management units, but is unclear if these regulations would be applied to onsite E&P waste management operations. The following paragraphs summarize waste management regulations that may apply to pits.

Table C-12. Summary of Regulations for E&P Wastes in California

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Leak detection monitoring is required for waste management units and should be conducted at least every 5 years to determine if "measurably significant" evidence of a release has occurred. Waste management units and their drainage control facilities should be constructed to manage 1000-year with 24-hour precipitation (Class II) or 100-year storm with 24-hour precipitation (Class III). These units should also be designed to withstand the maximum credible earthquake (Class II) or at least the maximum probable earthquake (Class III). Groundwater monitoring is required for waste management units. Inspection frequency information was available for production facilities, not sumps or waste management units. Aboveground production facilities shall be inspected at least monthly for leaks and corrosion; facilities not operating properly shall be repaired or replaced. Secondary containment berms shall be inspected monthly, and fluids, including rainwater, shall be removed from secondary containment areas or catch basins. Discharge permits, noncommercial fluid recycling pits and centralized pits are not specifically addressed in the regulations. As of January 2015, DOGGR must provide an annual inventory of unlined sumps to the State Water Resources Control Board and the California Regional Water Quality Control boards. Reports for produced water ponds, both lined and unlined, were available online. In January 2019 the requirement for reporting was repealed.
Pit Closure Requirements	Oil and gas regulations state that responsibility for sump closure lies with both RWQCB and DTSC, and DOGGR has responsibility for final site restoration. Under State Water Quality Control Board regulations onsite sumps used for well drilling operations are closed by either removing the wastes for offsite disposal, or removing free liquid and covering the residual wastes, provided that representative sampling of the sump contents show wastes to be nonhazardous. Sampling is required for waste characterization. Drilling mud is classified as a special waste and can be disposed at a special waste landfill. The lease restoration includes the locations of any existing or previously removed, where known, sumps, tanks, pipelines, and facility settings. Lease restoration includes the removal of all tanks, above-ground pipelines, debris, and other facilities and equipment. Financial security is required for the wells/site, not for pits specifically and a final inspection is required after completion of plugging operations to determine if Division environmental regulations (California Code of Regulations, Title 14, Subchapter 2) have been adhered to.
Spill Notification	A spill contingency plan is required for each facility. Oil spills shall be promptly reported by phone to the California Emergency Management Agency. Blowouts, fires, serious accidents, and significant gas or water leaks resulting from or associated with an oil or gas drilling or producing operation, or related facility, shall be promptly reported to the appropriate Division district office, but no specific time frame is given. An unauthorized release associated with well stimulation treatment requires a written report to the Division within 5 days and notifying the Regional Water Board and any other appropriate response entities for the location and the type of fluids involved.
Corrective Action	Corrective action for spills at well stimulation locations include clean up and remediation of the area, and disposal of any cleanup or remediation waste, as required by all applicable federal, state, and local laws and regulations. Regulations indicate that financial assurance is required for spill response and corrective action at production facilities.

Table C-12. Summary of Regulations for E&P Wastes in California

Topic Area	Summary
Off-site Landfills	Regulations do not clearly state which type of waste management unit may be used for E&P waste, but Class II or Class III solid waste management units may be allowed. A waste classification system is used to determine waste type. Alternative cover materials may be approved for use as daily cover, but it is unclear if E&P waste is allowed.
Land Application	Land treatment units (LTUs) are facilities where hazardous materials are applied onto or incorporated into the soil surface so that hazardous constituents are degraded, transformed or immobilized within the treatment zone. LTUs are a waste management option, but it is unclear if E&P waste is allowed. Regulations for LTUs include precipitation and drainage controls, and seismic design criteria.
Beneficial Use	Regulations and requirements for beneficial use of brine (produced water) are not provided in the oil and gas rules, however based on documented practices by RWQCB produced water can be reused for agricultural purposes. The RWQCBs may approve specific requests for beneficial reuse of produced water. In 2016, four oil companies sent oilfield produced water to four irrigation districts near Bakersfield. https://www.waterboards.ca.gov/publications_forms/publications/factsheets/docs/prod_water_for_crop_irrigation.pdf Some solid waste is allowed for beneficial use at a solid waste landfill and may include alternative daily cover, alternative intermediate cover, final cover foundation layer, liner operations layer, leachate and landfill gas collection system, construction fill, road base, wet weather operations pads and access roads, and soil amendments for erosion control and landscaping. However, it is unclear if the use of E&P waste is allowed. Beneficial reuse is restricted to those solid wastes appropriate for the specific use and must conform with engineering and industry guidelines, as specified in the planning documents.
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in the state regulations.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the state regulations.
NORM and TENORM	Regulations addressing NORM/TENORM were not identified. However, one facility (Buttonwillow Facility) was identified that accepts radionuclides (in the decay series of U-238, U-235 and Th-232) up to 1,800 pCi/g. This facility serves oil exploration and production companies, among other customers.

C.13. Arkansas

In 2016, Arkansas accounted for approximately 1.8% of U.S. oil and gas production including conventional and unconventional resources according to the U.S. Energy Information Agency. The Arkansas Oil and Gas Commission regulates oil and gas production, extraction and transportation in the state. The Arkansas Department of Environmental Quality regulates solid and hazardous waste disposal and water quality in the state. NORM is regulated by the Radiation Control Program under the State Board of Health. Regulations were updated in 2009 and 2015 to include unconventional resources in the Fayetteville Shale, Woodford Shale, Moorefield Shale and the Chattanooga Shale. Pit regulations were updated most recently in 2012, and stimulation regulations were updated in 2017. **Table C-13** provides a summary of the regulations identified for E&P wastes in Arkansas.

Table C-13. Summary of Regulations for E&P Wastes in Arkansas

Topic Area	Summary
Definitions	Oil and gas regulations include approximately 100 entries and have not been updated since 1991 rule book. Few definitions relate to E&P wastes. The following pits are defined within the text of the oil and gas regulations: circulation pit, completion pit, emergency pit, mud pit, reserve pit, test pit and workover pit.
Waste Unit Location Requirements	Requirements for floodplains, surface water and groundwater are dispersed in regulations. Prior authorization is required for pit construction in wetlands. Endangered species are not specifically addressed in the regulations. Setback are specified for storage tanks, such as 200 feet from an existing occupied habitable dwelling. If the water table is less than 10 feet below the ground surface, pits shall be constructed above ground or a closed loop system is required.
Tank Requirements	Containment dikes or other structures are required for tanks and shall have the capacity of at least 1.5 times the largest tank the containment structure surrounds. Netting is required for open top tanks to prevent birds and flying mammals from landing in the tank. Modular large volume tanks, construction materials, tank monitoring and tank bottom removal are not specifically addressed in the regulations.
Pit Construction and Operation Requirements	Multiple pit types are included in these regulations (circulation pit, completion pit, emergency pit, mud pit, reserve pit, test pit and workover pit) and are covered by a general APD permit. Liners are required and the type depends upon the pit contents. For example, synthetic or compacted clay liners are used for reserve pits; and synthetic, bentonite drilling mud or concrete liners may be used for mud and circulation pits. Additional requirements for pit construction include a minimum 2 feet of freeboard and minimum depth to groundwater of 10 feet. A stormwater erosion and sediment control plan (or appropriate guidance document) shall be prepared (or presented) for the well site. Inspections are not required but may be conducted when deemed necessary by the ADEQ staff. Requirements are not provided for leak detection/monitoring, fencing, netting, groundwater monitoring, discharge permits, temporary pits, non-commercial fluid recycling pits or centralized pits. Signs are required for the well and tank batteries but not for pits and other waste management facilities.
Pit Closure Requirements	Liquids removal is required prior to pit closure. Oily-based solids must be removed, while water-based solids can be buried in place. A schedule for pit closure, based on well type, is provided in the regulations. While inspection is not specified, additional analytical or disposal requirements may be required for oil-based drilling fluids. Financial security for pits is included as part of general APD bond.
Spill Notification	Spill notification is not specifically addressed in the state regulations.
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	E&P waste disposal is allowed at a permitted surface disposal facility, however, oil-based wastes must go to a Class I landfill (municipal). While testing of the waste is not required, RCRA and TSCA waste testing may be required. Use of E&P waste as a daily cover at landfills are not specifically addressed in the regulations.
Land Application	Disposal of water-based waste by land application is allowed with a permit. Specific limitations/conditions and location restrictions are not included in the regulations.

Table C-13. Summary of Regulations for E&P Wastes in Arkansas

Topic Area	Summary
Beneficial Use	Road spreading is an acceptable form of disposal for crude oil bottom sediments and does not appear to be considered beneficial use. Specifications for road spreading are provided in the regulations and indicate that the applied waste shall not have a produced water content greater than 10% free water by volume. Information about beneficial use of brine is not provided in the regulations.
Waste Minimization/ Management	If oil-based drilling fluids are to be used, and the location of the mud or circulation pit is within 100 feet of a pond, lake, stream, Extraordinary Resource Waters, Ecologically Sensitive Waterbody or Natural and Scenic Waterway, the Operator is required to use a Closed Loop System. As noted previously, if the water table is less than 10 feet below the ground surface, pits shall be constructed above ground or a closed loop system is required.
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in these regulations.
NORM and TENORM	NORM is regulated by the Radiation Program under the Arkansas State Board of Health. Disposal of NORM is allowed and details about the storage of NORM are provided. Waste is exempt when concentrations are less than 5 picocuries per gram of radium-226 and/or radium-228, 0.05% by weight of uranium or thorium, or 150 picocuries per gram of any other NORM radionuclide, provided that these concentrations are not exceeded at any time.

C.14. Utah

In 2016, the U.S. Energy Information Agency estimated that Utah accounted for approximately 1.2% of the nation's oil and gas production. Most of the production is from the northeast part of the state in the Uinta Basin where several different conventional and unconventional resources are targeted. The Division of Oil, Gas and Mining within the Department of Natural Resources regulates oil and natural gas production in the state. Utah Oil and Gas has oversight responsibility for all operations for and related to the production of oil or natural gas, disposal of salt water and oil-field wastes. The Utah Department of Environmental Quality, Waste Management and Radiation Control Division regulates solid and hazardous wastes. NORM/TENORM is not specifically addressed in state oil and gas regulations.

The Utah Administrative Code (UAC) Rule 649 contains oil and gas regulations. Several sections of the rule have been updated recently, including Section 3 (Drilling and Operating Practices updated in 2016) which contains most of the permitting, pits, and hydraulic fracturing requirements and Section 9 (updated in 2013) contains the waste management and disposal rules including evaporation facilities, landfarms, and other disposal facilities. Like many states, the waste management regulations specifically exclude pits associated with underground injection wells.

Utah Division of Oil, Gas and Mining provide additional resources on ranking criteria to determine waste containment requirements according to sensitivity level to protect the surface and near surface environment. **Table C-14** provides a summary of the regulations identified for E&P wastes in Utah.

Table C-14. Summary of Regulations for E&P Wastes in Utah

Topic Area	Summary
Definitions	Approximately 80 definitions are provided in the oil and gas regulations (Title R649), including definitions for E&P waste, pit, emergency pit, disposal pit and reserve pit. "E and P Waste" means exploration and production waste and is defined as those wastes resulting from the drilling of and production from oil and gas wells as determined by the EPA, prior to January 1, 1992, to be exempt from Subtitle C of the RCRA. The definition of reserve pit is broader than many other states, and includes pits used for drilling as well as completion and testing. Text in the regulation identifies additional types of pits including workover and completion pits, storage pits, pipeline drip pits, and sumps. UAC Rule 19, solid waste regulations state: "Solid waste does not include… : drilling muds, produced waters, and other wastes associated with the exploration, development, or production of oil, gas, or geothermal energy."
Waste Unit Location Requirements	Oil and gas regulations address floodplains, groundwater and surface water but do not include endangered species. Setbacks related to the waste management units (not just the well site) are specified. For example, "Disposal facilities shall be located a minimum of one mile from residences or occupied buildings; not within a floodplain; not within 500 feet of a wetland, water-course or lakebed; and not in permeable soil with groundwater less than 50 feet below the lowest elevation where waste will be placed." A simple reading of the definition of "disposal facility" indicates that pits used during the drilling and completion may not be considered disposal facilities.[C5] The Onsite Pit Guidance states that a pit/trench may not be constructed in fill material or in a drainage or floodplain of flowing or intermittent streams. Depth to groundwater, distances to surface water bodies and water wells, and population within a one-mile radius are factors when determining pit specifications (such as construction materials and liner requirements).
Tank Requirements	General tank requirements indicate that berms should be constructed of sufficient height and width to contain tank contents. Tank monitoring, netting for open tanks, modular large volume tanks, construction material and tank bottom removal are not specifically addressed in these regulations.
Pit Construction and Operation Requirements	Specifications and criteria for pit construction are not provided in the regulations, however the text of the regulation states that the pits shall be located and constructed according to the Division guidelines for onsite pits as provided on the Department web page (the Guidance Document), which does provide some specifications and criteria. General regulatory requirements say that pits shall be located and constructed in such a manner as to contain fluids and not cause pollution of waters and soils. Permits for pits are not required but a detailed description of the pit plan appears to be included as part of the APD. The Division conducts a predrill site evaluation to help define reserve pit location and construction requirements (including liner requirements). The Division appears to have significant flexibility and authority to define site specific requirements for pits.

C5) "Disposal Facility" means an injection well, pit, treatment facility or combination thereof that receives E and P Wastes *for the purpose of disposal* [emphasis added]. This includes both commercial and noncommercial facilities. (R 649-1-1 Definitions)

Table C-14. Summary of Regulations for E&P Wastes in Utah

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Regulations require fencing and netting (when determined necessary). General requirements for run-on/run-off control and secondary containment are also included. Any intentional discharge of water requires an additional permit from the Division of Water Quality. Freeboard requirements are only specified for evaporation ponds (two feet). Inspections are not required but may be conducted at the discretion of the agency. In addition, leak detection and monitoring may be required in a permit for sensitive areas. Signage is required for the site, not pits specifically. Regulations do not provide specific requirements for temporary and emergency pits, or address noncommercial fluid recycling pits or centralized pits.
Pit Closure Requirements	Regulations specify liquids and solids removal prior pit closure. Onsite pits must be closed within one year following drilling and completion of the well, and an inspection of the restored well site shall be conducted within 30 days of notification or as soon as weather conditions permit. Sampling of the final pit condition is required, and financial security is part of the well permit bond. Disposal facilities including land farms, composting, bioremediation, solidification and treatment facilities not associated with individual wells (either commercial or non-commercial) require a separate bond.
Spill Notification	Incident reporting is specified for both major and minor reportable events at oil or gas drilling, producing, transportation, gathering, or processing facility, or at any injection or disposal facility. Major reportable events include an unauthorized release of more than 25 barrels of oil, salt water, oil field chemicals or oil field wastes; and any spill, venting, or fire, regardless of the volume involved that occurs in a sensitive area (parks, recreation sites, wildlife refuges, lakes, reservoirs, streams, urban or suburban areas), and require a verbal notification within 24 hours and a written report within five days. Minor reportable events include unauthorized release of more than 5 barrels and up to 25 barrels of oil, salt water, oil field chemicals or oil field wastes; and require a written report within five days.
Corrective Action	The regulations include general waste management practices that specify "operators shall catch leaks, drips, contain spills and cleanup promptly." Additional requirements are not provided.
Off-site Landfills	Disposal of E&P waste is allowed at both commercial and non-commercial disposal facilities under the oil and gas regulations, but regulations do not specifically address offsite landfills. Utah Solid Waste regulations R315-304 allows E&P wastes to be disposed in Industrial Solid Waste Landfills (Class IIIb). Testing of waste and its use as daily cover are not specifically addressed in either of the regulations groundwater monitoring at Class III landfills is required.
Land Application	E&P waste may be land applied, and details are provided in the regulations. Specifications indicate waste should be liquid-free and applied to soil with a hydraulic conductivity no greater than 1×10^{-6} cm/sec. Other treatment facilities, such as composting, solidifying, other bioremediation, and water treatment, may be approved.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Based on the numerical risk ranking system for fluid containment describe above, Level I conditions require total containment by closed-loop drilling system, concrete structure or other type of total containment structure or material. Produced water recycling is not required but is recommended.

Table C-14. Summary of Regulations for E&P Wastes in Utah

Topic Area	Summary
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in these regulations.
NORM and TENORM	State oil and gas regulations do not address NORM/TENORM. General radioactive waste regulations address NORM management only and set a disposal limit of 15 pCi/g for Ra 226.

C.15. Kansas

According to the U.S. Energy Information Agency, Kansas accounted for approximately 1% of U.S. oil and gas production in 2016. Much of the oil and gas is produced from conventional resources but drilling in the unconventional Mississippian Lime Play has increased over the past several years. The Conservation Division of the Kansas Corporation Commission regulates oil and natural gas production in the state. The Kansas Department of Health and Environment, Waste Management Division regulates solid and hazardous waste disposal. NORM/TENORM is not specifically addressed in state oil and gas regulations. Oil and gas regulations, including those related to pits and hydraulic fracturing, were updated in 2009 and 2013, and solid waste regulations applicable to E&P wastes, including land-spreading of E&P wastes, were updated in 2013. **Table C-15** provides a summary of the regulations identified for E&P wastes in Kansas.

Table C-15. Summary of Regulations for E&P Wastes in Kansas

Topic Area	Summary
Definitions	Definitions in the oil and gas regulations include over 100 entries. The following pits are covered in the oil and gas regulations: drilling pit (reserve pits and working pits), work-over pit, emergency pit, settling pit, burn pit, and haul-off pit.
Waste Unit Location Requirements	Overarching regulations for solid waste facilities address siting requirements for floodplains, endangered species, surface water and groundwater. Floodplains and surface water are also addressed in the oil and gas regulations. Exceptions may be requested for siting emergency pits in sensitive groundwater areas. Buffer zones are provided for disposal of drilling waste by land-spreading. For example, land spreading must be at least 500 feet from each habitable structure and at least 100 feet from each intermittent stream.
Tank Requirements	Signage is required for tanks. No other requirements for tanks are provided in these regulations.
Pit Construction and Operation Requirements	Permits are required for drilling pits, work-over pits, emergency pits, settling pits, burn pits, and haul-off pits. Burn and confinement pits are defined as temporary. Liners are necessary when the Conservation Division requires pits to be sealed; all emergency pits must be sealed. Pit location must be 5 feet above the shallowest water table. Freeboard varies from 12 inches (for drilling, work-over, burn and containment pits) to 30 inches (for emergency and settling pits). Requirements are not provided for leak detection/monitoring, fencing, netting, berm requirements, run-on/run-off controls, groundwater monitoring, non-commercial fluid recycling pits or centralized pits.

Table C-15. Summary of Regulations for E&P Wastes in Kansas

Topic Area	Summary
Pit Closure Requirements	Regulations require that pit contents be disposed prior to pit closure. Timeframe for closure depends on the type of pit, which varies from 30 days after cessation for settling, burn and emergency pits to 365 days after the well spud date for drilling pits. Inspection and sampling during pit closure are not specifically addressed in the regulations, but chloride content of the waste is required during permitting. Pit contents can be disposed of in the annular well space, buried in place, or moved to an onsite or offsite disposal location as approved by the director. Financial security for pits is required as part of general APD bond.
Spill Notification	Spill notification is addressed in the regulations.
Corrective Action	Corrective action is addressed in the regulations.
Off-site Landfills	E&P waste disposal is allowed at a sanitary landfill, including a municipal solid waste landfill. Testing of waste and use as a daily cover at landfills are not specifically addressed in the regulations.
Land Application	Disposal of drilling waste by land-spreading requires approval, and conditions for disposal are provided in the regulations. Examples include waste characteristics (10,000 ppm limit for chloride content), as well as site characteristics (maximum slope is 8% and the uppermost aquifer is at least 10 feet below ground surface). Land application of E&P wastes is generally considered a disposal method, however an exception to classify the use as beneficial may be granted by KDHE Bureau of Waste Management with proper documentation. Water based drilling muds and cuttings are eligible for land application but brine and completion fluids are not eligible. Prior to application, KDHE requires information on the material to be applied as well as the characteristics of the application area, and a soil loading analysis.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in these regulations.
Commercial recycling and reclamation facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in these regulations.
NORM and TENORM	TENORM is not regulated in Kansas. Land spreading is an acceptable form of NORM disposal when the maximum predicted NORM level is no more than 1.5 times the highest NORM level found in the drilling waste samples and the maximum predicted NORM level is no more than 370 Bq/kg (10 pCi/g).

C.16. Montana

In 2016, Montana accounted for 0.4% of the U.S. oil and gas production as indicated by the U.S. Energy Information Agency. Wells include a large number of conventional reserves as well as unconventional Bakken production in the eastern part of the state. The Montana Board of Oil and Gas Conservation within the Natural Resources and Conservation Department regulates oil and natural gas production, and Montana Department of Environmental Quality (MDEQ) solid waste regulations address TENORM related to oil and gas production, in the state. The Montana Department of Environmental Quality, Solid Waste Management Section regulates solid/hazardous waste. Updates to the oil and gas regulations were made in 2009; these did not address pits and other waste management operations but rather clarified select definitions, production tests, and reporting. Additional updates in 2011 and 2018 addressed hydraulic fracturing and well stimulation activities. Most regulations were last updated or promulgated in 1992. As of 2018, revisions were being considered to TENORM rules in Montana. **Table C-16** provides a summary of the regulations identified for E&P wastes in Montana.

Table C-16. Summary of Regulations for E&P Wastes in Montana

Topic Area	Summary
Definitions	Regulations contain 81 regulatory definitions but few related to E&P waste. The definition of earthen pits includes reserve pits, skimming pits, settling pits, produced water pits, percolation pits, evaporation pits, emergency pits, and workover pit.
Waste Unit Location Requirements	Regulations are overarching for all pits with respect to floodplains and dispersed in regulations for surface water and groundwater. Endangered species are not specifically addressed in these regulations. Location restrictions are not provided; however, regulations require that earthen pits or ponds that receive produced water containing more than 15,000 ppm TDS must be constructed above the high groundwater table.
Tank Requirements	The only tank requirement specified is netting for "open storage vessels." No other tank requirements are included in the regulations.
Pit Construction and Operation Requirements	Permits are required for earthen pits and produced water pits with more than 15,000 ppm TDS. Synthetic liners are required for production pits and oil/salt mud reserve pits. Additional requirements include a minimum freeboard of 3 feet, fencing and netting, as well as requirements for temporary pits. Signage is required as part of the well site but not for pits specifically. Requirements are not provided for leak detection/monitoring, minimum depth to groundwater, berms or secondary containment, run-on/run-off controls, groundwater monitoring, inspection, discharge permits, non-commercial fluid recycling pits or centralized pits.
Pit Closure Requirements	Regulations specify liquids removal, solids removal and schedule for pit closure. Inspection and sampling for pit closure are not specifically addressed. Financial security for pit closure is a general requirement for bonding under the application for permit to drill.
Spill Notification	Spill notification is not specifically addressed in the state regulations.
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	E&P waste disposal is allowed at municipal landfills and possibly other radioactive waste facilities. Testing is only required for TENORM prior to disposal. Use of waste as daily cover is not specifically addressed in the regulations.
Land Application	Land application is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Waste minimization and management activities, such as closed loop drilling and produced water recycling, are not specifically addressed in these regulations.
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in these regulations.

Table C-16. Summary of Regulations for E&P Wastes in Montana

Topic Area	Summary
NORM and TENORM	TENORM is addressed by regulations for the MDEQ solid waste program. Disposal is allowed at permitted TENORM landfills. Testing/screening is required as acceptable radioactivity levels depend upon the permit for each facility. Action plan/management plan and storage requirements are not specifically addressed by these regulations.

C.17. Mississippi

According to the U.S. Energy Information Agency, Mississippi accounted for approximately 0.4% of the nation's oil and gas production in 2016. While some oil production comes from conventional vertical wells, the bulk of Mississippi's production (both oil and gas) is from the unconventional Tuscaloosa Shale in the southern part of the state. Wells in the Tuscaloosa are deep and the play is still in its early stages. The State Oil and Gas Board (OGB) regulates oil and natural gas production in the state. The Department of Environmental Quality, Waste Division is responsible for management of solid and hazardous waste. NORM related to oil and natural gas production is regulated by the Oil and Gas Board.

Oil and Gas Conservation statutes (Title 53, Chapters 1 and 3) contain mostly administrative rules related to permits, spacing, fees and authority of the OGB and were last updated in 2015. Statewide Rules and Regulations (Order No. 201-51, Rules 1 through 69) contain the detailed requirements for waste management including Rules 68 and 69 covering NORM-contaminated waste. Rule 61, relating to berms crude and saltwater tanks was updated in 2015 and Rule 68 related to NORM was updated in 2017. The Rulebook also contains 12 rules applicable to state offshore submerged lands (OS-1 through OS-12). Title 17 (Solid Waste) includes pertinent E&P waste definitions and authorizes the OGB to regulate oilfield wastes. The most recent date of revision for regulations was not always clear in the Rulebook, because the source often only referred to the original authorizing act. **Table C-17** provides a summary of the regulations identified for E&P wastes in Mississippi.

Table C-17. Summary of Regulations for E&P Wastes in Mississippi

Topic Area	Summary
Definitions	Approximately 20 definitions are provided in Title 53, Chapter 1 and 36 definitions are included in Rule 2 regarding oil and gas operations. Some rules include additional definitions. Five types of earthen pits are discussed: temporary salt water storage pits, emergency pits, burn pits, well test pits and drilling reserve pit (mud pits). Regulations are often performance based (e.g. "Mud Pits used in connection with drilling operations shall be sited and constructed so as to prevent the escape of any of the pit contents") and leave much of the technical requirements to the Supervisor and inspectors for approval.

Table C-17. Summary of Regulations for E&P Wastes in Mississippi

Topic Area	Summary
Waste Unit Location Requirements	Location and siting requirements for waste management units (pits and tanks) are general in nature. No specific setback distances from surface water, groundwater, floodplains or sensitive habitats were found in the regulations. These criteria may be specified in well and pit permits but were unavailable for review. Groundwater and surface water are addressed by the general requirement for non-polluting activities: "rules and regulations are hereby promulgated to prevent waste by pollution of air, fresh waters and soils. These rules shall be effective throughout the state of Mississippi and are for the purpose of prevention of waste by pollution of air, fresh waters and soils." Regulations do not address endangered species and only floodplains in NORM landfarms. Landfarming of NORM waste cannot be within 300 feet of an occupied dwelling, within 25-year floodplain or in an area with less than 5 feet to groundwater.
Tank Requirements	Unlike many states, Mississippi tank regulations specifically address saltwater tanks. Each permanent oil and/or saltwater tank or battery of oil and/or saltwater tanks require a dike (or firewall) with 150% capacity of the largest tank. No specific construction requirements are provided, but the dike (or firewall) should be constructed of impermeable material. Fencing is not allowed for tanks and netting is not mentioned.[C6] Modular large volume tanks, tank monitoring and permits regarding tank bottom removal are not specifically addressed in the regulations.
Pit Construction and Operation Requirements	Construction and operation requirements are provided for earthen pits,[C7] which include temporary salt water storage pits, emergency pits, burn pits, well test pits and drilling reserve pit (mud pits). Permits are issued for such pits, with the exception of drilling reserve pit (mud pits), which are included in the APD. Temporary salt water storage pits require lining with an impervious material acceptable to the Supervisor; liners are not mentioned for other pit types. Berm requirements and run-on/run-off controls are general stating the pit shall be protected from surface waters by dikes and drainage ditches. Fencing is not allowed (see footnote for tanks below). General performance-based requirements are provided for all five types of pits, including construction "so as to prevent the escape of any of the contents", and maintaining fluid levels (freeboard) of 1 to 2 feet, all pits require a sign placed conspicuously near the pit. Inspections are not required but a representative of the State Oil and Gas Board must be given an opportunity to inspect a pit prior to use. Discharge permits are not required for reserve pits. Pit fluids may be discharged to the land surface and/or streams, after notifying the Oil and Gas Board field representative, if mud contents meet specified criteria and proper approval is secured from the Department of Natural Resources.

C6) The regulation specifically prohibits facilities from having restricted access with fencing and either locked or unlocked gates. The regulation explains that insuring that this agency's Field Inspectors and other agency personnel have unrestricted access to all oil and gas wells, tanks, tank batteries and related oil and gas exploration and production facilities on a 24-hour a day, 7- day a week basis for inspection and regulatory enforcement purposes.

C7) The introduction of the earthen pits rule notes that earthen pits are to be phased out, unless done in accordance with the regulations. The term earthen pit is not defined in the regulations so it is unclear if it refers to unlined pits or any excavated area used for storage.

Table C-17. Summary of Regulations for E&P Wastes in Mississippi

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Leak detection/monitoring, minimum depth to groundwater, netting, groundwater monitoring, non-commercial fluid recycling pits and centralized pits are not specifically addressed in the regulations. Onshore regulations state that impervious containers be used in lieu of pits in areas where it is impossible or impractical to construct a pit, or to protect waters or environmental resources. Where impervious containers are used, the contents must be properly disposed of within ninety days following usage.
Pit Closure Requirements	Liquids removal is required prior to pit closure, and solids removal is not mentioned. Pit closure consists of removal of fluids, backfilling, leveling and compacting for all pits. A closure schedule is only provided for Reserve Pits, which states they should be closed within 3 months of completion of drilling. Inspections are required for Emergency Pits within 2 weeks after the emergency period to ensure the pit contains no more than 2 feet of water and is ready for future emergency use. Financial assurance is required for wells, not pits specifically. Sampling is not specifically addressed in the regulations.
Spill Notification	Spill notification and corrective action are included in these regulations for offshore wells only.[C8] The offshore rules require recording the cause, size of spill and action taken. The record must be maintained and available for inspection by the Supervisor All spills or leakage of oil and liquid pollutants of one barrel or more must be reported orally to the Supervisor "without delay" and then be confirmed in writing.
Corrective Action	Regulations state that corrective action should be taken immediately and in accordance with the approved emergency plan. Modifications to plans may be conducted as directed by the Supervisor.
Off-site Landfills	Off-site landfills are not specifically addressed in the regulations. The regulations allow downhole disposal of mud and other deleterious substances and allow other disposal methods to be approved by the Supervisor. Solid waste regulations exclude E&P wastes from solid waste regulations as well as in definitions of municipal and industrial waste, but U.S. DOE (1997) reported 10 municipal landfills that accept E&P waste.
Land Application	Land application of NORM-contaminated wastes is allowed in Mississippi, however the rule appears to exclude NORM impacted sludge, tank bottoms, drilling muds, drill cuttings or other materials, thus only allowing scale from equipment and NORM contaminated soils. Waste with ambient exposure rates in excess of 600 microR per hour cannot be land applied and the ambient exposure rate in the impacted area should not exceed eight (8) microR per hour above background or exceed a concentration of Radium 226 or Radium 228 of 5 pCi/g above background. These values are exceeded the operator shall take "appropriate remedial or corrective action. Land application restrictions include distance to groundwater (five feet), proximity to the 25-year floodplain, and distance from inhabited dwelling (300 feet).
Beneficial Use	No beneficial uses of E&P wastes such as road spreading are provided in the regulations but solid waste regulations allow Mississippi Department of Environmental Quality to make a determination that allows for the beneficial use of eligible nonhazardous solid wastes in the state, if applicants make a formal request.

C8) It is unclear if the offshore spill regulations provided in OS-8 (Prevention of Waste, including Pollution, and Waste Disposal) are also applicable to onshore wells.

Table C-17. Summary of Regulations for E&P Wastes in Mississippi

Topic Area	Summary
Waste Minimization/ Management	No regulations regarding waste minimization, closed loop drilling or produced water recycling were identified.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the oil and gas regulations. They are not explicitly addressed in the solid waste regulations.
NORM and TENORM	NORM in Mississippi is addressed by the Division of Radiological Health within the State Department of Health, as well as Rules 68 and 69 for NORM-contaminated wastes relating to oil and gas activities. Under the Radiation Division, NORM is exempt from regulations if less than 5 picocuries per gram of radium - 226 or radium - 228 above background; or, concentrations less than 30 picocuries per gram of technologically enhanced radium-226 or radium-228. NORM disposal requires a permit, which is issued for a period of time that is "reasonably necessary to complete the disposal activity not to exceed 5 years." NORM waste must be from oil and/or gas-related activities conducted within the territorial limits of the State. Acceptable methods of NORM disposal include (1) Placement between cement plugs; (2) Encapsulation in pipe then placed between cement plugs; (3) Mixed with gel or mud (slurried) and placed between cement plugs; (4) Slurried then placed into a formation; (5) Surface land spreading; (6) Subsurface land spreading; or (7) Disposal offsite at a licensed, low level radioactive waste or NORM disposal facility. Notification to the Supervisor is required at least 48 hours prior to beginning disposal operations, to allow a representative to observe, inspect the operation. Conditions for disposal by land spreading of NORM waste were described above. Limitations for other disposal methods were not provided. An action plan/management plan and storage requirements are not specifically addressed in the regulations.

C.18. Michigan

In 2016, Michigan accounted for approximately 0.3% of the nation's oil and gas production according to data from the U.S. Energy Information Agency. Production is from a combination of historic conventional fields and unconventional reserves including the Antrim Shale and more recent discoveries in the deeper Collingwood and Utica shales. The Department of Environmental Quality (DEQ), Office of Oil, Gas and Minerals Division regulates oil and natural gas production in the state. The DEQ is also responsible for management of solid and hazardous waste, and NORM waste related to oil and natural gas production is regulated by its Office of Waste Management and Radiological Protection.

Oil and gas regulations include Oil and Gas Operations (Rule 324, most recently amended in 2015) and Ionizing Radiation Rules for Radioactive Material (Rule 325, most recently amended in 2016). Michigan DEQ developed "Cleanup and Disposal Guidelines for Sites Contaminated with Radium-226" in November 2013. **Table C-18** provides a summary of the regulations identified for E&P wastes in Michigan.

Table C-18. Summary of Regulations for E&P Wastes in Michigan

Topic Area	Summary
Definitions	Approximately 50 definitions are provided in Rule 324 and 80 are included in Rule 325. Some sections include additional definitions. Drilling mud pits are the main pit type regulated, but flare pits and fresh water storage pits are mentioned in the regulations. The term "earthen pit" is used in the regulations but it is not defined. Based on context it appears to refer to unlined pits.
Waste Unit Location Requirements	The APD requires identification of floodplains, surface waters, rivers, and endangered species within 1,320 feet of the proposed well location but does not restrict siting based on these criteria. An environmental assessment is required to be submitted as part of the APD. [C9] Regulations provide setback distances for siting of wells and certain equipment (well separators, storage tanks, and treatment equipment) near public water supply wells, but does not address surface water. There is a general requirement for oil and gas operations to not be conducted "at a location where it is likely that a substance may escape in a quantity sufficient to pollute the air, soil, surface waters, or groundwaters." Regulations do not address siting or locations relative to endangered species or floodplains.
Tank Requirements	Surface facilities, including tanks, require a hydrogeological investigation of the facility area to establish local background groundwater quality prior to construction. Secondary containment (dikes or firewalls) is required and must be have a capacity 150% of a tank or tank battery. Secondary containment areas must have a leak monitoring system of either a groundwater monitor well or tertiary containment. Tanks that contain hydrocarbons or brine, or both, must be elevated and placed on impervious pads or constructed so that any leakage can be easily detected. Operators must inspect primary and secondary containment at surface facilities (including tanks) at least once per week. Netting for open tanks, modular large volume tanks, construction materials and permits regarding tank bottom removal are not specifically addressed in the regulations.
Pit Construction and Operation Requirements	Construction and operation requirements for drill mud pits are based on pit contents and formations drilled, and permits are required. Solid salt cuttings are not allowed in pits. Machine oil, refuse, completion and test fluids, liquid hydrocarbons, or other materials may not be placed in lined pits. Earthen pits may not be used for E&P waste, waste oil or tank bottoms. Impoundments for storage of fresh water (not wastes) are allowed for hydraulic fracturing, but tanks are required for containment of all flowback fluids. Drilling mud pits may not be constructed unless depth to groundwater is greater than 4 feet, and requirements for liners include 20-mil virgin PVC material, no seams, and large enough to encompass the drilling mud tank, salt washer and shale shaker. Pits must have round corners and slope of less than 20 degrees. Leak detection and monitoring is for the well site or hydraulic fracturing operations and not required for pits specifically. Fencing is required if a drilling mud pit is not closed immediately after drilling completion. Signage is required for a well or surface facility but not pits specifically. Discharge permits are required if discharges to the air, surface waters, or groundwater of the state are likely to occur at a surface facility.

C9) The Environmental Impact Assessment is a 3 page form (Form 7200-19) that requires information on the impacts and mitigations for proposed drilling program and disposal of drilling wastes and the surface facilities to be use for production.

Table C-18. Summary of Regulations for E&P Wastes in Michigan

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Netting, freeboard, berms, run-on/run-off controls, inspections and non-commercial fluid recycling pits are not specifically addressed in the regulations. Centralized production facilities are mentioned but centralized pits are not. The application process allows the Supervisor to evaluate permit applications based on the site-specific conditions and require any necessary controls to avoid or control pollution.
Pit Closure Requirements	Liquids removal is required prior to pit closure. Solids removal is not required, and all drilling mud pits shall be stiffened before encapsulation, and the liner folded over the waste prior to covering with soil. Closure specifications for flare pits are not described in the regulations. Drilling mud pits should be closed "as soon as practical after drilling completion but not more than 6 months after drilling completion." Financial responsibility or conformance bond is required for wells, not pits specifically. Inspection and sampling during pit closure is not specifically addressed in the regulations.
Spill Notification	Spill notification requires owners to "promptly report and record all reportable losses, spills, and releases of brine, crude oil, oil or gas field waste, products and chemicals used in association with oil and gas exploration, production, disposal, or development."
Corrective Action	Corrective action details should be in an approved spill or loss response and remedial action plan that is put on file before a facility is used. Follow-up requirements after the corrective action are not specified.
Off-site Landfills	No prohibition for offsite disposal of E&P wastes was found in the Solid Waste or Oil and Gas regulations but off-site landfilling was not specifically identified as a disposal method.
Land Application	Land application of oil and gas-related wastes is not allowed in Michigan
Beneficial Use	Roadspreading of brine may be approved by the Supervisor, however brine may not be used by the well owner and must be transferred to another party for use. Concentration limits are provided for hydrogen sulfide, calcium and BTEX, and annual testing of the brine source (tanks) is required.
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in the state regulations.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the state regulations.
NORM and TENORM	NORM wastes relating to oil and gas activities are regulated by the Department of Environmental Quality, Waste Management and Radiological Protection Division. Oil and gas regulations in the state do not address NORM waste. Downhole disposal is allowed for well plugging and abandonment waste (i.e., pipe scale). Disposal of other NORM waste depends on the concentration, and testing is required prior to disposal. Wastes below 50 pCi/g Ra-226 may be disposed in a hazardous waste or Type 2 landfill and wastes greater than 50 pCi/g at a licensed radioactive waste facility. An action plan/management plan and storage requirements are not specifically addressed in the regulations.

C.19. Virginia

In 2016, Virginia accounted for approximately 0.3% of the nation's oil and gas production according to data from the U.S. Energy Information Agency. All current production is from the southwest part of the state where oil is produced from conventional reservoirs and most gas is produced from unconventional coalbed methane wells. Virginia has the potential for future exploitation of unconventional shale and tight gas resources. The Department of Mines and Energy regulates oil and natural gas production in the state. The Department of Environmental Protection, along with the Department of Mines and Energy are responsible for management of solid and hazardous waste. TENORM waste related to oil and natural gas production is regulated by the Department of Health. **Table C-19** provides a summary of the regulations identified for E&P wastes in Virginia.

Table C-19. Summary of Regulations for E&P Wastes in Virginia

Topic Area	Summary
Definitions	Approximately 90 definitions are provided in Chapter 150 of the Virginia Gas and Oil Regulation. Specific pit types were not discussed. Most of the oil and gas regulations reviewed in the Virginia Gas and Oil Regulation (Chapter 150) became effective/amended in 2013 or 2016. Most of the TENORM regulations (Sections 3470 through 3560 of Chapter 481, Virginia Radiation Protection Regulations) were issued in September 2006 or amended in June 2008.
Waste Unit Location Requirements	Setback and location requirements related to groundwater and surface water are only addressed with respect to land application of pit and produced fluids. Regulations do not address endangered species or floodplains. Wells have a residential setback of 200 feet from an inhabited building, unless approved by the director. There are no specific setback requirements for waste units.
Tank Requirements	Secondary containment for tanks are required to have a capacity 1-1/2 times the volume of the largest tank, be maintained in good condition and kept free of brush, water, oil or other fluids. Construction details are not included, but a general requirement states that tanks should be "designed and constructed to contain the fluids to be stored in the tanks and prevent unauthorized discharge of fluids." Inspections are required at least annually for tanks and tank installations. Netting for open tanks, modular large volume tanks and permits regarding tank bottom removal are not specifically addressed in the regulations.
Pit Construction and Operation Requirements	Specific pit types are not provided in the regulations, and all pits are considered temporary. Permits are not required for pits, but are included as part of the general well permit. Construction requirements for pits include a liner of 10 mil or thicker high-density polyethylene or its equivalent and a minimum freeboard of 2 feet. "Pits may not be used as erosion and sediment control structures or storm water management structures, and surface drainage may not be directed into a pit." Specific secondary containment/berm requirements are for the entire site, not pit-specific. Fencing is required to secure the site from the public and wildlife. Signage is also required for the site, not pits specifically. Groundwater monitoring is required for the site, and each well permit must include a groundwater plan that consists of initial baseline groundwater sampling and testing followed by subsequent sampling and testing after pit installation. Netting, minimum depth to groundwater, leak detection/monitoring, inspections, discharge permits, noncommercial fluid recycling pits and centralized pits are not specifically addressed in the regulations.

Table C-19. Summary of Regulations for E&P Wastes in Virginia

Topic Area	Summary
Pit Closure Requirements	All free liquids must be removed prior to pit closure. Drill cuttings and solids may remain in the on-site pit for disposal, and testing is not required. Regulations state that pits should be reclaimed within 180 days. Financial security is required for the site, not pits specifically. Inspections are not specifically addressed in the regulations.
Spill Notification	If the lining or pit fail, notification should be given by the quickest available means, and operations shall cease until the liner and pit are repaired or rebuilt. Other onsite and off-site leaks require oral and written reporting as part of the monthly report.
Corrective Action	On-site corrective action for spills should be "consistent with the requirements of an abatement plan, if any has been set, in a notice of violation or closure, emergency or other order issued by the director." Spills reported in the mothy report must include a description of the corrective actions taken.
Off-site Landfills	Disposal of E&P waste at a permitted offsite facility (including landfills) is the recommended practice for all other solid waste from gas, oil or geophysical operations.
Land Application	Land application of oil and gas-related wastes in Virginia does not require a permit. Fluids to be land-applied must meet groundwater criteria (alkalinity, chloride, iron, manganese, oil and grease, pH and SAR). Site conditions, such as slope, soils and vegetation should be considered when determining the rate and volume of land application at each site. Fluids may not be applied if the ground is saturated, frozen or snow-covered. Fluids also shall not be applied closer than 25 feet from highways or property lines, closer than 50 feet from surface watercourses, wetlands, natural rock outcrops, or sinkholes, closer than 100 feet from water supply wells or springs.
Beneficial Use	Virginia has beneficial use regulations, which may be applicable but are not specific for E&P waste.
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in the regulations.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the regulations.
NORM and TENORM	TENORM wastes relating to oil and gas activities are regulated by the Department of Health. TENORM is exempt from such regulations if any combination of Ra-226 and Ra-228 is less than 5 pCi/g excluding natural background. Oil and gas regulations in the state do not address TENORM waste. TENORM waste shall be disposed in a facility licensed under requirements for uranium and thorium byproduct materials. Alternate methods of disposal may be authorized. An action plan/management plan, on-site or landfill testing/screening requirements, and storage requirements are not specifically addressed in the regulations.

C.20. Kentucky

According to the U.S. Energy Information Agency, in 2016, Kentucky accounted for approximately 0.2% of the US oil and gas production. Oil and gas production is regulated by the Kentucky Cabinet for Energy and Environment, Department of Natural Resources, Oil & Gas Division. Wastes from oil and gas facilities and disposal of wastes offsite are both addressed by the Kentucky Cabinet for Energy and

Environment, Department of Environmental Protection. TENORM is regulated by the Kentucky Cabinet for Health and Family Services. Oil and gas regulations were most recently updated in 2007, and solid waste regulations regarding exemptions for special wastes (includes E&P wastes) were updated in 2016. **Table C-20** provides a summary of the regulations identified for E&P wastes in Kentucky.

Table C-20. Summary of Regulations for E&P Wastes in Kentucky

Topic Area	Summary
Definitions	Water pollution control regulations for oil and gas facilities (401 KAR 5:090) include 29 definitions, and o not include definitions for individual pit types or definition of E&P waste. Definitions for the following pit types are provided in the subsections of oil and gas regulations: holding pits for produced water and drilling pits for fluids other than produced water associated with well drilling, construction, acidizing or fracturing an oil or gas well.
Waste Unit Location Requirements	Overarching regulations for waste sites and facilities in the solid waste regulations address floodplains, endangered species, surface water and groundwater. Special waste landfills have setback requirements (for example, 100 feet from the property line or 250 feet of an intermittent or perennial stream unless a water quality certification has been issued). Minimum depth to groundwater for waste units is not specified.
Tank Requirements	Requirements for tanks are not provided in these regulations. Best management practice includes recycling of tank bottoms as waste oil.
Pit Construction and Operation Requirements	Holding pits and drilling pits are specified in these regulations and are covered under permits-by-rule. Such pits may not be used for the ultimate disposal of produced waters. Holding pits must be designed with a synthetic liner (20 mils or equivalent), a continuous bermed area at least two feet above ground level, and a minimum freeboard of one foot. Regulations require all surface water to be diverted away from the holding pit. Discharge permits are required for produced water. Groundwater monitoring is required for special waste sites and signage is required for general well sties, however, neither is for pits specifically. Inspections for pits are not specified, but the Cabinet may inspect any oil and gas facility. Requirements are not provided for leak detection/monitoring, fencing, netting, minimum depth to groundwater, temporary pits, non-commercial fluid recycling pits or centralized pits.
Pit Closure Requirements	Oil and Gas Well Operator's Manual (Department for Natural Resources, Division of Oil & Gas) indicates that solid and liquid wastes shall be removed from pits prior to closure. The Manual also provides a closure timeframe of 30 days. Details about inspection and sampling are not included. Note: this information is based on a manual, not regulations. A general APD bond is required for special waste landfills but not pits specifically.
Spill Notification	Operators must develop and implement Spill Prevention Control and Countermeasure plans as required, and report spills, discharges and bypasses as necessary.
Corrective Action	Corrective action is not specifically addressed in the regulations.
Off-site Landfills	E&P waste is allowed at special waste landfills and other unspecified permitted facilities. Testing of waste and use as a daily cover are not specifically addressed in the regulations.
Land Application	Special waste, including E&P wastes, may be applied at landfarming or composting facilities. An application is required.
Beneficial Use	Beneficial reuse/brine spreading is not allowed.

Table C-20. Summary of Regulations for E&P Wastes in Kentucky

Topic Area	Summary
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in these regulations.
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in these regulations.
NORM and TENORM	TENORM is regulated by the Kentucky Cabinet of Health and Family Services. Oil and gas regulations only address the downhole disposal of TENORM. Testing/screening is required, and waste profile/manifest is necessary for possession and transportation of TENORM. The type of landfill, well or low-level radioactive waste disposal facility depends on ranges of activity concentration. An activity concentration greater than 200 pCi/g of combined Ra-226 and Ra-228 in a landfill in Kentucky shall be prohibited.

C.21. Illinois

In 2016, Illinois accounted for approximately 0.1% of the nation's oil and gas production according to U.S. Energy Information Agency data. Oil is produced from conventional reservoirs in the southern part of the state, and only a small amount of gas is produced. Most production is from stripper wells, but there is a potential for future exploration of unconventional reserves in the deep New Albany Shale. The Department of Natural Resources, Oil and Gas Program regulates oil and natural gas production in the state. The Illinois Environmental Protection Agency is responsible for management of solid and hazardous waste. NORM waste related to oil and natural gas production is regulated by the Illinois Environmental Protection Agency, Emergency Management Agency, and Central Midwest Interstate Low-Level Radioactive Waste Commission. **Table C-21** provides a summary of the regulations identified for E&P wastes in Illinois.

Table C-21. Summary of Regulations for E&P Wastes in Illinois

Topic Area	Summary
Definitions	Approximately 50 definitions are provided in Section 240.10 of Title 62 of the Illinois Administrative Code. Additional definitions are also provided in other sections of Part 240 (The Illinois Oil and Gas Act). Several types of pits including sediment pits (used for drill cuttings), drilling fluid pits (circulation pits) reserve pits (for drilling fluid waste storage) and completion pits are discussed, along with tanks and concrete storage structures. Title 62, Chapter 1, Part 240 (The Illinois Oil and Gas Act) has an amended effective date of March 18, 2018. Part 245 (Hydraulic Fracturing Regulations) is a recent act with extensive regulations effective November 14, 2014.
Waste Unit Location Requirements	Concrete storage structures and tanks are prohibited within 200 feet of an existing inhabited structure, stream, body of water or marshy land. Concrete storage structures are also prohibited in floodplains. A permit is required for any tank, structure, measure or device intended or used for storage of hydraulic fracturing fluid, hydraulic fracturing flowback, or produced water within a floodplain. Protection of groundwater and surface water from discharges are addressed in the regulations but endangered species are not. Minimum depth to groundwater for waste management units is not specified.

Table C-21. Summary of Regulations for E&P Wastes in Illinois

Topic Area	Summary
Waste Unit Location Requirements (Cont.)	Hydraulic fracturing regulations require assessment of the potential for seismic activity and accounting for the risks in all well drilling and operations plans. If the well is in a seismic risk zone (as defined in the regulations) the well insurance policy is required to have a rider providing coverage against loss or claims resulting from impacts from any aspect of the permitted operations following earthquakes of magnitude 4.5 or more.
Tank Requirements	Secondary containment (dikes) for tanks should be have a capacity 1-1/2 times the volume of the largest tank. Construction specifications for tanks are general and indicate materials should be compatible with the expected fluids being contained and netting is required for tanks. Modular large volume tanks and tank monitoring are not specifically addressed in the regulations. Permits for tank bottom removal are not required, but haulers of liquid oilfield wastes (including tan bottoms) must be permitted. Crude oil bottom sediments may be disposed of in at permitted special waste landfills, injected at a permitted facility, bioremediated by landfarming or used for road oiling on the lease (if approved).
Pit Construction and Operation Requirements	Specific pit types include drilling, reserve, sediment, circulation, completion and workover/plugging, and production pits, and permits are required. Pits for freshwater and saltwater/oil drilling fluids have separate regulations. Liners are not required for fresh water drilling pits but other pit types require a synthetic flexible liner that is at least 30 mils in thickness and compatible with the fluid contained. Leak detection/monitoring, fencing, netting, run-on and run-off controls, groundwater monitoring and inspections are required. A permit is required to discharge waste onto the surrounding land surface or into a body of water. Minimum depth to groundwater, freeboard and berm requirements, signage, temporary pit requirements, noncommercial fluid recycling pits and centralized pits are not specifically addressed in the regulations.
Pit Closure Requirements	All oilfield brine and produced waters shall be removed and disposed in a Class II UIC well. Fresh water drilling fluid wastes may be disposed of by on-site burial or surface application in accordance with the regulations. Saltwater and oil-based muds can be buried onsite but must be enclosed in the liner and covered with 5 feet of soil. Pit closure inspections, sampling and financial security are not specifically addressed in the regulations.
Spill Notification	Immediate notification is required for spills of crude oil in excess of 1 barrel, or produced water in excess of 5 barrels, onto the surface of the land; and all crude oil spills, regardless of amount, which enter streams, rivers, ponds, lakes, wetlands or other bodies of water.
Corrective Action	For saltwater spills water must be removed and disposed in permitted injection wells and the area treated with lime immediately. Loading rate and tilling requirements for lime are provided in the regulations. Remediation requirements are presented separately for crude oil spills and produced water spills. For saltwater spills, the Department will determine if additional remediation action needs to be taken by the permittee, which may include flushing of the area with freshwater, the addition of organic material (e.g., peat moss, straw), additional chemical treatment, additional disking the soil, or soil removal.
Off-site Landfills	Liquid oilfield waste, including tank bottoms and other RCRA exempt wastes, can be disposed of at special waste landfills. Special Waste landfills fall under the Inert Waste landfill construction and operation requirements and are subject to stringent siting standards and require liners, and groundwater monitoring.

Table C-21. Summary of Regulations for E&P Wastes in Illinois

Topic Area	Summary
Land Application	Crude oil bottom sediments may be bioremediated on-site through land spreading. Requirements for land spreading include addition of fertilizer and lime, tilling, watering to promote plant growth and limit runoff.
Beneficial Use	Lease road oiling is allowed and requires a permit and should not be conducted when the ground is frozen or during precipitation events, or in areas subject to frequent flooding. Material used for lease road oiling must contain less than 10% produced water. Beneficial use of brine is not specifically addressed in the regulations.
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in the regulations.
Commercial Recycling and Reclamation Facilities	The recently added hydraulic fracturing regulations recommend recycling of flowback and produced water. Requirements for commercial water or other waste recycling facilities are not provided in the regulations.
NORM and TENORM	NORM waste related to oil and natural gas production is regulated by the Illinois Environmental Protection Agency, Emergency Management Agency, and Central Midwest Interstate Low-Level Radioactive Waste Commission. Oil and gas regulations in the state do not address NORM waste. E&P waste is treated as a low-level radioactive waste and managed under the Commission's Regional Management Plan. Off-site disposal of NORM waste is permitted in non-hazardous special waste landfills if NORM is at background levels. If greater than background levels, disposal may be required at a waste facility permitted by the Illinois Department of Nuclear Safety. Residue containing NORM from concrete storage structures may also require disposal at a waste facility permitted by the Illinois Department of Nuclear Safety. Wells targeting black shale formations (New Albany) are subject to additional regulations due to the potential for elevated radioactivity content of the cuttings and fluids. Permits required developing a radioactive materials management strategy to test for and identify, manage, transport and dispose of any radioactive materials utilized or generated during the course of operations. Testing of drill cuttings for radioactivity is required. Drilling fluid, drilling cuttings and drilling waste from any black shale zones that test positive for levels of radioactive contamination shall not be stored in open pits and must be disposed of offsite at a permitted facility.

C.22. Indiana

In 2016, Indiana produced approximately 0.04% of total U.S. oil and gas production, according to the U.S. Energy Information Agency. The Division of Oil and Gas within the Indiana Department of Natural Resources regulates oil and natural gas production, as well as NORM related to oil and gas production, in the state. The Indiana Department of Environmental Management regulates solid and hazardous wastes. The oil and gas regulations, Title 29 (312 IAC 29), were promulgated in 2017. **Table C-22** provides a summary of the regulations identified for E&P wastes in Indiana.

Table C-22. Summary of Regulations for E&P Wastes in Indiana

Topic Area	Summary
Definitions	The oil and gas regulations include 134 definitions including many related waste management. The definition of "E&P waste" is very general and does not reference the RCRA exemption. Several entries relate to hydraulic fracturing, stimulation, and NORM wastes. Definitions are provided for circulation pit, completion pit, production fluid storage pit, reserve pit, workover pit, and concrete production fluid storage structures.
Waste Unit Location Requirements	Requirements for facility locations in floodplains, and proximity to surface water and groundwater are dispersed throughout the subsections in the regulations. Endangered species are not specifically addressed in these regulations. Location restrictions are provided (for example, pits shall not be located within 200 feet of an occupied dwelling or a water body). Pits must also be located 3 feet above the seasonally high groundwater table.
Tank Requirements	Indiana regulations include detailed technical and operational requirements for tank batteries. The regulations address tank and berm design, tank construction materials, and the treatment of storm water within secondary containment. The regulations specify netting for open top tanks.
Pit Construction and Operation Requirements	Regulations include definitions for the following types of pits: circulation pit, completion pit, production fluid storage pit, reserve pit and workover pit. Permits are required for construction of a pit in a floodway. Indiana pit and tank regulations include numerous requirements for "concrete production fluid storage structures" , a structure not specifically regulated in other states in this study. Pits containing saltwater-based, oil-based and production fluids require synthetic liners. Construction details are provided in the regulations, and a visual inspection is required. Additional requirements for freeboard, fencing, netting, berms, run-on/run-off controls, signage and inspections are also included. Temporary pits are also addressed. Requirements are not provided for groundwater monitoring, inspection, discharge permits, non-commercial fluid recycling pits or centralized pits.
Pit Closure Requirements	Regulations specify liquids removal, liner removal and schedule for pit closure (within one hundred twenty (120) days after conclusion of well drilling operations or sixty (60) days of well completion operations, whichever occurs first). Inspection and sampling for pit closure are not specifically addressed. Financial security for pit closure is a general requirement for bonding under the application for permit to drill.
Spill Notification	Spill notification is not specifically addressed in the state regulations.
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	E&P waste disposal is allowed at "permitted landfills", including municipal solid waste landfills. Testing of waste and its use as daily cover in municipal landfills are not specifically addressed in the regulations.
Land Application	Water-based mud and completion fluids may be land applied. A permit is required if not applied at the lease site. Conditions for use and location restrictions are provided in the regulations, such as land application may not be performed during a precipitation event, chloride content must be less than 1,000 mg/L, and the site must be located at least 100 feet from a water body.

Table C-22. Summary of Regulations for E&P Wastes in Indiana

Topic Area	Summary
Land Application (Cont.)	Crude oil and tank bottoms are allowed for oiling lease and county roads with a permit. Conditions for its use are provided in the regulations. Examples specify that road oiling shall not be conducted when the ground is frozen and the produced water content of the crude oil tank bottoms shall not be greater than 10% free water by volume. Disposal of oil and gas NORM on lease or county roads is prohibited.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Closed loop drilling is noted in the regulations but it not specifically designated as a best management practice. Closed loop systems must be maintained in a leak-free condition when used Produced water recycling is not required.
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in these regulations.
NORM and TENORM	Oil and gas NORM waste may be disposed in plugged and abandoned wells, disposed or land applied at the lease site, or disposed at an off-site facility that is permitted to accept such waste. Notification and disposal plan are required but a permit is not. Land application limits indicate that after application and mixing, radioactivity concentration in the area may not exceed five (5) pCi/g above background of Radium-226 combined with Radium-228 or one hundred fifty (150) pCi/g above background of any other radionuclide. Additional disposal limitations/conditions are provided in the regulations.

C.23. New York

According to the U.S. Energy Information Agency, New York accounted for approximately 0.04% of the total US production in 2016. The New York Department of Environmental Conservation regulates oil and gas production and facilities (Division of Mineral Resources), solid waste disposal (Division of Materials Management) and NORM/TENORM/NARM (Division of Environmental Remediation). **Table C-23** provides a summary of the regulations identified for E&P wastes in New York.

Table C-23. Summary of Regulations for E&P Wastes in New York

Topic Area	Summary
Definitions	Only brine pits are discussed in the regulations. Other pit types are not defined.
Waste Unit Location Requirements	Solid waste regulations include general requirements for siting solid waste facilities. Overarching requirements include a general prohibition of pollution in oil and gas operations. General well location restrictions are 100 feet from any inhabited private dwelling house without written consent, or 150 feet from any public building and 50 feet from a public stream, river or other body of water. Minimum depth to water is not specified.
Tank Requirements	Tank requirements are provided for solid waste facilities, not oil and gas facilities specifically. All tanks must be chemically compatible with the waste being stored and inspections are required. If necessary, above ground tanks must have a secondary containment system designed and built to contain 110% of the volume of either the largest tank within the containment system or the total volume of all interconnected tanks, whichever is greater. A minimum freeboard of 2 feet is required if the top of the tank is open.

Table C-23. Summary of Regulations for E&P Wastes in New York

Topic Area	Summary
Tank Requirements (Cont.)	Modular large volume tanks, netting, tank monitoring and tank bottom removal are not specifically addressed in the regulations.
Pit Construction and Operation Requirements	Drilling muds are not considered to be polluting fluids. The only pit type included in these regulations is earthen pits for brine. A "watertight material" is required for brine pits; unlined brine pits are prohibited. Permits are not required, however, the operator must submit and receive approval for a plan for the environmentally safe and proper ultimate disposal of fluids. A permit for discharge may be required depending on the disposal method. Signage is necessary for the oil and gas facility, not pits specifically. Requirements are not provided for leak detection/monitoring, fencing, netting, depth to groundwater, freeboard, berms or secondary containment, run-on/run-off controls, groundwater monitoring, signage, inspection, temporary pits, non-commercial fluid recycling pits or centralized pits.
Pit Closure Requirements	Pit closure should be conducted within 45 days after cessation of drilling operations, unless the Department approves an extension. No other details regarding pit closure are included in the regulations. Financial security for pits is included as part of oil and gas facility bond.
Spill Notification	Spill notification is addressed in the regulations.
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	E&P waste disposal is allowed at a solid waste facility. It is unclear about whether testing of waste is required or if E&P waste may be used as daily cover, although it was noted that the waste may not be within 10 feet of the final cover.
Land Application	Land application of E&P waste is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use of brine requires a written petition, and brine must meet specific criteria for roadspreading. Specifics are provided in the regulations for its application and usage. For example, brine application for dust control and road stabilization is prohibited between sundown and sunrise on unpaved roads and brine may not be applied directly to vegetation.
Waste Minimization/ Management	Waste minimization and management activities, such as closed loop drilling and produced water recycling, are not specifically addressed in these regulations.
Commercial Recycling and Reclamation Facilities	Commercial and stationary recycling and reclamation facilities are not specifically addressed in these regulations.
NORM and TENORM	New York applies the term "naturally occurring and/or accelerator-produced radioactive material (NARM)" to drill cuttings. A permit is not required for NARM disposal; however, the disposal of TENORM is more restrictive. Storage requirements and disposal limitations/conditions are extensive and difficult to navigate in the regulations. There is also a specific regulation for screening if drill cuttings are being disposed.

C.24. Florida

According to U.S. Energy Information Agency data, Florida accounted for approximately 0.03% of the nation's oil and gas production in 2016. All production is from conventional reservoirs with most coming from fields located near Pensacola, and a small producing area in the southern part of the state.

The Department of Environmental Protection, Division of Water Resource Management, Oil and Gas Program regulates oil and natural gas production in the state. The Division of Waste Management, Solid Waste and Recycling Program is responsible for management of solid waste. NARM waste related to oil and gas production is regulated by the Florida Department of Health, Radiation Control.[C10] **Table C-24** provides a summary of the regulations identified for E&P wastes in Florida.

Table C-24. Summary of Regulations for E&P Wastes in Florida

Topic Area	Summary
Definitions	The oil and gas regulations are relatively concise and do not provide detailed specifications and requirements for most waste management topics. Approximately 60 definitions are provided in Chapter 62C-25 (Conservation of Oil and Gas: General). The types of pits discussed include mud pits and reserve pits. Most of the oil and gas rules (Sections 62C-25 through 29) were amended on March 24, 1996, with a few sections being amended since. Section 64E-5.101 (Definitions) in Control of Radiation Hazards was published on December 26, 2013.
Waste Unit Location Requirements	Location restrictions (residential and environmental setbacks) and minimum depth to groundwater are not specifically addressed in the oil and gas regulations for any waste management units. Groundwater, surface water and endangered species are not specifically addressed in the oil and gas regulations. Solid waste regulations state "A landfill or solid waste disposal unit shall not be located in the 100-year floodplain where it will restrict the flow of the 100-year flood, reduce the temporary water storage capacity of the floodplain unless compensating storage is provided, or result in a washout of solid waste."
Tank Requirements	There are few technical requirements for tanks in the regulations. Secondary containment must be two times the capacity of the tank. General construction requirements indicate materials should be "relatively impermeable and of sufficient size and strength." Netting, modular large volume tanks and removal of tank bottoms are not specifically addressed. A general requirement for operating facilities includes monitoring all equipment and facilities to immediately detect any leak which may cause pollution.
Pit Construction and Operation Requirements	Specific pit types addressed in the regulations include mud pits and reserve pits. Earthen pits for active drill fluids are prohibited. Sensitive areas (including wetlands and national/state forests and parks) require prefabricated tanks and drip pans for all waste fluid, or reserve pits that must be either lined with impermeable material or intermittently pumped to reduce hydrostatic head. Reserve pits should also not exceed 75% capacity to ensure adequate freeboard. General dike requirements for sites include installation of berms and run-on/run-off controls. Permits and signage for pits are part of the general APD. Leak detection/monitoring, fencing, netting, minimum depth to groundwater, groundwater monitoring, inspections, discharge permits, temporary pit requirements, noncommercial fluid recycling pits and centralized pits are not specifically addressed in the regulations.

C10) Florida uses the term naturally occurring or accelerator-produced radioactive material (NARM) in regulations, but the definition is consistent with TENORM in other states.

Table C-24. Summary of Regulations for E&P Wastes in Florida

Topic Area	Summary
Pit Closure Requirements	Liquids and recoverable slurry must be removed from the pit and disposed either downhole or at a landfill. Financial security is included in the general well bond, not for pits specifically. Pit closure schedule, inspections, and sampling are not specifically addressed in the regulations.
Spill Notification	Spills of crude petroleum or associated fluids into the environment require immediate notification and written confirmation for spills greater than 5 barrels.
Corrective Action	Corrective actions should be immediate and conducted in accordance with Spill Prevention and Clean Up Plan.
Off-site Landfills	Off-site disposal of E&P waste is allowed, but the type of facility is not specified. Requirements for testing of waste and use of E&P wastes as daily cover are not specifically addressed in the state regulations.
Land Application	Land application is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in the regulations.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the regulations.
NORM and TENORM	Florida Department of Health defines "NARM" as any naturally occurring or accelerator-produced radioactive material. To meet the definition of licensing state, NARM only refers to discrete sources of NARM. Diffuse sources of NARM, which are large in volume and low in activity, are excluded from consideration by the Conference of Radiation Control Program Directors, Inc., for licensing state designation purposes. Florida has comprehensive regulations for radioactive materials, but none specifically address oil and gas or TENORM. Regulations appear to allow TENORM type materials to be disposed at permitted facilities, however specific permitting and testing requirements are unclear. An action plan/management plan, on-site or landfill testing/screening and storage requirements are not specifically addressed in the regulations.

C.25. Idaho

The U.S. Energy Information Agency estimated that Idaho accounted for approximately 0.01% of the nation's oil and gas production in 2016. Oil exploration has occurred in Idaho since the early 1900's but commercial production just started in 2016 from a small conventional gas field in southwestern Idaho. The Idaho Department of Lands, Oil and Gas Conservation Commission regulates oil and natural gas production in the state. The Oil and Gas Division serves as the administrative arm of the Commission. The Department of Environmental Quality, Waste Management and Remediation Division, Solid Waste and Hazardous Waste Programs regulate solid and hazardous waste, respectively. The Department of Environmental Quality regulates NORM/TENORM waste related to oil and natural gas production.

Idaho oil and gas regulations underwent a major revision in 2012 in response to increased drilling activity. Additional changes have been made as recently as 2015 which included new regulations for pits and tanks. Department of Water Resources recently announced that it would ask the EPA to run the Class II injection program in Idaho because it is new to the industry and is the only hydrocarbon-producing state without a Class II program in place. **Table C-25** provides a summary of the regulations identified for E&P wastes in Idaho.

Table C-25. Summary of Regulations for E&P Wastes in Idaho

Topic Area	Summary
Definitions	Approximately 60 definitions are provided in Section 010 (Definitions) of ID07, Chapter 02 – Rules Governing Conservation of Oil and Natural Gas in the State of Idaho. Pits are defined as any excavated or constructed depression or reservoir used to contain reserve, drilling, well treatment, produced water, or other fluids at the drill site. This does not include enclosed, mobile, or portable tanks used to contain fluids. Regulations for waste management provide a combination of detailed technical specifications (pit construction, for example) and more general requirements (pit content disposal).
Waste Unit Location Requirements	Regulations related to siting pits near floodplains, surface water and groundwater are dispersed in the oil and gas regulations. Solid waste regulations provide general overarching location and siting requirements for floodplains, surface water, groundwater and endangered species. Specific setback distances for pits are not specifically addressed in the regulations. Tank batteries cannot be placed in a recognized source water assessment or protection area, or within 300 feet of existing occupied structures, water wells, canals, ditches, natural or ordinary high water mark of surface waters, or within 50 feet of highways. Pits located in a one hundred-year floodplain must be in conformance with any applicable floodplain ordinances. A minimum depth to groundwater is not included in the regulations.
Tank Requirements	Regulations state that dikes for tank batteries have a capacity of 1½ times the volume of the largest tank and a permeability of 10^{-9} cm/sec. Construction specifications, netting, monitoring, modular large volume tanks and removal of tank bottoms are not specifically addressed.
Pit Construction and Operation Requirements	Mud pits are specifically discussed in the oil and gas regulations. Separate requirements are provided for short-term pits (reserve, well treatment and other pits used less than 1 year) versus long-term pits (used longer than 1 year). Separate pit permits are required only if the pit is not included under the original APD. Liners with a thickness of 20 mils are required for reserve, well treatment and other short-term pits, while long-term pits require liners of 60 mils. All liners should have a permeability of 10^{-9} cm/sec. Leak detection/monitoring is required for long-term pits but not short-term ones. Fencing is required for the well site but not pits specifically. Fencing and netting are implied for pits based on "site-specific methods for excluding people, terrestrial animals, and avian wildlife from the pits." Bermed pit walls must be a minimum of 2 feet wide at the top. Pits that have berms more than 10 feet in height or hold 50 acre-feet of fluid must comply with dam safety requirements. A minimum freeboard of 2 feet is required for pits.

Table C-25. Summary of Regulations for E&P Wastes in Idaho

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Run-off/run-on controls and signage are required for Tier II/III solid waste facilities and groundwater monitoring is also required for Tier III facilities, not pits specifically. Short-term pits are considered temporary pits. The owner/operator must notify the Department within 24 hours of an emergency situation that requires an emergency pit. Regulations require removal of oil skims from both short term and long-term pits. Inspections, discharge permits, noncommercial fluid recycling pits and centralized pits are not specifically addressed in the regulations.
Pit Closure Requirements	Liquid removal is required prior to pit closure. Pit liners and accumulated solids should be removed and testing of the solids is necessary to determine an appropriate disposal facility. After removal of the liner and solids, the pit must be inspected by the Department and remediated if there are signs of leakage. All reclamation work should be completed within 12 months of plugging and abandonment of a well or closure of other oil and gas facilities. Bonds are required for the wells/site, not for pits specifically.
Spill Notification	Notification is required for leaks from pits. "If a pit or closed-loop system develops a leak, or if any penetration of the pit liner occurs below the liquid's surface, then the owner or operator shall remove all liquid above the damage or leak line within forty-eight (48) hours, notify the appropriate Department area office within forty-eight (48) hours of the discovery, and repair the damage or replace the pit liner."
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	Off-site disposal of E&P waste is not clearly stated but appears to be allowed at non-municipal solid waste landfills (NMSWLF). Routine characterization of waste is required at both Tier II (low risk) and Tier III (higher risk) NMSWLF facilities. Both types of facilities have stringent design criteria and require liners and groundwater monitoring. Use of E&P waste as daily cover is not specifically addressed.
Land Application	Land application is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Closed loop drilling is described as an option to pits, but not required. Produced water recycling is not specifically addressed in the regulations.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the regulations.
NORM and TENORM	Idaho Board of Environmental Quality regulates NORM/TENORM related to oil and gas activities. Oil and gas regulations do not address NORM/TENORM. While the regulation is not clear for NORM/TENORM, radioactive materials can be disposed at appropriately permitted RCRA C facilities. Disposal of radioactive materials is not allowed at a municipal solid waste landfill. An action plan/management plan, on-site or landfill testing/screening and storage requirements are not specifically addressed in the regulations.

C.26. Tennessee

According to the U.S. Energy Information Agency, in 2016, Tennessee accounted for approximately 0.01% of the nation's oil and gas production. Small quantities of oil and gas are produced from both conventional wells and new unconventional wells targeting the Chattanooga Shale. The Department of Environment and Conservation, division of Water Resources Oil and Gas Board regulates oil and natural gas production in the state. The Department of Environment and Conservation, Division of Radiological Health regulates NORM/TENORM waste related to oil and natural gas production.

Chapters 0400-51 through 0400-58 contain rules for the Oil and Gas Programs and were most recently updated in June 2013. Four sections address issues related to waste management: Definitions, Drilling, Testing and Completion, and Production. Chapter 0400-20 (Division of Radiological Health) is dated May 22, 2012. **Table C-26** provides a summary of regulations identified for E&P wastes in Tennessee.

Table C-26. Summary of Regulations for E&P Wastes in Tennessee

Topic Area	Summary
Definitions	Nearly 100 definitions are provided in Chapter 0400-51-01 (Definitions) of the Rules of the Oil and Gas Program. Discussion of waste management addresses only tanks and pits and is fairly brief in Chapter 0400-53-03 (Prevention of Hazards and Pollution). Regulations address hydraulic fracturing controls and chemical disclosure. The types of pits discussed include mud circulation pits, reserve pits and saltwater pits.
Waste Unit Location Requirements	Overarching regulations indicate wells, pits or storage facilities in wetlands or flood-prone areas are prohibited. Regulations for surface water are dispersed and state that a pit cannot be within 100 feet of the normal high-water line of any stream or lake. Pits and tanks should also be located at least 100 feet from any fire hazard or dwelling. Endangered species are not specifically addressed in the oil and gas regulations. While a minimum depth to groundwater is not specified, there is a general requirement that pits should be constructed above ground where shallow groundwater may be encountered, or closed loop drilling should be used.
Tank Requirements	Regulations provide a limited amount of detail and requirements for construction and operation of tanks. Secondary containment is required and should be 1½ times the capacity of the largest tank in the battery. Regulations include a diagram of an excavated tank pad and pit containment system. Construction requirements, netting, monitoring, modular large volume tanks and removal of tank bottoms are not specifically addressed in the regulations.
Pit Construction and Operation Requirements	The types of pits discussed include mud circulation and reserve pits, as well as saltwater and fracturing fluid pits. Pits for saltwater and fracturing fluids are considered temporary storage. Pits require synthetic liners with a minimum thickness of 10-mil thickness (or equivalent measures, such as clay). However, mud circulation and reserve pits require a liner of 20-mil thickness with a 4-inch welded seam overlap. These pits also have additional minimum requirements, such as a freeboard of 2 feet, 2:1 side slopes and berm walls at least 2 feet wide. Only runoff from the immediate area may enter the pit. While no specific minimum depth to groundwater is provided, regulations state "In areas where groundwater is close enough to the surface that it will be encountered in construction of a pit, pits shall be constructed above ground, or the operator shall use a closed-loop system."

Table C-26. Summary of Regulations for E&P Wastes in Tennessee

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Signage is required for the well, and groundwater monitoring (sampling drinking water wells is done at the request of the owner, and is not pits specifically. Groundwater monitoring is only required for hydraulically fractured wells that use more than 200,000 gallons of fluid. Permits, leak detection/monitoring, fencing, discharge permits, noncommercial fluid recycling pits and centralized pits are not specifically addressed in the regulations.
Pit Closure Requirements	Pits should be drained and filled within 30 days of the initial disturbance. All drilling supplies and equipment (including liners) that are not contained and covered in the pit shall be removed from the site. Financial security is included in the general well permit, not for pits specifically. Inspections and sampling are not specifically addressed in the regulations.
Spill Notification	A spill of oil, saltwater, or other drilling or production associated materials requires notification within 12 hours.
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	Off-site disposal of E&P waste is not specifically mentioned in the regulations.
Land Application	Land application is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Closed loop drilling is a possible alternative in wetlands but is not required. As stated above, "In areas where groundwater is close enough to the surface that it will be encountered in construction of a pit, pits shall be constructed above ground, or the operator shall use a closed-loop system." Produced water recycling is not specifically addressed in the regulations.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the regulations.
NORM and TENORM	Tennessee Division of Radiological Health defines "NARM" as any naturally occurring or accelerator-produced radioactive material. It does not include byproduct, source or special nuclear material. Oil and gas regulations do not define NARM but rather reference radiation regulations. Disposal of NARM is determined on a case by case basis. ASTSWMO indicates that disposal of NARM waste is allowed in a MSWLF if less than 30 pCi/g. An action plan/management plan and on-site or landfill testing/screening are not specifically addressed in the regulations.

C.27. Nevada

The U.S. Energy Information Agency data indicates that Nevada accounted for less than 0.01% of the nation's oil and gas production in 2016. There is no commercial gas production in Nevada and a very small volume of oil is produced from two shallow producing areas with fewer than 20 oil fields. The Nevada Commission on Mineral Resources, Division of Minerals, Oil and Gas – Oil and Gas Program regulates oil and natural gas production in the state. The Department of Environmental Conservation, Division of Environmental Protection regulates solid and hazardous waste. The Department of Health and Human Services, Division of Public and Behavioral Health regulates NORM/TENORM waste related to oil and natural gas production.

Nevada oil and gas regulations (Chapter 522) are clear but with limited details. For example, the only discussion of pits is in Chapter 522.225 containing two short paragraphs without any technical specifications. The Oil and Gas Division appears to have significant flexibility to address issues on a site-specific basis. In 2014, the oil and gas regulations were updated to include a section on hydraulic fracturing which provides a much greater level of detail and technical specifications. **Table C-27** provides a summary of the regulations identified for E&P wastes in Nevada.

Table C-27. Summary of Regulations for E&P Wastes in Nevada

Topic Area	Summary
Definitions	Approximately 36 definitions are provided in Chapter 522.010 (Definitions) and 522.700 (Hydraulic Fracturing) of Chapter 522 - Oil and Gas. Definitions are not provided for specific pit types or wastes.
Waste Unit Location Requirements	Oil and gas regulations do not provide location or setback requirements for pits. The only location or setback requirement potentially related to waste management units is that the edge of the drilling pad must not be less than 100 feet from any known perennial water source, existing water well or existing permitted structure. Dikes or fire walls are required around oil tanks located within the corporate limits of any city or town, where tanks for storage are less than 500 feet from any highway or inhabited dwelling, less than 1,000 feet from any school or church. Regulations are dispersed in the solid waste regulations and provide several location requirements. For example, Class 1 landfills are (1) allowed within 100 feet of a floodplain but must demonstrate no impact to the floodplain; (2) must not jeopardize existence or habitat for endangered species; (3) must not be within 1,000 feet of surface water; and (4) must not be within 100 feet of upper aquifer. A residential setback is not included in the regulations.
Tank Requirements	As described above, dikes or fire walls are required around permanent tanks for under certain conditions, but regulations provide no further details on construction operation or protection requirements. Tanks are required for containment of all fluids during hydraulic fracturing operations. Water regulations are referenced for requirements. Secondary containment requirements, construction specifications, netting, monitoring, modular large volume tanks and removal of tank bottoms are not specifically addressed.
Pit Construction and Operation Requirements	The following types of pits are mentioned in the oil and gas regulations: collecting pits, reserve pits, burning pits and pits "for storage of brines." Unlined pits for oil, brines or oilfield waste are prohibited unless approved by the Division. In addition, a reserve pit for drilling liquids must not be subsequently used for the discharge of wellbore fluids during the testing of the well. Hydraulic fracturing fluids must be stored in tanks, not pits. The requirement for liners is inferred from the prohibition of unlined pits, however, no specifications are provided. Signage is required for wells, not pits specifically. Groundwater monitoring of nearby residential wells must be sampled prior to hydraulic fracturing (this requirement is not limited to pits).

Table C-27. Summary of Regulations for E&P Wastes in Nevada

Topic Area	Summary
Pit Construction and Operation Requirements (Cont.)	Permits, leak detection/monitoring, fencing, netting, depth to groundwater, freeboard and berm requirements, run-off/run-on controls, inspections, discharge permits, temporary pits, noncommercial fluid recycling pits and centralized pits are not specifically addressed in the regulations.
Pit Closure Requirements	Pit closure shall be conducted "as soon as weather and ground conditions permit, upon final abandonment and completion of the plugging of any well." As practicable, the site should be restored to its condition when operations commenced. Financial security is included in the general well permit, not for pits specifically. Removal of pit contents, inspections and sampling are not specifically addressed in the regulations.
Spill Notification	Notification is required after an incident, such as a fire, lightning strike, leak, break or overflow and should include the following information: exact location of the incident; steps being taken to remedy the situation; and details about the amount of oil or gas lost, destroyed or permitted to escape.
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	Off-site disposal of E&P waste is not specifically mentioned in the regulations but appears to be allowed. Testing of waste and use as daily cover were not specifically addressed.
Land Application	Land application is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use is not specifically addressed in the state regulations.
Waste Minimization/ Management	Closed loop drilling and produced water recycling are not specifically addressed in the regulations.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the regulations.
NORM and TENORM	NORM and TENORM in the state currently have limited regulations; it is unclear if they are regulated under NAC 459 (Hazardous Materials). Nevada Department of Health and Human Services has an exemption for naturally occurring radioactive material that contains less than 5 picocuries (0.185 becquerel) of radium-226 per gram of material. Oil and gas regulations do not address NORM/TENORM. A licensee shall dispose of licensed radioactive material only using one of the following methods: transfer to an authorized recipient; permitted land disposal facility; by decay in storage; by release in effluents within the limits specified, or as otherwise approved. An action plan/management plan, on-site or landfill testing/screening and storage requirements are not specifically addressed in the regulations.

C.28. Missouri

In 2016, Missouri accounted for less than 0.01% of the nation's oil and gas production according to the U.S. Energy Information Agency. A small number of oil wells produced from shallow conventional reservoirs, and one commercial gas well was reported in 2017. Missouri has some unconventional reserves in coalbed methane, heavy oil and tar sands. The Department of Natural Resources, Missouri Geological Survey is responsible, in part, for activities associated with oil and natural gas production in the state. The Department of Natural Resources, Solid Waste Management Program is responsible for management of solid waste. NORM/TENORM is not specifically addressed in state oil and gas regulations.

Many sections of the oil and as regulations were updated in 2016 including drilling and completion, production and well spacing. None of these sections appear to have regulations controlling waste management. **Table C-28** provides a summary of the regulations identified for E&P wastes in Missouri.

Table C-28. Summary of Regulations for E&P Wastes in Missouri

Topic Area	Text
Definitions	Approximately 70 definitions are provided in 10 CSR 50-1. No pits are defined. Missouri regulations are relatively silent on E&P waste. No technical specifications for waste management structures (pits, tanks, etc.) are provided. The review found no guidance, regulations or policies addressing criteria and siting of waste units, tanks, pits. Spill notification and corrective actions, land application, beneficial use, waste minimization, commercial recycling or NORM/TENORM.
Waste Unit Location Requirements	Waste unit location requirements are not specifically addressed in the state regulations.
Tank Requirements	Tank requirements are not specifically addressed in the state regulations.
Pit Construction and Operation Requirements	Pit construction and operation requirements are not specifically addressed in the state regulations.
Pit Closure Requirements	Pit closure requirements are not specifically addressed in the state regulations.
Spill Notification	Spill notification is not specifically addressed in the state regulations.
Corrective Action	Corrective action is not specifically addressed in the state regulations.
Off-site Landfills	E&P wastes are not excluded from landfills under 10 CSR 80-3.010 Design and Operation (3) Solid Waste Excluded); and may be allowed under (2) Solid Waste Accepted…"Only the following solid wastes shall be accepted for disposal in a sanitary landfill: municipal waste; bulky waste; demolition and construction wastes; brush and wood wastes; cut, chipped, or shredded tires as defined in 10 CSR 80-8; soil; rock; concrete; related inert solids relatively insoluble in water; E&P waste may be considered a Special Waste "(108) Special waste means waste which is not regulated hazardous waste, which has physical or chemical characteristics, or both, that are different from municipal, demolition, construction and wood wastes, and which potentially require special handling.
Land Application	Land application is not specifically addressed in the state regulations.
Beneficial Use	Beneficial use not specifically addressed in the state regulations.
Waste Minimization/ Management	Waste minimization and management are not specifically addressed in the state regulations.
Commercial Recycling and Reclamation Facilities	Commercial recycling and reclamation facilities are not specifically addressed in the state regulations.
NORM and TENORM	NORM and TENORM are not specifically addressed in the state regulations.

C.29. References

CalEPA (California Environmental Protection Agency). 2002. "Oil Exploration and Production Wastes Initiative." Prepared by the Department of Toxic Substances Control. Sacramento, CA. May.

PADEP (Pennsylvania Department of Environmental Protection). 2018. "Office of Oil and Gas Management: At a Glance."

TXCEQ (Texas Commission on Environmental Quality). 2014. "Management of Oil and Gas Waste at TCEQ Regulated Facilities." [Power Point presentation].

U.S. DOE (United Stated Department of Energy). 1997. "Costs for Off-site Disposal of Nonhazardous Oil Field Wastes: Salt Caverns versus Other Disposal Methods." Prepared by Argonne National Laboratory under Contract W-31-109-Eng-38. Argonne, IL. April.

WVDEP (West Virginia Department of Environmental Protection). 2015. "Final Report on the Examination of Drill Cuttings and Related Environmental, Economic, and Technical Aspects Associated with Solid Waste Facilities in West Virginia.'" Prepared by the Marshall University Center for Environmental, Geotechnical and Applied Science. Charleston, WV. June.

Attachment C-1:

Summary of State Regulatory Elements

[Due to the large file size, this spreadsheet is maintained as a separate file.]

Attachment C-2:

Compilation of State Regulatory Language

[Due to the large file size, this spreadsheet is maintained as a separate file.]

EXHIBIT A-38

Establishment of Cleanup Levels for CERCLA Sites with Radioactive Contamination

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

AUG 22 1997

OSWER No. 9200.4-18

MEMORANDUM

SUBJECT: Establishment of Cleanup Levels for CERCLA Sites with Radioactive Contamination

FROM: Stephen D. Luftig, Director Steph D. Luftig
Office of Emergency and Remedial Response

Larry Weinstock, Acting Director
Office of Radiation and Indoor Air

TO: Addressees

PURPOSE

This memorandum presents clarifying guidance for establishing protective cleanup levels[1] for radioactive contamination at Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) sites. The policies stated in this memorandum are inclusive of all radioactive contaminants of concern at a site including radon.[2] The directive is limited to providing guidance regarding the protection of human health and does not address levels necessary to protect ecological receptors.

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[1] This directive provides guidance on cleanup levels expressed as a risk, exposure, or dose level and not as a soil concentration level. The concentration level for various media, such as soil, that corresponds to a given risk level should be determined on a site-specific basis, based on factors such as the assumed land use and the physical characteristics (e.g., important surface features, soils, geology, hydro geology, meteorology, and ecology) at the site. This guidance does not alter the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) expectations regarding treatment of principal threat waste and the use of containment and institutional controls for low level threat waste.

[2] Since radon is not covered in some Federal radiation regulations it is important to note that the cleanup guidance clarifications in this memorandum include radon. Attachment A is a listing of standards for radionuclides (including radon) that may be applicable or relevant and appropriate requirements (ARARs) for Superfund sites.

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This document provides guidance to EPA staff. It also provides guidance to the public and to the regulated community on how EPA intends that the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) be implemented. The guidance is designed to describe EPA's national policy on these issues. The document does not, however, substitute for EPA's statutes or regulations, nor is it a regulation itself. Thus, it cannot impose legally-binding requirements on EPA, States, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA may change this guidance in the future, as appropriate.

BACKGROUND

All remedial actions at CERCLA sites must be protective of human health and the environment and comply with Applicable or Relevant and Appropriate Requirements (ARARs) unless a waiver is justified. Cleanup levels for response actions under CERCLA are developed based on site-specific risk assessments, ARARs, and/or to-be-considered material[3] (TBCs).

A listing is attached of radiation standards that are likely to be used as ARARs to establish cleanup levels or to conduct remedial actions. Cleanup standards have been under development by EPA under the Atomic Energy Act (AEA) and will be ARARs under certain circumstances if issued.

ARARs are often the determining factor in establishing cleanup levels at CERCLA sites. However, where ARARs are not available or are not sufficiently protective, EPA generally sets site-specific remediation levels for: 1) carcinogens at a level that represents an excess upper bound lifetime cancer risk to an individual of between 10^{-4} to 10^{-6}; and for 2) non-carcinogens such that the cumulative risks from exposure will not result in adverse effects to human populations (including sensitive sub-populations) that may be exposed during a lifetime or part of a lifetime, incorporating an adequate margin of safety. (See 40 CFR 300.430(e)(2)(i)(A)(2).) Since all radionuclides are carcinogens, this guidance addresses carcinogenic risk. If non-carcinogenic risks are posed by specific radionuclides, those risks should be taken into account in establishing cleanup levels or suitable remedial actions. The site-specific level of cleanup is determined using the nine criteria specified in Section 300.430(e)(9)(iii) of the NCP.

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[3] To-be-considered material (TBCs) are non-promulgated advisories or guidance issued by Federal or State governments that are not legally binding and do not have the status of potential ARARs. However, TBCs will be considered along with ARARs as part of the site risk assessment and may be used in determining the necessary level of cleanup for protection of health and the environment.

It is important to note that a new potential ARAR was recently promulgated : NRC's Radiological Criteria for License Termination (See 62 FR 39058, July 21, 1997). We expect that NRC's implementation of the rule for License Termination (decommissioning rule) will result in cleanups within the Superfund risk range at the vast majority of NRC sites. However, EPA has determined that the dose limits established in this rule as promulgated generally will not provide a protective basis for establishing preliminary remediation goals (PRGs) under CERCLA.[4] The NRC rule set an allowable cleanup level of 25 millirem per year (equivalent to approximately 5×10^{-4} increased lifetime risk) as the primary standard with exemptions allowing dose limits of up to 100 millirem per year (equivalent to approximately 2×10^{-3} increased lifetime risk). Accordingly, while the NRC rule standard must be met (or waived) at sites where it is applicable or relevant and appropriate, cleanups at these sites will typically have to be more stringent than required by the NRC dose limits in order to meet the CERCLA and NCP requirement to be protective.[5] Guidance that provides for cleanups outside the risk range (in general, cleanup levels exceeding 15 millirem per year which equates to approximately 3×10^{-4} increased lifetime risk) is similarly not protective under CERCLA and generally should not be used to establish cleanup levels.

The lack of a protective comprehensive set of regulatory cleanup levels for radiation, together with the possibility of confusion as to the status of other Federal Agency regulations and guidance as ARARs or TBCs, may cause uncertainty as to the cleanup levels deemed protective under CERCLA. Until a protective comprehensive radiation cleanup rule is available, this guidance clarifies the Agency's position on CERCLA cleanup levels for radiation.

OBJECTIVE

This guidance clarifies that cleanups of radionuclides are governed by the risk range for all carcinogens established in the NCP when ARARs are not available or are not sufficiently protective. This is to say, such cleanups should generally achieve risk levels in the 10^{-4} to 10^{-6} range. EPA has a consistent methodology for assessing cancer risks and determining PRGs at CERCLA sites no matter the type of contamination.[6]

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[4] See letter, Carol Browner, Administrator, EPA, to Shirley Jackson, Chairman, Nuclear Regulatory Commission, February 7, 1997.

[5] See attachment B for a detailed discussion of the basis for the conclusion that the dose limits in the NRC rule are not adequately protective.

[6] U.S. EPA, "Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A) Interim Final," EPA//540/1-89/002, December 1989. U.S. EPA, "Risk Assessment Guidance for Superfund: Volume I - Human Health Evaluation Manual (Part B, Development of Risk-based Preliminary Remediation Goals", EPA/540/R-92/003, December 1991.

Cancer risks for radionuclides should generally be estimated using the slope factor approach identified in this methodology. Slope factors were developed by EPA for more than 300 radionuclides in the *Health Effects Assessment Summary Tables* (HEAST).[7] Cleanup levels for radioactive contamination at CERCLA sites should be established as they would for any chemical that poses an unacceptable risk and the risks should be characterized in standard Agency risk language consistent with CERCLA guidance.

Historically, radiation exposure and cleanup levels have often been expressed in units unique to radiation (e.g., millirem or picoCuries). It is important for the purposes of clarity that a consistent set of existing risk-based units (i.e., $\# \times 10^{-\#}$) for cleanups generally be used. This will also allow for ease and clarity of presenting cumulative risk for all contaminants, an objective consistent with EPA's policy on risk characterization.[8]

Cancer risk from both radiological and non-radiological contaminants should be summed to provide risk estimates for persons exposed to both types of carcinogenic contaminants. Although these risks initially may be tabulated separately, risk estimates contained in proposed and final site decision documents (e.g., proposed plans, Record of Decisions (RODs), Action Memos, ROD Amendments, Explanation of Significant Differences (ESDs)) should be summed to provide an estimate of the combined risk to individuals presented by **all** carcinogenic contaminants.

IMPLEMENTATION

The approach in this guidance should be considered at current and future CERCLA sites for which response decisions have not been made.

Overall Exposure Limit:

Cleanup should generally achieve a level of risk within the 10^{-4} to 10^{-6} carcinogenic risk range based on the reasonable maximum exposure for an individual. The cleanup levels to be specified include exposures from all potential pathways, and through all media (e.g., soil, ground water, surface water, sediment, air, structures,

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[7] U.S. EPA, "Health Effects Assessment Summary Tables FY-1995 Annual," EPA/540/R-95/036, May 1995; and U.S. EPA, "Health Effects Assessment Summary Tables FY-1995 Supplement," EPA/540/R-95/142, Nov. 1995.

[8] For further discussion of EPA's policy, see memorandum from EPA Administrator Carol Browner entitled: "EPA Risk Characterization Program," March 21, 1995.

biota). As noted in previous policy, "the upper boundary of the risk range is not a discrete line at 1 x 10^{-4}, although EPA generally uses 1 x 10^{-4} in making risk management decisions. A specific risk estimate around 10^{-4} may be considered acceptable if justified based on site-specific conditions".[9]

If a dose assessment is conducted at the site[10] then 15 millirem per year (mrem/yr) effective dose equivalent (EDE) should generally be the maximum dose limit for humans. This level equates to approximately 3 x 10^{-4} increased lifetime risk and is consistent with levels generally considered protective in other governmental actions, particularly regulations and guidance developed by EPA in other radiation control programs.[11]

Background Contamination:

Background radiation levels will generally be determined as background levels are determined for other contaminants, on a site-specific basis. In some cases, the same constituents are found in on-site samples as well as in background samples. The levels of each constituent are compared to background to determine its impact, if any, on site-related activities. Background is generally measured only for those radionuclides that are contaminants of concern and is compared on a contaminant specific basis to cleanup level. For example, background levels for radium-226 and radon-222 would generally not be evaluated at a site if those radionuclides were not site-related contaminants.

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[9] Memo from Assistant Administrator Don Clay to the Regions; "Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions'" OSWER Directive 9355.0-30; April 22, 1991.

[10] Cleanup levels not based on ARARs should be expressed as risk, although levels may at the same time be expressed in millirem.

[11] Further discussion and analysis of the basis for this recommendation is contained in the materials in the docket for the AEA standard under development by EPA, which is available at the following address: U.S. EPA, 401 M Street, S.W., Room M1500, Air Docket No. A-93-27, Washington D.C. 20460. The material is also available via computer modem through the Cleanup Regulation Electronic Bulletin Board (800-700-7837 outside the Washington area and 703-790-0825 locally), or on-line through the Radiation Site Cleanup Regulation HomePage (http://www.epa.gov/radiation/cleanup/). Cleanup levels based on some older ARARs that use a 25/75/25 mrem/yr standard (i.e., 25 mrem/yr to the whole body, 75 mrem/yr to the thyroid, and 25 mrem/yr to any other critical organ) may appear to permit greater risk than those based on 15 mrem EDE but on average correspond to approximately 10 mrem/yr EDE, using current risk methodologies. Similarly, ARARs based on a 25/75 mrem/yr standard used as an ARAR (i.e., 25 mrem/yr to whole body and 75 mrem/yr to any critical organ) would on average correspond to those cleanups based on 15 mrem/yr EDE. (See also "Comparison of Critical Organ and EDE Radiation Dose Rate Limits for Situations Involving Contaminated Land;" Office of Radiation and Indoor Air; April 1997.) See also Attachment B.

In certain situations background levels of a site-related contaminant may equal or exceed PRGs established for a site. In these situations background and site-related levels of radiation will be addressed as they are for other contaminants at CERCLA sites.[12]

Land Use and Institutional Controls:

The concentration levels for various media that correspond to the acceptable risk level established for cleanup will depend in part on land use at the site. Land uses that will be available following completion of a response action are determined as part of the remedy selection process considering the reasonably anticipated land use or uses along with other factors.[13] Institutional controls (ICs) generally should be included as a component of cleanup alternatives that would require restricted land use in order to ensure the response will be protective over time. The institutional controls should prevent an unanticipated change in land use that could result in unacceptable exposures to residual contamination, or at a minimum, alert future users to the residual risks and monitor for any changes in use.

Future Changes in Land Use:

Where waste is left on-site at levels that would require limited use and restricted exposure to ensure protectiveness, EPA will conduct reviews at least once every five years to monitor the site for any changes including changes in land use. Such reviews should analyze the implementation and effectiveness of any ICs with the same degree of care as other parts of the remedy. Should land use change in spite of land use

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[12] For further information regarding EPA's approach for addressing background at CERCLA sites see: National Oil and Hazardous Substances Pollution Contingency Plan, 55 FR 8717-8718, March 8, 1990; U.S. EPA "Guidance on Remedial Actions for Contaminated Ground Water at Superfund Sites," EPA/540/G-88/003, December 1988, pg. 4-9; U.S. EPA "Soil Screening Guidance: User's Guide," EPA/540/R-96/018, April 1996, pg. 8; and U.S. EPA "Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A)," EPA/540/1-89/02, December 1989, pp. 4-5 to 4-10 and 5-18 to 5-19. It should be noted that certain ARARs specifically address how to factor background into cleanup levels. For example, some radiation ARAR levels are established as increments above background concentrations. (See attached chart for a listing of radiation standards that are likely to be used as ARARs.) In these circumstances, rather then follow the general guidance cited above, background should be addressed in the manner prescribed by the ARAR ARARs, such as 40 CFR 192, are available to establish cleanup levels for those naturally occurring radionuclides that pose the most risk (such as radium-226 or Thorium in soil, and indoor radon) when those radionuclides are site related contaminants.

[13] In developing Land use assumptions, decision makers should consult the guidance provided in the memorandum from Elliott Laws A.A., OSWER entitled: "Land Use in the CERCLA Remedy Selection Process" (OSWER Directive No. 9355.7-04), May 25, 1995.

restrictions, it will be necessary to evaluate the implications of that change for the selected remedy, and whether the remedy remains protective (e.g., a greater volume of soil may need to be removed or managed to achieve an acceptable level of risk for a less restrictive land use).

Ground Water Levels:

Consistent with CERCLA and the NCP, response actions for contaminated ground water at radiation sites must attain (or waive as appropriate) the Maximum Contaminant Levels (MCLs) or non-zero Maximum Contaminant Level Goals (MCLGs) established under the Safe Drinking Water Act, where the MCLs or MCLGs are relevant and appropriate for the site. This will typically be the case where ground waters are a current or potential source of drinking water.[14] The ARARs should generally be attained throughout the plume (i.e., in the aquifer).

Modeling Assessment of Future Exposures:

Risk levels, ground water cleanup, and dose limits should be predicted using appropriate models to examine the estimated future threats posed by residual radioactive material following the completion of the response action.[15] The modeling assessment should: (1) assume that the current physical characteristics (e.g., important surface features, soils, geology, hydrogeology, meteorology, and ecology) will continue to exist at the site; (2) take into account for each particular radionuclide that is a site-related contaminant, the following factors:

- radioactive decay and the ingrowth of radioactive decay products when assessing risk levels;
- the year of peak concentration in the ground water when assessing protection (e.g., remediating previous contamination and preventing future contamination) of ground water, and;
- the year of peak dose when assessing dose limits; and,

(3) model the expected movement of radioactive material at the site both within media (i.e., soil, ground water, surface water, sediment, structures, air, biota) and to other media.

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[14] In making decisions on ground water protection, decision makers should consult the guidance provided in "Presumptive Response Strategy and Ex-Situ Treatment Technologies for Contaminated Ground Water at CERCLA Sites" (OSWER Directive No. 9355.7-04) October 1996.

[15] For further information regarding the basis for this recommendation, see U.S. EPA, "Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A) Interim Final," EPA//540/1-89/002, December 1989, pp. 10-22 and 10-24.

FURTHER INFORMATION

The subject matter specialists for this directive are Jeffrey Phillips of OERR and John Karhnak of ORIA. General questions about this directive, should be directed to 1-800-424-9346.

Attachments

Addressees
- National Superfund Policy Managers
- Superfund Branch Chiefs (Regions I-X)
- Superfund Branch Chiefs, Office of Regional Counsel (Regions I-X)
- Radiation Program Managers (Regions I, IV, V, VI, VII, X)
- Radiation Branch Chief (Region II)
- Residential Domain Section Chief (Region III)
- Radiation and Indoor Air Program Branch Chief (Region VIII)
- Radiation and Indoor Office Director (Region IX)
- Federal Facilities Leadership Council
- OERR Center Directors

CC:
- Jim Woolford, FFRRO
- Elizabeth Cotsworth, OSW
- Craig Hooks, FFEO
- Barry Breen, OSRE
- Joanna Gibson, HOSC/OERR
- Earl Salo, OGC

Attachment A:

Likely Federal Radiation Applicable or Relevant and Appropriate Requirements (ARARs)

The attached draft table of Federal standards is a listing of Federal radiation regulations that may be "Applicable or Relevant and Appropriate Requirements" (ARARs) for Superfund response actions. This list is not a comprehensive list of Federal radiation standards. It must also be cautioned that the selection of ARARs is site-specific and those site-specific determinations may differ from the attached analysis for some of the following ARARs.

Likely Federal Radiation (AEA, UMTRCA, CAA, CWA, SDWA) ARARs

Standard	Citation	When is standard Applicable (Conduct/Operation or Level of Cleanup[1])	When is standard potentially a Relevant and Appropriate Requirement
Maximum contaminant levels (MCLs). Drinking water regulations designed to protect human health from the potential adverse effects of drinking water contaminants.	40 CFR 141	*Rarely:* At the tap where water will be provided directly to 25 or more people or will be supplied to 15 or more service connections.	Where ground or surface water is considered a potential or current source of drinking water
Concentration limits for liquid effluents from facilities that extract and process uranium, radium, and vanadium ores.	40 CFR 440 Subpart C	*Very Unlikely:* Applies to surface water discharges from certain kinds of mines and mills	Discharges to surface waters of some kinds of radioactive waste.

Likely Federal Radiation (AEA, UMTRCA, CAA, CWA, SDWA) ARARs			
Standard	**Citation**	**When is standard Applicable (Conduct/Operation or Level of Cleanup[1])**	**When is standard potentially a Relevant and Appropriate Requirement**
Federal Water Quality Criteria (FWQC) and State Water Quality Standards (WQS). Criteria/standards for protection of aquatic life and/or human health depending upon the designated water use.	Water Quality Criteria; Report of the National Technical Advisory Committee to the Secretary of the Interior; April 1, 1968.	Discharge from a CERCLA site to surface water. (C/O)	Restoration of contaminated surface water. (LC)
Concentration limits for cleanup of radium-226, radium-228, and thorium in soil at inactive uranium processing sites designated for remedial action.[2]	40 CFR 192.12(a), 192.32(b)(2), and 192.41	*Never*: Standards are applicable only to UMTRCA sites that are exempt from CERCLA	Sites with soil contaminated with radium-226, radium-228, and/or thorium

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[2] For further information, see OSWER directive entitled “Use of Soil Cleanup Criteria in Subpart B of 40 CFR Part 192 as Remediation Goals for CERCLA sites.”

Likely Federal Radiation (AEA, UMTRCA, CAA, CWA, SDWA) ARARs

Standard	**Citation**	**When is standard Applicable (Conduct/Operation or Level of Cleanup[1])**	**When is standard potentially a Relevant and Appropriate Requirement**
Combined exposure limits for cleanup of radon decay products in buildings at inactive uranium processing sites designated for remedial action	40 CFR 192.12(b)(1) and 192.41(b)	*Never*: Standards are applicable only to UMTRCA sites that are exempt from CERCLA	Sites with radioactive contamination that is currently, or may potentially, result in radon that is caused by site related contamination migrating from the soil into buildings
Concentration limits for cleanup of gamma radiation in buildings at inactive uranium processing sites designated for remedial action	40 CFR 192.12(b)(2)	*Never*: Standards are applicable only to UMTRCA sites that are exempt from CERCLA	Sites with radioactive contamination that is currently, or may potentially, emit gamma radiation
Design requirements for remedial actions that involve disposal for controlling combined releases of radon-220 and radon-222 to the atmosphere at inactive uranium processing sites designated for remedial action	40 CFR 192.02	*Never*: Standards are applicable only to UMTRCA sites that are exempt from CERCLA	Sites with radon-220 or radon-222 as contaminants which will be disposed of on-site.

Likely Federal Radiation (AEA, UMTRCA, CAA, CWA, SDWA) ARARs			
Standard	**Citation**	**When is standard Applicable (Conduct/Operation or Level of Cleanup[1])**	**When is standard potentially a Relevant and Appropriate Requirement**
Performance objectives for the land disposal of low level radioactive waste (LLW).	10 CFR 61.41	*Unlikely:* Existing licensed LLW disposal sites at the time of license renewal. (LC) *Unlikely that this would occur*.	Previously closed sites containing LLW if the waste will be permanently left on site.
National Emission Standards for Hazardous Air Pollutants (NESHAPs) under the Clean Air Act, that apply to radionuclides.	40 CFR 61 Subparts H and I	Airborne emissions during the cleanup of Federal Facilities and licensed NRC facilities. (CO)	Cleanup of other sites with radioactive contamination.
Radiological criteria for license termination.	10 CFR 20 Subpart E	Existing licensed sites at the time of license termination. (LC)	Previously closed sites.

1.Conduct/operation (C/O) refers to those standards which are typically ARARs for the conduct or operation of the remedial action. Level of Cleanup (L/C) refers to those standards which are typically ARARs for determining the final level of cleanup.

August 20, 1997

Attachment B:

Analysis of what Radiation Dose Limit is Protective of Human Health at CERCLA Sites (Including Review of Dose Limits in NRC Decommissioning Rule)

Introduction

The Nuclear Regulatory Commission ("NRC") has finalized a rule titled "Radiological Criteria for License Termination" (see 62 FR 39058, July 21, 1997). EPA has determined that the dose limits established in this rule generally will not provide a protective basis for establishing preliminary remediation goals ("PRGs")under the Comprehensive Environmental Response, Compensation and Liability Act ("CERCLA").[1] The NRC rule sets an allowable cleanup level of 25 millirem per year effective dose equivalent (EDE) (equivalent to approximately 5 x 10^{-4} lifetime cancer risk) as the primary standard with exemptions allowing cleanup levels of up to 100 millirem per year (mrem/yr) EDE (equivalent to approximately 2 x 10^{-3} lifetime risk).[2] While the NRC standards must be met (or waived) at sites where it is applicable or relevant and appropriate, cleanups at these sites will typically have to be more protective than required by the NRC rule dose limits in order to meet the requirement to be protective established in CERCLA and the 1990 revisions to the National Oil and Hazardous Substances Pollution Contingency Plan ("NCP").[3]

Protectiveness for carcinogens under CERCLA is generally determined with reference to a cancer risk range of 10^{-4} to 10^{-6} deemed acceptable by EPA. Consistent with this risk range, EPA has considered cancer risk from radiation in a number of different contexts, and has consistently concluded that levels of 15 mrem/yr EDE (which

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[1] See letter, Carol Browner, Administrator, EPA, to Shirley Jackson, Chairman, Nuclear Regulatory Commission, February 7, 1997.

[2] Throughout this analysis risk estimates for dose levels were derived using a risk assessment methodology consistent with CERCLA guidance for assessing risks.

[3] Similarly, guidance that provides for radiation cleanups outside the risk range is generally not protective and should not be used to establish preliminary remediation goals .

equate to approximately a 3 x 10^{-4} cancer risk) or less are protective and achievable.[4] EPA has explicitly rejected levels above 15 mrem/yr EDE as being not sufficiently protective.

The dose levels established in the NRC Decommissioning rule, however, are not based on this risk range or on an analysis of other achievable protective cleanup levels used for radiation and other carcinogenic standards. Rather, they are based on a different framework for risk management recommended by the International Commission on Radiation Protection (ICRP) and the National Council on Radiation Protection and Measurements (NCRP). NRC's application of this framework starts with the premise that exposure to radiation from all man-made sources, excluding medical and natural background exposures, of up to 100 mrem/yr., which equates to a cancer risk of 2 x 10^{-3}, is acceptable. Based on that premise, it concludes that exposure from decommissioned facilities of 25 mrem/yr, which equates to a cancer risk of approximately 5 x 10^{-4}, is acceptable, and allows the granting of exceptions in certain instances permitting exposure up to the full dosage of 100 mrem/yr from these facilities. EPA has carefully reviewed the basis for the NRC dose levels and does not believe they are generally protective within the framework of CERCLA and the NCP. Simply put, NRC has provided, and EPA is aware of, no technical, policy, or legal rationale for treating radiation risks differently from other risks addressed under CERCLA and for allowing radiation risks so far beyond the bounds of the CERCLA risk range.

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[4] It should be noted that 15 mrem/yr is a dose level, not a media remediation level. Accordingly, this level could be achieved at CERCLA sites through appropriate site-specific combinations of active remediation and land-use restrictions to ensure no unacceptable exposures.

1. Rationale for 15 mrem/yr as Minimally Acceptable Dose Limit

To determine an acceptable residual level of risk from residual radioactive materials following a response action that would be protective of human health, EPA examined the precedents established by EPA for acceptable exposures to radiation in regulations and site-specific cleanup decisions in light of the CERCLA risk range for carcinogens. EPA's conclusion is that to be considered protective under CERCLA, remedial actions should generally attain dose levels of no more than 15 mrem/yr EDE for those sites at which a dose assessment is conducted. This dose level corresponds to an excess lifetime cancer risk of approximately 3×10^{-4}.

1.1 The CERCLA risk range

Under CERCLA, all remedies are required to attain cleanup levels that "at a minimum. . . assure protection of human health and the environment." CERCLA §121(d)(1). The NCP provides that, for carcinogens, preliminary remediation goals should generally be set at levels that represent an upper-bound lifetime cancer risk to an individual of between 10^{-4} and 10^{-6}. 40 CFR § 300.430(e)(2)(I)(A)(1). This regulatory level was set based on EPA's conclusion that the CERCLA protectiveness mandate is complied with "when the amount of exposure is reduced so that the risk posed by contaminants is very small, i.e., at an acceptable level. EPA's risk range of 10^{-4} to 10^{-6} represents EPA's opinion on what are generally acceptable levels." 55 Fed. Reg. at 8716 (March 8, 1990). EPA's adoption of this risk range was sustained in judicial review of the NCP. State of Ohio v. EPA, 997 F.2d 1520, 1533 (D.C. Cir. 1993).

Under appropriate circumstances, risks of greater than 1×10^{-4} may be acceptable. CERCLA guidance states that "the upper boundary of the risk range is not a discrete line at 1×10^{-4}, although EPA generally uses 1×10^{-4} in making risk management decisions. A specific risk estimate around 10^{-4} may be considered acceptable if justified based on site-specific conditions."[5] Other EPA regulatory programs have developed a similar approach to determining acceptable levels of cancer risk. For example, in a Clean Air Act rulemaking establishing NESHAPs for NRC licensees, Department of Energy facilities, and many other kinds of sites, EPA concluded that a risk level of "3×10^{-4} is essentially equivalent to the presumptively safe level of 1×10^{-4}." 54 Fed. Reg. at 51677 and 51682 (December 15, 1989). EPA explicitly rejected a risk level of 5.7×10^{-4} as not being equivalent to the presumptively safe level of 1×10^{-4} (in the case of elemental phosphorus plants) in this rulemaking. 54 Fed. Reg. at 51670.

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[5] "Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions" from EPA Assistant Administrator Don R. Clay, April 22, 1991.

1.2 Prior rulemaking decisions

EPA has examined the protectiveness of various radiation levels on a number of occasions. In each case, EPA's determination of what constitutes an adequate level of protection was reached in a manner consistent with EPA's regulation of other carcinogens. The conclusions from these efforts support the determination that 15 mrem/yr EDE should generally be the maximum dose level allowed at CERCLA sites. For example, EPA's Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes ("High-Level Waste Rule," 40 CFR Part 191) sets a dose limit of 15 mrem/yr EDE for all pathways.

In addition, EPA set an effective dose equivalent of 10 mrem/yr EDE (excluding radon-222) for air emissions of radionuclides from federal facilities, NRC licensees, and uranium fuel cycle facilities under the National Emissions Standards for Hazardous Air Pollutants (NESHAP, 40 CFR Part 61). This lower limit included all air pathways, but excluded releases to surface and ground waters.

Not all EPA rules apply the current dose methodology of effective dose equivalent (EDE). A dose limit of 15 mrem/yr EDE is also consistent with the dose levels allowed under older multi-media standards that were based on the critical organ approach to dose limitation. Critical organ standards developed by EPA and NRC consist of a combination of whole body and critical organ dose limits. Three of these critical organ standards (EPA's uranium fuel cycle rule, 40 CFR 190.10(a), developed for NRC licensees; NRC's low level waste rule, 10 CFR 61.41; and EPA's management and storage of high level waste by NRC and agreement states rule, 40 CFR 191.03(a)), referred to here as '25/75/25 mrem/yr' dose limits, are expressed as 25 mrem/yr to the whole body, 75 mrem/yr to the thyroid, and 25 mrem/yr to any critical organ other than the thyroid. One standard (EPA's management and storage of high level waste by DOE rule, 40 CFR 191.03(b)), referred to here as a "25/75 mrem/yr" dose limit, is expressed as 25 mrem/yr to the whole body and 75 mrem/yr to any critical organ (including the thyroid). To compare the dose level allowed under standards expressed in terms of EDE with the dose levels allowed under the critical organ approach to dose limitation, EPA has analyzed the estimated effective dose equivalent levels that would result if sites were cleaned up to the numerical dose limits used in these standards.[6] The analysis indicates that if sites were cleaned up under a 25/75/25 mrem/yr dose limit, the residual contamination would correspond to approximately 10 mrem/yr EDE. For sites cleaned up under a 25/75 mrem/yr dose limit, the residual contamination would correspond to approximately 15

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[6] "Comparison of Critical Organ and EDE Radiation Dose Rate Limits for Situations Involving Contaminated Land" Office of Radiation and Indoor Air; April 1997.

mrem/yr EDE. These findings are similar to those mentioned in the preamble to the high-level waste rule (40 CFR Part 191; December 20, 1993; 58 FR 66402). In that rulemaking, EPA noted that the dose limit of 25 mrem/yr to the whole body or 75 mrem/yr to any critical organ, which was used in a previous high-level waste rule (September 19, 1985; 50 FR 38066) corresponds to the same level of risk as that associated with a 15 mrem/yr EDE. A cleanup level of 15 mrem/yr EDE is thus generally consistent with all of these other standards, although there are minor differences.

Finally, standards for the cleanup of certain radioactively contaminated sites have been issued under the Uranium Mill Tailings Radiation Control Act (UMTRCA), P.L. 95-604. Those standards are codified at 40 CFR Part 192. Among other provisions, the UMTRCA standards limit the concentration of radium-226, radium-228, thorium-230 and thorium-232, within 15 centimeters (cm) of the surface to no more than 5 picoCuries per gram (pCi/g) over background. They also limit the concentration of these radionuclides below the surface to no more than 15 pCi/g over background. Since these standards were developed for the specific conditions found at the mill sites to which they apply (for example, all mill sites are required by law to remain in federal control), correlating these concentrations to dose requires a site-specific determination considering both the distribution and nature of contaminants at the site and the selected land use. Therefore, those standards are less relevant for determining if 15 mrem/yr EDE is consistent. However, analysis indicates that the cleanup of UMTRCA sites is consistent with the minimally acceptable dose limit of 15 mrem/yr EDE under a residential exposure scenario for radium-226, radium-228, and thorium-232, and is much more stringent for thorium-230.[7] For land uses other than residential (e.g., commercial/industrial, recreational) the UMTRCA cleanup standards are more stringent for all four radionuclides.[8]

1.3 Site-Specific Decisions

EPA has examined the cleanup decisions made under Superfund to address sites contaminated with radioactive wastes. Many of these cleanup actions used the UMTRCA

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[7] *Reassessment of Radium and Thorium Soil Concentrations and Annual Dose Rates*. Office of Radiation and Indoor Air, July 22, 1996.

[8] A level of 15 mrem/yr is also supported by EPA's draft Federal Radiation Protection Guidance for Exposure of the General Public (59 FR 66414, December 23, 1994). The draft guidance recommends that the maximum dose to individuals from specific sources or categories of sources be established as small fractions of a 100 mrem/yr upper bound on doses from all current and potential future sources combined, and cites the regulations that are discussed in Section 1.2 of this paper as appropriate implementation of this recommendation. All of the regulatory examples cited support the selection of cleanup levels at 15 mrem/yr or less. However, because this guidance is in draft form and is subject to continued review within EPA prior to finalization, it should not be used as a basis for establishing acceptable cleanup levels.

cleanup standard (40 CFR Part 192) as an ARAR. Some of the sites used State regulations as ARARs. For a number of major DOE cleanup actions such as those at the Hanford reservation and Rocky Flats, a 15 mrem/yr EDE cleanup level has been decided upon or proposed. In other cases of CERCLA radiation cleanup actions that are not based on ARARs, cleanup levels between 1×10^{-5} and 1×10^{-6} have been selected (Bomark, NJ; Fernald, OH; Charleston Naval Shipyard, SC; and Mare Island Naval Shipyard, CA). Overall EPA finds that a 15 mrem/yr EDE level (with a risk of 3×10^{-4}) is at the upper end of remediation levels that have generally been selected at radioactively contaminated CERCLA sites.

2.0 Dose Limits in NRC's Rule are not Protective

EPA reviewed the dose limits that are contained in NRC's Radiological Criteria for License Termination (see 62 FR 39058, July 21, 1997). The NRC rule allows a cleanup level of 25 mrem/yr EDE (equivalent to approximately 5×10^{-4} lifetime risk) with exemptions allowing cleanup levels of up to 100 mrem/yr EDE (equivalent to approximately 2×10^{-3} lifetime risk). These limits are beyond the upper bound of the risk range generally considered protective under CERCLA. In addition, they present risks that are higher than levels EPA has found to be protective for carcinogens in general and for radiation, in particular, in other contexts. EPA has no technical or policy basis to conclude that these levels are protective under CERCLA.

The risk levels corresponding to the 25 to 100 mrem/yr EDE range allowed by the NRC rule (5×10^{-4} to 2×10^{-3}) are unacceptably high relative to 1×10^{-4}, which is the risk level generally used as the upper boundary of the CERCLA risk range for making risk management decisions at CERCLA sites. This determination is consistent with EPA's explicit rejection of a risk level of 5.7×10^{-4} for elemental phosphorus plants in the preamble for a NESHAP rulemaking (54 FR 51670). In the same preamble, EPA stated that a risk level of "3×10^{-4} is essentially equivalent to the presumptively safe level of 1×10^{-4}" (54 FR 51677). It was during this same NESHAP rulemaking that NCRP first recommended to EPA its regulatory scheme (a dose limit of 25 mrem/yr EDE for a single source that if met would not require analyzing other sources, otherwise a dose limit of 100 mrem/yr EDE from all sources combined) that NRC cites as a source for the regulatory approach taken in its decommissioning rule.[9] EPA rejected NCRP's recommended regulatory scheme, and promulgated dose limits of no more than 10 mrem/yr EDE in its NESHAP rulemaking for radionuclides, while concluding that "individual dose levels greater than 10 mrem/y ede are inconsistent with the requirements of section 112" of the Clean Air Act. 54 Fed. Reg. at 51686.

The documentation and analysis supporting the NRC rule dose levels provide no basis for such a significant departure from the CERCLA risk range. Indeed, as discussed above, EPA's past analyses and experience have demonstrated that exposures of 15 mrem/yr EDE or less are attainable and that such a departure is unwarranted. A dose limit of 25 mrem/yr EDE represents almost a doubling of the allowable risk from previous radiation rulemakings; the risk represented by a dose limit of 100 mrem/yr EDE is seven times as high as previously allowed. As note in Section 1.2, a dose limit of 25 mrem/yr effective dose equivalent is inconsistent with the dose levels allowed under older

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[9] "Control of Air Emissions of Radionuclides" NCRP Position Statement No. 6. The report cited by NRC, NCRP No. 116, merely references this previous NCRP position statement.

standards using a previous dose methodology (multi-media standards that were based on the critical organ approach to dose limitation). If these older dose standards were to be applied to the cleanup of contaminated sites, the average dose level would correspond to approximately 10 or 15 mrem/yr EDE on average.[10] Also, analysis indicates that the cleanup of UMTRCA sites using the 5 pCi/g and 15 pCi/g soil standards under 40 CFR 192 is consistent with an upper bound of 15 mrem/yr EDE under a rural residential exposure scenario for radium-226, radium-228, and thorium-232, and is much more stringent for thorium-230.[11] For land uses other than residential (e.g., commercial/industrial, recreational) the UMTRCA cleanup standards are more stringent for all four radionuclides.

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[10] "Comparison of Critical Organ and EDE Radiation Dose Rate Limits for Situations Involving Contaminated Land" Office of Radiation and Indoor Air; April 1997.

[11] *Reassessment of Radium and Thorium Soil Concentrations and Annual Dose Rates*. Office of Radiation and Indoor Air, July 22, 1996.

MEMORANDUM

TO: Lisa Biddle, EPA
Karen Milam, EPA

FROM: Sarah Yates, ERG

DATE: June 6, 2016

SUBJECT: **Radioactive Materials in the Unconventional Oil and Gas (UOG) Industry (DCN SGE01185)**

This memorandum describes UOG extraction wastewater concentrations for certain radioactive materials for the *Technical Development Document for Effluent Limitations Guidelines and Standards for Oil and Gas Extraction* (TDD) (DCN SGE01188). Radioactive materials, such as radium, radon, and uranium, have been detected in wastewater generated by the UOG extraction industry (DCN SGE00241, DCN SGE01188). Specifically, this memorandum provides background information about radioactive materials in UOG extraction wastewater, including general background about radioactivity and how it is measured, issues related to the analysis of radioactive materials in UOG extraction wastewater, ongoing studies, and potential concerns about radioactive materials in UOG extraction wastewater. The *Crosswalk Memorandum between Proposed and Final Technical Development Document for Effluent Limitations Guidelines and Standards for Oil and Gas Extraction: Tables and Figures* (DCN SGE01334) contains a crosswalk of all tables and figures in the TDD. Appendix F of the TDD contains the name of the relevant supporting memorandum for each TDD table and figure, where applicable. This memorandum is organized into the following sections:

- Section 1.0 Background: radioactivity and how it is measured
- Section 2.0 Measurement of radioactivity in UOG extraction industry wastewater
- Section 3.0 Studies of radioactive material in UOG extraction industry wastewater
- Section 4.0 radioactive materials in UOG extraction wastewater and associated concerns
- Section 5.0 describes ERG’s quality assurance procedures.
- Section 6.0 lists the references used for these analyses.

For definitions of common terms used throughout the TDD, the supporting memoranda, and memoranda attachments, please refer to the Glossary in the introduction of the TDD.

1.0 BACKGROUND: RADIOACTIVITY AND HOW IT IS MEASURED

Radioactivity and Ionizing Radiation. Radioactivity is the property of some unstable atoms that causes them to spontaneously decay and give off energy (radiation) as particles or rays. This phenomenon is known as radioactive decay. Because the radiation emitted during radioactive decay has enough energy to break chemical bonds, it is referred to as ionizing radiation. The three main kinds of ionizing radiation are (DCN SGE00936):[1]

- *Alpha particles*, which include two protons and two neutrons (essentially a helium nucleus);
- *Beta particles*, which are essentially high-speed electrons; and
- *Gamma rays and x-rays*, which are pure energy (photons).

The descriptions of these types of ionizing radiation provided below are taken from Keenan 1971 (DCN SGE00179) and EPA's radiation protection website (DCN SGE00936).

Alpha particles emitted from a given nuclide[2] have energies confined to a few discrete values, so that the energies of alpha particles can identify the nuclide from which they are emitted. Some nuclides emit alpha particles at more than one speed. For example ^{226}Ra (radium-226) emits alpha particles at either 1.517e9 or 1.488e9 centimeter/second (cm/sec). The emission of the slower particle is followed by the emission of a gamma ray, such that equal energy is emitted in each case. The loss of an alpha particle reduces the mass of the nucleus and also changes the atom to a different element (the number of protons determines the element). For example, when radium-226 (^{226}Ra) emits an alpha particle, it loses two protons and two neutrons. The atomic mass is reduced from 226 to 222 and the ^{226}Ra atom becomes an atom of ^{222}Rn (radon-222), a radioactive gas.

Beta particle emission occurs when the ratio of neutrons to protons in the nucleus is too high. In this case, an excess neutron transforms into a proton, which stays in the nucleus, and a beta particle (high speed electron) is ejected energetically. Unlike alpha particles, beta particles are emitted at all possible speeds (term of art: beta spectrum). When the ejection of the beta particle does not rid the nucleus of sufficient energy, the nucleus releases the remaining excess energy in the form of gamma radiation. Like alpha particle emission, emission of a beta particle also changes the atom to a different element. For example, ^{228}Ra (radium-228) is a beta emitter. During its radioactive decay, a neutron in the nucleus converts to a proton and the nucleus emits a beta particle. The number of protons increases from 88 to 89, changing the atom from radium to actinium (DCN SGE00936). Even though the atom is a different element, because neutrons and protons have the same mass, the atom retains the same atomic mass number: beta decay converts ^{228}Ra to ^{228}Ac (actinium-228).

Gamma radiation emission occurs when the nucleus of a radioactive atom has too much energy. It often follows the emission of a beta particle and can also follow the emission of an alpha particle (there are no pure gamma emitters). In either case, the energies of the gamma radiation from a given nuclide are limited to a few discrete values, that is, discrete wavelengths, and can be used to identify the nuclide.

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[1] Other kinds of ionizing radiation exist but are not germane to this discussion (e.g., neutrons).

[2] *Nuclide* is an atomic species characterized by the specific constitution of its nucleus, i.e., by its number of protons, its number of neutrons, and its energy state. An element is a substance in which all atoms have the same number of protons; atoms of the same element with different numbers of neutrons have differing atomic weights and are called isotopes (DCN SGE00179). ^{226}Ra and ^{228}Ra are isotopes of radium with atomic weights of 226 and 228, respectively.

Measuring Radioactivity. Radioactivity is measured using electronic detectors coupled to instrumentation used to count the number of atomic disintegrations per unit of time. Whether a radioactive material emits alpha particles, beta particles, or gamma rays, the quantity of radioactive material is expressed in terms of its radioactivity (or simply its activity), in units of measure of the curie (Ci) or becquerel (Bq) (DCN SGE00977).

A curie (Ci) is a non-SI unit for radioactivity, defined as 37 billion disintegrations per second[3]. Thus, a radioactive sample that has an activity of 74 billion disintegrations per second has an activity of 2 curies. The curie is a very large unit for quantities found in the environment. Scientists use the following fractions of a curie as well:

- Picocuries (pCi) are 1 trillionth of a curie (1 x 10^{-12} Ci). Picocuries are used in measuring the typically small amount of radioactivity in air and water.

- Other fractions such as millicuries (mCi), or 1/1000 Ci and nanocuries (nCi), or 1 billionth of a curie, are used as needed (DCN SGE00936).

A Becquerel (Bq) is the SI unit for radioactivity and is defined as the activity of a quantity of radioactive material in which one nucleus decays per second. Therefore, the Becquerel is the same as an inverse second (s^{-1}). The conversion between Becquerel and curie is $1\ \text{Ci} = 3.7 \times 10^{10}\ \text{Bq}$.

Measuring Radiation. The units for exposure in air are the roentgen (R) and coulomb/kilogram (C/kg). There are also similar units for measuring absorbed dose in tissue (rad and Gray) and dose equivalent for the absorbed dose and biological effects (rem and Sievert).

Instrumentation for Detecting Radioactivity. The energy of radioactive decay can be detected by a variety of instruments that quantify the amount of radioactivity present in a sample (the disintegrations per second). Some techniques can also measure the detected energy and identify the radioactive isotope that is emitting the radiation. The following descriptions of common radioactivity measurement techniques are taken from U.S. EPA, 2011 (DCN SGE00937).

Liquid Scintillation Counting – a radioactive sample is mixed with solvent and chemicals that emit light pulses when they are excited by radiation. This technique is typically used to measure the radioactivity of beta emitting radionuclides, such as ^3H (tritium). With analysis of the energy of the emitted radiation and the duration of pulses, liquid scintillation counters can identify the alpha and beta emitting isotopes present in a sample.

Gas Flow Proportional Counting – a radioactive sample causes a gas inside a detector tube to ionize and release electrons. The released electrons move to the anode and the signal is recorded. Gas proportional counters are sensitive detectors for alpha and beta particle emissions and are used for EPA Method 900.0 (gross alpha and gross beta radioactivity screening).

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[3] The curie was originally a comparison of the activity of a sample of radioactive material to the activity of one gram of radium, which at the time was measured as 37 billion disintegrations per second. When more accurate techniques measured a slightly different activity for radium, the reference to radium was dropped (DCN SGE00936).

Alpha Spectrometry – alpha particles emitted from a radioactive sample collide with atoms in a germanium or silicon crystal detector, releasing electrons that are amplified and detected as an electric pulse. Because nuclides emit alpha particles at discrete energies, alpha spectrometry can sometimes identify the radionuclide in a purified sample, in addition to counting its activity.

Gamma Spectrometry – crystal detectors interact with gamma rays from a radioactive sample by absorbing energy and re-emitting it as light. Crystals used for gamma ray detectors include thallium-doped sodium iodide and high-purity germanium (HPGe). HPGe crystals must be cooled to liquid nitrogen temperature[4] for use in gamma spectrometry. HPGe detectors can distinguish energy of gamma ray sources and identify the radionuclides in a sample. Activity of radionuclides that emit only alpha particles and beta particles with no accompanying gamma radiation will not be detected by gamma spectrometry.

Naturally Occurring Radioactive Materials. Certain radionuclides occur naturally in minerals and rocks in the earth's crust. As radioactive elements decay, the parent elements form new elements (progeny or daughter products). If the progeny are also radioactive, they will continue to decay in a chain that continues until a stable (non-radioactive) end product is reached. Uranium and thorium are naturally occurring radioactive elements found in trace amounts in most rocks and soils (DCN SGE00782, DCN SGE00783), including formations from which UOG resources are extracted. Uranium and thorium decay chains include radium, radon, and other radionuclides, and ultimately reach a stable non-radioactive lead isotope that does not decay further (DCN SGE00795). Uranium and thorium decay chains are depicted in Figure 1-1. Other naturally-occurring elements that are non-series radionuclides include ^{40}K (potassium-40) and ^{87}Ru (rubidium-87). ^{40}K is often present in mineral samples. Rubidium is also ubiquitous and used in dating mineral samples.

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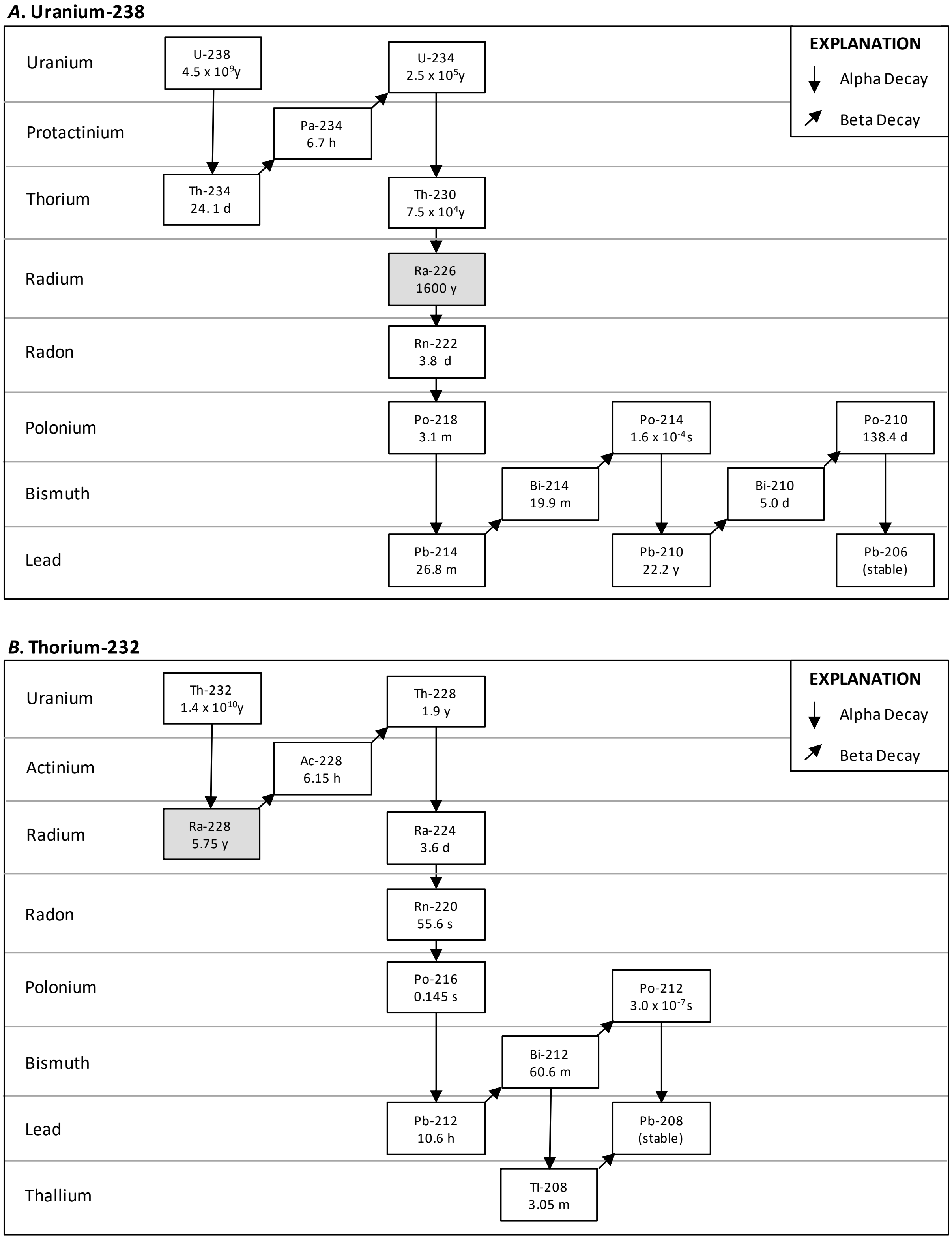
[4] Liquid nitrogen held at atmospheric pressure maintains a temperature of −321° F/ −196 ° C, its boiling point.



Source: DCN SGE00241.

Figure 1-1. Decay Chains for (A.) ^{238}U and (B.) ^{232}Th

Naturally occurring radioactive material (NORM) is a term often used to refer collectively to material that contains radionuclides at concentrations found in nature. Radionuclides found in NORM associated with UOG extraction include uranium, thorium, and their respective decay products (DCN SGE00795). The term technologically enhanced naturally occurring radioactive materials (TENORM) is now used to distinguish clearly between radionuclides as they occur naturally (NORM) and NORM radionuclides that human activity has concentrated or exposed to the environment (TENORM) (DCN SGE00973, DCN SGE01126). Examples of human activity that exposes and/or concentrates NORM are oil and gas extraction, mining, and water and wastewater processing.

The radioactive elements uranium and thorium commonly occur in the same sedimentary sandstones and shale formations as UOG resources (DCN SGE00241). For example, Rowan et al., 2011 (DCN SGE00241) studied radium content in a UOG formation (the Marcellus Shale, an organically-rich black shale). They explain that organic carbon, the source of oil and gas, is known to play a role in concentrating uranium. As shown in the decay chains depicted in Figure 1-1, ^{238}U (uranium-238) decays to ^{226}Ra, while ^{232}Th decays to ^{228}Ra. Water found in the pores of UOG formation rocks (i.e., formation water) is typically highly saline and found in oxygen-poor, reducing environments. Uranium and thorium are poorly soluble under these conditions, but radium solubility is enhanced (DCN SGE00241). For this reason, formation water is relatively enriched in radium isotopes compared to their parent nuclides, ^{238}U and ^{232}Th (DCN SGE00975).

2.0 MEASUREMENT OF RADIOACTIVITY IN UOG EXTRACTION WASTEWATER

Chapter C.3 of the TDD (DCN SGE01188) presents the concentrations of ^{226}Ra, ^{228}Ra, and the parameters gross alpha and gross beta in UOG extraction wastewater. This section discusses the methods used for measuring radioactivity in UOG extraction wastewater reported in the TDD.

2.1 EPA Approved Test Procedures for Radioactive Materials in Wastewater

EPA identifies approved test procedures (methods) for the analysis of pollutants in wastewater in 40 CFR Part 136. EPA requires the use of these test procedures whenever the waste constituent is required to be measured for NPDES permit applications and NPDES permit compliance reports. As shown in Table 2-1, for radioactive materials, 40 CFR Part 136 includes test procedures for:

- Gross alpha and gross beta radioactivity (Method 900.0);
- Alpha emitting radioisotopes of ^{223}Ra, ^{224}Ra and ^{226}Ra(Method 903.0); and
- ^{226}Ra, radon emanation technique (Method 903.1).

Table 2-1. List of Approved Radiologic Test Procedures

Parameter and Units	Method	EPA Reference[1]
Alpha-Total, pCi per liter	Proportional or Scintillation Counter	900.0
Beta-Total, pCi per liter	Proportional Counter	900.0
Radium Total, alpha emitting isotopes, pCi per liter	Proportional Counter	903.0
^{226}Ra, pCi per liter	Scintillation Counter	903.1

Source: 40 CFR Part 136. Table IE.

[1] Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032 (1980), U.S. Environmental Protection Agency, August 1980. Appendix B provides method for measuring alpha and beta counting error.

EPA does not have an approved method for measuring uranium and thorium in wastewater. EPA approved methods are described in this section.

900.0 Gross Alpha and Gross Beta Radioactivity *Summary:* This method covers the measurement of gross alpha and gross beta particle activities. The method is a screening technique for alpha and beta particle activities. An aliquot of a preserved sample is evaporated to a small volume and transferred quantitatively to a tared 2-inch stainless steel counting planchet. The sample residue is dried to constant weight, reweighed to determine dry residue weight, and then counted for alpha and/or beta radioactivity using a gas-flow proportional counting system or scintillation detector system. Counting efficiencies for both alpha and beta particle activities are selected according to the amount of sample solids from counting efficiency vs. sample solids standard curves.

Interference Issues: Alpha and beta particles have lower energy than gamma radiation with limited ability to pass through solids. Because Method 900.0 requires drying a standard volume water sample, a sample with high salt concentration typical of some UOG wastewater will produce a thick solids residue. To ensure the alpha and beta particles in the sample can be counted, the solids thickness must be limited by reducing the sample volume. This reduces the method sensitivity, making it difficult to measure low levels of radioactivity in a sample of highly saline UOG wastewater.

As further explained in DCN SGE00974: “The amount of [suspended and dissolved] solids in a sample limits the size of sample that can be processed and thereby the sensitivity of the measurement. Method 900.0 restricts residue thickness for gross alpha measurements to a maximum of 5 mg/cm^2. In a 50-mm diameter stainless-steel planchet, this is equivalent to 100 milligrams of solid residue. While this method is applicable to samples which generally have solids content under 500 mg/L … [UOG wastewater] samples may have solids content in the hundreds of thousands of mg/L and sample sizes would be restricted to a small fraction of a milliliter in order not to exceed the maximum residue thickness. For this reason, the capability of the method to detect activity could be decreased by a factor of one-thousand and the ability of the evaporation approach to detect radioactivity in … [UOG wastewater] becomes questionable at best.”

903.0 Alpha-Emitting Radium Isotopes *Summary:* This method covers alpha emitting radioisotopes of radium: ^{223}Ra, ^{224}Ra, and ^{226}Ra. Radium in a water sample is collected by co-precipitation with barium and lead sulfate, and purified by re-precipitation from ethylenediaminetetracetic acid (EDTA) solution. Citric acid is added to the sample to assure that complete interchange occurs before the first precipitation step. The final barium sulfate ($BaSO_4$) precipitate, which includes ^{226}Ra, ^{224}Ra, and ^{223}Ra is alpha counted to determine the total disintegration rate of the radium isotopes.

Interference Issues: Because Method 903.0 requires a co-precipitation of radium with barium sulfate, high test sample concentrations of Group II elements (magnesium, calcium, strontium, barium) will interfere with the radium recovery and result in inaccurate measurements. As shown in TDD Tables C-16 and C-17, Group II element concentrations in UOG extraction wastewater can reach hundreds of thousands of mg/L, so that the accuracy of Method 903.0 for UOG wastewater may be reduced.

903.1 ^{226}Ra, Radon Emanation Technique. *Summary:* This method is specific for ^{226}Ra, and is based on the emanation and scintillation counting of ^{222}Rn, a daughter product of ^{226}Ra. ^{226}Ra in the water sample is concentrated and separated by coprecipitation on barium sulfate. The precipitate is dissolved in EDTA reagent, placed in a sealed bubbler and stored for ingrowth of ^{222}Rn. After ingrowth, the gas is purged into a scintillation cell. When the short-lived ^{222}Rn daughters are in equilibrium with the parent (after about four hours), the scintillation cell is counted for alpha activity.

All of the alpha-emitting radium isotopes ^{226}Ra, ^{224}Ra, and ^{223}Ra undergo decay to radon isotopes. However, only the progeny of ^{226}Ra, ^{222}Rn, has a half-life long enough to be useful for analytical measurements. The other radon isotopes have half-lives of less than one minute. Thus when the ^{222}Rn is separated from all the other radium isotopes, the other radon progeny decay quickly enough so that they do not interfere with the measurement of ^{222}Rn and its progeny.

Interference Issues: The method reports that there are no radioactive interferences in this method. Because the method requires a co-precipitation of radium with barium sulfate, high test sample concentrations of Group II elements (magnesium, calcium, strontium, barium) may interfere with the radium recovery and result in inaccurate measurements. As shown in TDD Table C-16 and C-17, Group II element concentrations in UOG extraction wastewater can reach hundreds of thousands of mg/L, so that the accuracy of Method 903.1 for UOG wastewater may be reduced.

2.2 EPA Approved Test Procedures for Radioactive Materials in Drinking Water

Only the methods listed in Table 2-1 are approved for use in the NPDES permit program. EPA has additional approved test procedures for radiological parameters in drinking water that researchers have applied to UOG wastewater. These methods include test procedures for:

- ^{228}Ra in drinking water (method 904.0);
- Gamma emitting radionuclides in drinking water (method 901.1).

904.0 ^{228}Ra *Summary:* This method covers the measurement of ^{228}Ra in drinking water. Although it is not approved for use in the NPDES program, researchers have used it to measure ^{228}Ra in UOG wastewater. Radium in the water sample is collected by co-precipitation with barium and lead sulfate and purified by re-precipitation from EDTA solution. Both ^{226}Ra and

^{228}Ra are collected in this manner. After a 36 hour ingrowth of ^{228}Ac from ^{228}Ra, the ^{228}Ac is carried on yttrium oxalate, purified, and beta counted. If ^{226}Ra is also desired, the activity in the supernatant can be reserved for co-precipitation on barium sulfate, dissolved in EDTA and stored for ingrowth in a sealed radon bubbler (see Method 903.1).

Interference Issues: Because the Method 904.0 requires a co-precipitation of radium with barium sulfate, high test sample concentrations of Group II elements (magnesium, calcium, strontium, barium) will interfere with the radium recovery and result in inaccurate measurements. As shown in TDD Table C-16 and C-17, Group II element concentrations in UOG extraction wastewater can reach hundreds of thousands of mg/L, so that the accuracy of Method 904.0 for UOG wastewater may be reduced.

901.1 Gamma Emitting Radionuclides in Drinking Water *Summary:* This method covers the use of gamma spectroscopy for the measurement of gamma photons emitted from radionuclides without separating them from the sample matrix. This technique is used to measure concentrations of specific gamma emitters in a drinking water sample. Although it is not approved for use in the NPDES program, researchers have used it with modern gamma spectrometers to measure ^{226}Ra and ^{228}Ra in UOG wastewater. The method requires:

- The container configuration for the standards and the samples to be identical (i.e., geometry of the sample with respect to the detector), and

- The sample to be properly acidified and not contain any sediment.

Interference Issues: Interferences result from the presence of more than one gamma emitting radionuclide in the sample. Resolution of modern (HPGe) detectors is very good; however, they cannot resolve gamma-ray energies that are within ~ 0.5 kiloelectron volt (keV) of each other. Evaluation of the spectra by a trained spectroscopist is necessary to ensure proper reporting.

2.3 Development of Methods for Determination of Gross Alpha and Gross Beta and Radium Levels Specific to UOG Extraction Wastewater

Because of the generally high ionic strength (i.e., salt concentration) of UOG extraction wastewater, the accuracy of methods such as EPA Methods 900.0, 903.0, and 904.0 is questionable for analysis of UOG extraction wastewater. To address these difficulties, EPA and other researchers are developing methods tailored to UOG extraction wastewater. This section summarizes published results of the development of two methods specific to UOG extraction wastewater.

Gross Alpha and Gross Beta Activity. In response to the difficulty of applying approved methods to UOG extraction wastewater samples, EPA's National Analytical Radiation Environmental Laboratory and National Exposure Research Center cooperated in the development of the *Rapid Radiochemical Method for Gross Alpha and Gross Beta Activity in Flowback and Produced Water from Hydraulic Fracturing Operations (FPWHFO)*(DCN SGE00974). As reported in this document, the optimized method consists of measuring activity of alpha emitters by two methods (liquid scintillation counting and gamma spectrometry). The results of these measurement methods, described further below, may be summed to represent total gross alpha. Beta emission activity of ^{228}Ra is measured separately by gamma spectrometry, as described below (DCN SGE00974).

Thorium (Th), uranium (U), and polonium (Po) Gross Alpha by Liquid Scintillation Counting. A 300 mL sample is treated with permanganate in ammoniacal solution to coprecipitate all radionuclides in the naturally occurring series. The mixture is settled and the supernatant solution discarded. The residue is dissolved in hydrochloric acid and passed through a TRU Resin™ column (Eichrom Technologies, LLC, Lisle, IL).Thorium, uranium, and polonium are eluted from the resins using ammonium oxalate. The eluent is transferred to a liquid scintillation vial as the final sample test source and counted in the alpha emission region of the liquid scintillation spectrum. The final sample test source is counted for 30 minutes.

^{226}Ra Alpha by Gamma Spectrometry. A sample test source of 3 L is counted directly by gamma ray spectrometry. The activity concentration of ^{226}Ra is determined by gamma ray analysis using a specified energy gamma ray region (the 186 keV photopeak) and assumes no significant amount of ^{235}U (uranium-235) compared to the amount of ^{226}Ra in the sample[5]. The sample is counted for 12 hours or long enough to achieve the required method uncertainty.

^{228}Ra Beta by Gamma Spectrometry. The sample test source of 3 L is counted directly by gamma ray spectrometry. In addition to ^{228}Ra being determined indirectly by analysis of its first progeny, ^{228}Ac, several other radionuclides are determined directly by their gamma ray emission and others may be determined indirectly through analysis of a parent or progeny radionuclide that is a gamma ray emitter. The sample is counted for 12 hours or long enough to achieve the required method uncertainty.

The method developers noted that additional work was needed to optimize and validate portions of the method. Also, because the activity of samples containing natural decay chain activity, especially ^{226}Ra and ^{224}Ra, changes over time due to radioactive ingrowth and decay processes, questions about timing of wastewater generation, sample collection, preparation and counting must be addressed (DCN SGE00974).

^{226}Ra and ^{228}Ra. Researchers from the University of Iowa examined alternative methods for determining radium levels in UOG extraction wastewater. Working with a sample of Marcellus shale wastewater from northeastern Pennsylvania, Nelson et al., 2014 (DCN SGE00975), found that barium sulfate coprecipitation, the basis for EPA method 903.0, resulted in very poor recovery of radium (<1% of spiked activity of ^{226}Ra). The researchers explored four alternative methods and determined that HPGe gamma spectroscopy was the most promising method for determining levels of ^{226}Ra in UOG extraction wastewater, using a 3 L sample (stabilized with agar) counted for 17 hours. Researchers are continuing to evaluate the use of an electronic radon detector (Durridge RAD7) to quantify radium by measuring radon decay products. Although counting times with the radon detector method are shorter than HPGe gamma spectroscopy, sufficient hold time for radon ingrowth, 4 to 30 days, is required. Researchers are continuing development of this method.

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[5] Gamma-ray spectrometry may also be used to determine the activity of the ^{226}Ra beta-gamma emitting progeny, ^{214}Pb (lead-214) and ^{214}Bi (bismuth-214); however, these emissions are not included in the quantitation of ^{226}Ra by the method described in DCN SGE00974.

3.0 STUDIES OF RADIOACTIVE MATERIAL IN UOG EXTRACTION WASTEWATER

The following subsections describe studies related to radioactivity in the UOG industry. This is not a comprehensive review but includes studies that EPA identified during the development of the pretreatment standards for UOG extraction wastewater.

3.1 Pennsylvania Department of Environmental Protection (PA DEP) TENORM Study (DCN SGE01028)

In January 2015, PA DEP announced the results of a study of radioactive elements in UOG extraction wastewater, sludge, and drill cuttings. Liquid and solid samples were analyzed for alpha, beta, and gamma radiation and gas samples were analyzed for radon using the following methods (DCN SGE01028):

- EPA Method 901.1: Gamma spectroscopy to identify TENORM radionuclides;
- DOE Health and Safety Laboratory (HASL) 300: Alpha spectroscopy to identify isotopic uranium and isotopic thorium; and
- EPA Method 900.0: Gross alpha and gross beta.

In samples of flowback fluid and produced water, ^{226}Ra concentrations were elevated, ranging up to 26,600 pCi/L. ^{228}Ra was also detected in these samples, at up to 1,900 pCi/L. Although PA DEP concluded, "…[t]here is little potential for radiological exposure to workers and members of the public from handling and temporary storage of [flowback fluid and] produced water on natural gas well sites," they did conclude "…[t]here is a potential for radiological environmental impacts from spills of produced water [and flowback fluid] on natural gas well sites and from spills that could occur from the transportation and delivery of …[these] fluid[s]."

At ten POTWs, PADEP sampled treated and untreated wastewater and wastewater treatment sludge (filter cake). Six of the 10 POTWs are considered influenced (POTW-I) by having received wastewater from the oil and gas (O&G) industry, mainly the effluent of CWTs. Four of the sampled POTWs never received wastewater from the O&G industry. Because the measured concentrations shown in Table 3-1 are higher than concentrations found in surface water (see TDD Table C-20) and soil (DCN SGE01028 Table 2-2), there may be some potential for radiological contamination by discharges from POTWs treating UOG extraction wastewater.

Table 3-1. Radium Concentrations, Influent vs. Effluent for Six POTWs receiving Oil and Gas Wastewater

Sample Description	^{226}Ra (pCi/L)	^{228}Ra (pCi/L)
Influent, Unfiltered (Average)	190	28.1
Effluent, Unfiltered (Average)	103	10.4

Source: DCN SGE01028 Table 4-18

Samples of filter cake from the six POTWs receiving O&G wastewater showed "Ra-226 and Ra-228 present above typical background concentrations in soil. The average Ra-226 result was 20.1 pCi/g with a large variance in the distribution, and the maximum result was 55.6 pCi/g.

The average Ra-228 result was 8.32 pCi/g, and the maximum result was 32.0 pCi/g Ra-228." (DCN SGE01028)

PADEP concluded, "…[t]here is little potential for radiological exposure to workers and members of the public from handling and temporary storage of filter cake at POTW-I's. However, there is a potential for radiological environmental impacts from spills and the long-term disposal of POTW-I filter cake". (DCN SGE01028)

3.2 Argonne National Laboratories (ANL) Bakken NORM Study

The North Dakota Department of Health contracted Argonne National Laboratories to conduct a risk assessment of radioactive waste generated from UOG drilling in North Dakota's Bakken formation. North Dakota does not allow disposal, within the state, of radioactive waste containing greater than or equal to 5 pCi/L. However, North Dakota has experienced problems with trucking companies illegally dumping radioactive waste, including waste generated from the management of UOG extraction wastewater (DCN SGE00968, DCN SGE00970).

The study focused on the concentrations of radioactive elements in UOG industry solid waste generated during the management of UOG wastewater (e.g., scale, sludge, filter cakes, filter socks) and provided background information on TENORM waste streams. It also evaluated the radiological doses associated with a number of scenarios associated with oil and gas well site operations, improperly managed wastes, transportation of TENORM, and disposal of TENORM in Industrial Waste and Special Waste Landfills. Study results were released in November 2014 (DCN SGE01018). The study supported revisions to North Dakota's rules for radioactive waste disposal (DCN SGE01333).

4.0 RADIOACTIVE MATERIALS IN UOG EXTRACTION WASTEWATER AND ASSOCIATED CONCERNS

Oil and gas formations contain varying levels of NORM resulting from uranium decay, which may be transferred to UOG extraction wastewater. This section presents the concentrations of radioactive constituents compiled for the TDD, discusses, in general terms, the harm caused by ionizing radiation (whether from UOG extraction wastewater or other sources), and discusses the particular concerns associated with TENORM in UOG extraction wastewater.

4.1 Radioactive Materials Measured in UOG Extraction Wastewater

The EPA identified only limited radioactive constituent concentration data for UOG extraction wastewater. As presented in Table 4-1[6], most available data characterize produced water from the Marcellus formation; limited data were available from the Niobrara formation. ^{226}Ra and ^{228}Ra are both found in UOG produced water in both of these UOG formations, with ^{226}Ra concentrations generally two to five times greater than ^{228}Ra concentrations. The EPA also identified limited data about radioactivity in drilling wastewater[7]; Table C-18 in the TDD (DCN

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[6] The generation of the data in Table 4-1 is explained in the *Unconventional Oil and Gas (UOG) Produced Water Volumes and Characterization Data Compilation* memorandum (DCN SGE01184). This memorandum includes a description of the underlying data sources, data analysis, and QC procedures.

[7] Information about radioactive constituent concentrations in UOG drilling wastewater can be found in the *Unconventional Oil and Gas (UOG) Drilling Wastewater* memorandum (DCN SGE01181).

SGE01188) presents a summary of 5 data points for gross alpha and gross beta concentrations in UOG drilling wastewater from the Marcellus shale formation.

Table 4-1. Concentrations of Radioactive Constituents in UOG Produced Water

Parameter	Formation	Method(s)	Range[a] (pCi/L)	Median (pCi/L)	Number of Data Points	Number of Detects
Gross alpha	Marcellus	900.0	4.7 - 24,000	8,700	103	101
Gross alpha	Niobrara	900.0	300 - 820	1,800	3	3
Gross beta	Marcellus	900.0	0.66 - 1,700	1,600	94	92
Gross beta	Niobrara	900.0	170 - 420	760	3	3
^{226}Ra	Marcellus	901.1 Mod., 903.0, 903.1, γ-spectrometry	10 - 88,000	1,700	74	74
^{226}Ra	Niobrara	901.1 Mod.	960 - 3,300	620	3	3
^{228}Ra	Marcellus	901.1. 903.0, 904.0, γ-spectrometry	15 - 16,000	470	73	72
^{228}Ra	Niobrara	901.1 Mod.	400 - 1,100	330	3	3

a – Range values represent the 10th and 90th percentile values of the data
Source: DCN SGE01184

4.2 General Information about Harm Caused by Ionizing Radiation

Ionizing radiation is known to harm living tissue in humans and other organisms. The extent of harm depends on routes and duration of exposure and the energy and types of ionizing radiation (alpha and beta particles and gamma rays). Radiation exposure can occur externally, when the radiation source is outside of the organism. External exposure is of particular concern for radionuclides that emit gamma rays which have sufficient energy to penetrate containers, clothing, and skin. Internal exposure is a greater concern for radionuclides (such as radium) that emit alpha and beta particles. Although alpha and beta particles do not penetrate far into tissue, inside the body they will deposit their energy in a small volume of tissue, causing greater damage (DCN SGE01020). Internal exposure results mainly from ingestion (e.g., drinking water, food) and inhalation (e.g., inhaling a radioactive gas such as radon or contaminated dust).

All of the radionuclides present in UOG wastewater generate ionizing radiation that is potentially harmful to human health and the environment; however, as discussed previously, because of their greater solubility in UOG formation water[8], radium isotopes (particularly ^{226}Ra and ^{228}Ra) are present in UOG wastewater at higher concentrations than other radionuclides (DCN SGE00975). Further, radium is of particular concern because its chemical behavior is similar to calcium, magnesium and other Group II elements. Whereas external radiation is instantaneous (i.e., does not remain in the body after the exposure), internal deposition of radionuclides can present a hazard for long periods of time after the initial exposure. Because it behaves similarly to calcium, ingested radium may be stored in the body and can replace calcium in tissues, particularly bone. Long-term internal exposure to radium increases the risk of developing bone and other cancers. Because radium readily accumulates in the body, it is

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[8] Formation water is water that occurs naturally within the pores of rock.

considered to pose a greater cancer risk than most other radioactive elements (DCN SGE00980). Additionally, near-surface radium deposits may be a source of indoor radon in the future if homes are built over radium-contaminated soils.

In addition to potential harm to human health, radium that accumulates in river and stream sediments could harm benthic organisms. Warner, et al write, “Bioaccumulation of radium is known to occur in freshwater fish [and] invertebrates…Radium also accumulates in freshwater plants…” (DCN SGE00629).

4.3 Potential Concerns Associated with TENORM in UOG Extraction Wastewater

Transfer of TENORM to the environment may result from management of UOG extraction wastewater. UOG operators use three primary practices to manage UOG extraction wastewater (DCN SGE01188):

- Dispose of wastewater via underground injection for disposal wells (“disposal wells”);
- Reuse/recycle wastewater in subsequent fracturing jobs; and
- Transfer wastewater to a centralized waste treatment (CWT) facility.

While implementing these practices, radioactive materials may be removed from the wastewater stream in sludges that accumulate in tanks and equipment, during filtration of suspended solids from wastewater, or by chemically changing radium from a soluble to insoluble form during wastewater treatment. The following bullets summarize the potential concerns identified in the literature associated with TENORM during the management of UOG extraction wastewater.

- *Build-up of Radioactive Elements in Scale* – During transport of UOG extraction wastewater, radium may precipitate with other scale-contributing constituents (e.g., calcium, strontium) resulting in a TENORM-containing scale in pipes and valves (DCN SGE00622). Conventional oil and gas (COG) wastewaters, which have constituents similar to UOG wastewater, have been documented to generate radioactive scale. As discussed in DCN SGE00136, in studies of the COG industry, the American Petroleum Institute found the highest concentrations of radioactivity in wellhead piping scale. Radium concentrations measured in the scale on pipes and valves used to manage COG extraction wastewater averaged 480 pCi/g, ranging up to 400,000 pCi/g, depending on regional geology (DCN SGE00136). ^{226}Ra and ^{224}Ra, contained in the scale, decay into radon gas and present an inhalation hazard when workers contact the scale. Buildup of ^{210}Pb (lead-210) and ^{210}Po (polonium-210) in thin films and scales on the interior of equipment on natural gas wells and equipment are also a concern. People working with scale-encrusted equipment, pipes, and valves may be exposed to radiation, either externally or internally via inhalation or ingestion of radioactive materials.
- *Sludge and Filter Residues* – As reported in DCN SGE01018, “TENORM-contaminated sludges can accumulate in the bottom of vessels that are used to

> store or otherwise manage… [UOG extraction wastewater], including water storage tanks, oil/water separators, and heater treaters. Sludges typically are composed of solid debris, such as sand, scale, or rust particles, that settle out of the production stream. The primary… [radionuclides of concern] in sludges in the United States are ^{226}Ra, ^{228}Ra, and their decay products… Typically, the radium takes the form of a co-precipitate with sulfate or carbonate deposits. In addition, filters that are used to separate particulates from produced water generate a solid waste referred to as filter cake. This material is likely to have a similar composition to the sludge that is removed from produced water storage and handling equipment…. Disposable filter socks are used to filter particulates out of produced water prior to transport and disposal. These filters accumulate sludges and scales over time and must be changed and disposed of on a regular basis. In the past year, the improper disposal of these filter socks has been a problem in the State of North Dakota". (DCN SGE00970)

- *Radioactivity in Discharges of UOG Extraction Wastewater from Treatment Plants* – The treatment technologies used by wastewater treatment plants may not remove all of the pollutants contributing to radioactivity. As a result, these pollutants will be discharged to surface waters. Researchers measured sediment concentrations at the point of discharge from a brine treatment facility that accepted UOG extraction wastewater. They found ^{226}Ra at 8,732 Bq/kg (236 pCi/g) and ^{228}Ra at 2,072 Bq/kg, (56 pCi/g) about 200 times greater than upstream and background sediment concentrations. The researchers speculated that the contaminated sediments could pose ecological risks, particularly to benthic organisms (DCN SGE00629).

- *Site Contamination Potential* – Solid wastes generated during management of UOG wastewater (e.g., drilling wastewater filter residues, scale, sludge, treatment residuals) may contain TENORM. These wastes are often disposed of at the drilling site or in landfills. Improper disposal may lead to soil and/or groundwater contamination and/or airborne releases of radon gas (DCN SGE00622).

5.0 QUALITY CONTROL PROCEDURES

All of the analyses presented adhered to the *Environmental Engineering Support for Clean Water Regulations Programmatic Quality Assurance Project Plan (PQAPP)* (DCN SGE00957) and the *Unconventional Oil and Gas (UOG) Supplemental Quality Assurance Project Plan (SQAPP)* (DCN SGE00958), including collecting, evaluating, and analyzing existing data and information about radioactive materials in the UOG industry.

Specifically, ERG used the procedures described in Section 4 of the PQAPP to gather and manage existing data in support of the rulemaking. ERG staff entered reference information for relevant sources into the UOG Literature Review database. The ERG index keeper reviewed all reference information, assigned each reference a Document Control Number (DCN), imported the reference information into the UOG Project File Index database, and saved referenced files in the Electronic Project File folder.

ERG also used the procedures described in Section 3 of the SQAPP when collecting existing data for use in the UOG rulemaking. ERG used a combination of sources, including reports, papers, and online databases from state regulatory agencies such as departments of environmental protection and oil and gas commissions. As shown in Table 6-1, ERG assigned a source flag (A, B, C or D) to all references used in these analyses.

ERG defines each source flag as follows:

- Source Flag A - Journal articles and documents prepared by or for a government agency (e.g., site visit reports, industry meeting notes);
- Source Flag B - Documents prepared by a verified[9] source that include citation information (e.g., operator reports, vendor documents, university publications);
- Source Flag C - Documents prepared by a verified source that do not include citation information (e.g., operator reports, vendor documents, conference presentations); and
- Source Flag D - Documents prepared by a source that could not be verified and that do not include citation information.

ERG collected data and information that were specific to the radioactive elements, analysis procedures, and UOG wastewater of concern. The references were reviewed for relevance and comparability, and summarized for use in this memo. ERG searched for the best available information, and all but three sources qualify as Source Flag A, as described above. Beginning with federal, state, and local government reports and documents, ERG conducted a thorough literature search, with a particular interest in recent sources and sources that used the EPA Methods of interest (900.0, 901.0, 903.0, 903.1, and 904.0). Where available, ERG included information from site visits and industry meetings.

6.0 REFERENCES

Table 6-1 lists the sources ERG used along with their DCN and source flag.

Table 6-1. References

DCN	Source Citation	Source Flag[a]
SGE00136	U.S. EPA. 2011. Oil and Gas Production Wastes. https://www.epa.gov/radiation/tenorm-oil-and-gas-production-wastes	A
SGE00179	Keenan, Charles W. and Jesse H. Wood. General College Chemistry. Chapter 14 Nuclear Changes. Harper & Row Publishers, Inc., New York. 1971.	A
SGE00241	Rowan, E.L., et al. 2011. Radium content of oil and gas field prod waters in the Northern App Basin. USGS Scientific Investigations Report 2011–5135.	A
SGE00544	Marcellus Shale Coalition (MSC) and PA Independent Oil and Gas Association (PIOGA). 2013. Field Sampling Plan.	B
SGE00622	U.S. Geological Survey (USGS). 2013. Water Resources and Shale Gas/Oil Production in the Appalachian Basin. (August).	A

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[9] ERG considered sources as “verified” if we were able to find information about the author outside of the reference document. ERG primarily verified information by looking for company/organization websites that confirmed the author’s affiliation with the UOG industry

Table 6-1. References

DCN	Source Citation	Source Flag[a]
SGE00629	Warner et al. 2013. Impacts of Shale Gas Wastewater Disposal on Water Quality in Western PA. Environmental Science & Technology 47(20):11849–11857	A
SGE00782	U.S. EPA. 2012. (October 1). Available online at: https://www.epa.gov/radiation/radionuclide-basics-uranium	A
SGE00783	U.S. EPA. 2014. Thorium. (February 28). Available online at: https://www.epa.gov/radiation/radionuclide-basics-thorium	A
SGE00793	ERG. 2014. Unconventional Drilling/Hydraulic Fracturing and Natural Radioactivity Webinar Notes. (July 3)	C
SGE00795	U.S. EPA. 2012. About TENORM. (August 30). Available online at: https://www.epa.gov/radiation/technologically-enhanced-naturally-occurring-radioactive-materials-tenorm.	A
SGE00936	Understanding Radiation. Available online at: https://www.epa.gov/radiation/radiation-basics.	A
SGE00937	U.S. Environmental Protection Agency (U.S. EPA). 2011. Enhancing Radiological Laboratory Testing for Radionuclides in Drinking Water Training.	A
SGE00957	ERG. 2013. Environmental Engineering Support for Clean Water Regulations Programmatic Quality Assurance Project Plan (PQAPP).	A
SGE00958	ERG. 2014. Unconventional Oil and Gas (UOG) Supplemental Quality Assurance Project Plan (SQAPP).	A
SGE00968	Glatt, Dave; Tillotson, Steve. 2014. Contractor Selected for Cleanup of Filter Socks in Noonan	A
SGE00970	Donovan, Lauren. 2014. Bismarck Tribune Second dump site reported in Divide County.	D
SGE00973	U.S. EPA. 2013. Radiation Glossary.	A
SGE00974	U.S. EPA. 2014. Development of Rapid Radiochemical Method for Gross Alpha & Gross Beta Activity Concentration in Flowback & Produced Waters from HF Operations	A
SGE00975	Nelson, A. et al. 2014. Matrix Complications in the Determination of Radium Levels in Hydraulic Fracturing Flowback Water from Marcellus Shale.	A
SGE00977	USNRC. 2013. Measuring Radiation.	A
SGE00978	PA DEP. 2014. PA DEP TENORM Study - Update 2nd Quarter 2014 Update.	A
SGE00979	PA DEP. 2013. Sampling and Analysis Plan Part II Quality Assurance Project Plan	A
SGE00980	USGS. 2014. Trace Elements National Synthesis Project Radium Frequently Asked Questions.	A
SGE01018	Harton, C. 2014. Radiological Dose And Risk Assessment of Landfill Disposal of TENORM in North Dakota	A
SGE01020	U.S. EPA. 2012. Radiation Protection Health Effects.	A
SGE01028	PA DEP. 2015. Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) Study Report.	A
SGE01126	U.S. EPA. 2015. Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas in Drinking Water Resources. ORD.	A
SGE01181	ERG. 2016. Unconventional Oil and Gas (UOG) Drilling Wastewater Memorandum	A
SGE01184	ERG. 2016. Unconventional Oil and Gas (UOG) Produced Water Volumes and Characterization Data Compilation Memorandum	A
SGE01188	U.S. EPA. 2016. Technical Development Document for Effluent Limitations Guidelines and Standards for Oil and Gas Extraction.	A

Table 6-1. References

DCN	Source Citation	Source Flag[a]
SGE01333	North Dakota. Regulation and Licensing of Technologically Enhanced Naturally Occurring Radioactive Material Chapter 33-10-23.	A
SGE01334	ERG. 2016. Memorandum Providing a Crosswalk between Tables and Figures in the Proposed and Final Technical Development Document for Effluent Limitations Guidelines and Standards for Oil and Gas Extraction.	A

a— Source Flag A - Journal articles and documents prepared by or for a government agency (e.g., site visit reports, industry meeting notes).

Source Flag B - Documents prepared by a verified source that include citation information (e.g., operator reports, vendor documents, university publications);

Source Flag C - Documents prepared by a verified source that do not include citation information (e.g., operator reports, vendor documents, conference presentations); and

Source Flag D - Documents prepared by a source that could not be verified and that do not include citation information.

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Information Requirements under the Essential-Use Concept: PFAS Case Studies

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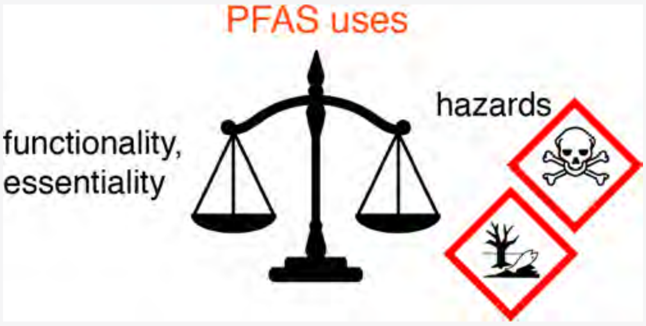
ABSTRACT: Per- and polyfluoroalkyl substances (PFAS) are a class of substances for which there are widespread concerns about their extreme persistence in combination with toxic effects. It has been argued that PFAS should only be employed in those uses that are necessary for health or safety or are critical for the functioning of society and where no alternatives are available ("essential-use concept"). Implementing the essential-use concept requires a sufficient understanding of the current uses of PFAS and of the availability, suitability, and hazardous properties of alternatives. To illustrate the information requirements under the essential-use concept, we investigate seven different PFAS uses, three in consumer products and four industrial applications. We investigate how much information is available on the types and functions of PFAS in these uses, how much information is available on alternatives, their performance and hazardous properties and, finally, whether this information is sufficient as a basis for deciding on the essentiality of a PFAS use. The results show (i) the uses of PFAS are highly diverse and information on alternatives is often limited or lacking; (ii) PFAS in consumer products often are relatively easy to replace; (iii) PFAS uses in industrial processes can be highly complex and a thorough evaluation of the technical function of each PFAS and of the suitability of alternatives is needed; (iv) more coordination among PFAS manufacturers, manufacturers of alternatives to PFAS, users of these materials, government authorities, and other stakeholders is needed to make the process of phasing out PFAS more transparent and coherent.



KEYWORDS: *PFAS, essential use, chrome plating, fluoropolymer, carpet*

1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a class of thousands of substances[1,2] most of which are either persistent themselves or are transformed into persistent compounds in the environment. Further, the few PFAS studied to date have shown a wide range of biological activity in cell-based, animal, and human epidemiological studies.[3] Because of these concerns, it has been argued that PFAS should only be employed in those uses that are necessary for health, safety, or are critical for the functioning of society and where no alternatives are available.[4−6] This concept of "essential uses" has been incorporated into a working paper on "Elements for an EU strategy for PFAS"[7] and also into the European Commission's Chemicals Strategy for Sustainability as well as the accompanying "Commission Staff Working Document − Poly- and Perfluoroalkyl Substances (PFAS)".[8]

Implementing the essential-use concept requires a sufficient understanding of the current uses of PFAS and of the availability, suitability, and hazardous properties of alternatives. Cousins et al. (2019a)[4] analyzed nine different use areas of PFAS and the availability of alternatives. Other research groups and institutions have also looked into alternatives to PFAS in certain use areas,[9−15] and additional information is available on the OECD Portal on PFAS.[16] Glüge et al. (2020)[17] characterized more than 200 uses of more than 1400 individual PFAS. This work has shown that PFAS uses are very diverse, and this diversity is a challenge to the implementation of the essential-use concept. In many cases, it is not clear whether the use of PFAS is essential. Accordingly, there is a need for a better understanding of where PFAS are used, what their specific functions in these uses are, and how easy or difficult it is to find alternatives.

To address this need, we investigate here a set of seven different PFAS uses, three in consumer products and four

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industrial applications. We investigate how much information is available on the types and functions of PFAS in these uses and, if needed, how much information is available on alternatives, their performance and hazardous properties, and finally, whether this information is sufficient as a basis for deciding on the essentiality of a PFAS use. On this basis, we aim to make a contribution to a broader understanding of the information requirements of the essential-use concept and to illustrate the type of questions that are brought up for decision makers by the essential-use concept.

2. METHODS

2.1. Selection of Case Studies. The intention of the case studies selected is to cover a range of different PFAS uses from relatively simple to more complex cases for which there is at least some information on alternatives available in the public domain. By looking into PFAS uses in consumer products and in industrial processes, the diversity of PFAS uses is reflected, and different types of assessment tasks and decision-making situations are illustrated. In addition, several of the case studies are in areas where PFAS have caused serious contamination problems, for example, fluoropolymer[17−20] or semiconductor production.[21,22]

Given the large number of PFAS and PFAS uses,[16] the seven case studies are a limited selection. Nevertheless, they show an interesting and relevant range of assessment tasks that may be typical for future applications of the essential-use concept. In particular, the industrial uses may deserve more discussion and further analysis.

The three case studies of PFAS uses in consumer products are on PFAS in bicycle lubricants, carpets, and cleaning products. The four industrial uses of PFAS are in fluoropolymer production, in the semiconductor industry, in chrome plating, and in chemical-driven oil production. For each case study, an extensive search of the available literature was conducted, including peer-reviewed journal articles, monographs, industry reports, product descriptions, and patents. In addition, we contacted PFAS manufacturers and downstream users and received additional input from technical experts for most of the case studies, in particular for bicycle lubricants, chrome plating, fluoropolymer production, and PFAS uses in the semiconductor industry. Details of the contacted businesses are provided in the Supporting Information (SI-1, Table S4).

2.2. Alternatives Assessment. Alternatives for each of the PFAS uses in the seven case studies were mainly found through literature searches. Confirmation of the information was obtained through discussions with providers of alternatives. Alternatives for which chemical identification information (CAS number or SMILES code) was found are listed in the accompanying MS Excel document "Gluege_et_al_SI-2.xlsx" (SI-2). In some cases, the chemical identity of alternatives was declared as confidential business information and not shared.

Where the chemical identity of the alternatives could be determined, their human-health and environmental hazards were compared with those of the PFAS currently used. Data on the hazards were taken from three sources: the ECHA Classification & Labeling (C&L) Inventory, the ECHA REACH registration database, and the EPI Suite estimation tool,[23] where appropriate. Where a charged organic substance was identified, a neutral form of the substance was run through EPI Suite. This may introduce error into the calculation. Data were collected or generated for the following hazards: carcinogenicity, mutagenicity, reproductive toxicity (human health) and persistence, bioaccumulation, ecotoxicity, and mobility (environment). The data collected are provided in the SI-2.

When a brand name is mentioned in this work, this does not constitute endorsement of the brand or its product. The chemical identity of the PFAS in the different uses was taken from Glüge et al. (2020).[16]

In addition to cases where an alternative is a direct replacement of PFAS by other chemicals with the same technical function, there are also cases where the design of the product or technical process can be modified such that the technical need for PFAS no longer exists. Depending on the chemicals used in the modified products or processes (if any), an alternative assessment may or may not be needed.

2.3. Essentiality Categories. Where possible, we applied the categories of "non-essential", "substitutable", and "essential" uses, as defined by Cousins et al. (2019a),[4] to the PFAS identified in the seven case studies. We did not judge whether or not a product or process is essential for health, safety or the functioning of society. Instead, the classification is based on whether the function provided by PFAS is needed in a specific product or process and on the availability of suitable alternatives. Products or processes where PFAS are not needed at all are classified as "non-essential". Products or processes where PFAS can be replaced by other substances or processes are classified as "substitutable". Cases where PFAS cannot (yet) be replaced are classified as essential. A further discussion and development of criteria for essential uses is not part of this work.

3. CASE STUDIES ON ALTERNATIVES TO PFAS

3.1. Bicycle Lubricants. *Uses.* Polytetrafluoroethylene (PTFE) is added to different kinds of bicycle lubricants including dry lubes, wet lubes, and wax lubes. Dry lubes are designed for riding in dry conditions and are often made by mixing ca. 10% lubricant (synthetic oils and additives) and 90% carrier fluid (solvent). Wet lubes contain larger quantities of higher-viscosity synthetic oils and additives such as PTFE and are intended for riding in wet conditions.[24] There are also lubricants based on paraffin wax mixed with additives such as PTFE and a carrier fluid. PTFE may be used within a range of 5−25% by weight in dry lubes to reduce friction and wear.[25] Wet lubricants seem to contain less PTFE; the safety data sheet of a wet PTFE lubricant reveals a PTFE content of 1−3% by weight.[26] Another aspect is that a PTFE content of less than 1% may be added just for marketing purposes.[27] For a substantial effect on performance, at least 4−5% PTFE is needed.[27]

Availability of Alternatives and Alternatives Assessment. There are lubricants on the market that do not contain PTFE and perform well according to tests and user experiences.[28−30] The providers of alternative lubricants state that their lubricants are "plant based“ and decompose rapidly,[31] but no information about biodegradability test results is provided. However, it can be assumed that, compared to the extreme persistence of PTFE, the persistence of these alternatives is much lower.

Conclusion. Although PFAS in bicycle lubricants may increase lubricating performance, they are technically not needed to keep chains lubricated. In addition, PFAS-free products have always been available on the market. In conclusion, the use of PFAS in bicycle lubricants is non-essential.

3.2. Carpets. *Uses.* PFAS have been used in carpets to impart water and oil repellency, stain resistance, and soil release to synthetic carpet face fibers.[32] The reason is that nylon and other synthetic fibers are both oleophilic and hydrophobic and, thus, have a great affinity for soils. Soil removal on untreated nylon is therefore more difficult than on treated nylon.

Availability of Alternatives. One carpet manufacturer, Interface, changed the formulation of the nylon used in face fibers so that the fibers themselves are stain-resistant.[33] The yarn producer, Aquafil, offers stain-free fibers based on the nylon-6 fiber "Econyl StayClean".[34] This fiber is made from nylon waste that was depolymerized and recycled.[35] No PFAS are added to the recycled fiber. Another yarn manufacturer, Universal Fibers, describes the use of a "sulfonated nylon copolymer" for a PFAS-free stain protection.[32] In this case PFAS are not needed because the modified nylon fiber is stain-resistant itself. The carpet manufacturer, Tarkett, on the other hand, treats its "Tandus Centiva"-branded products with fluorine-free soil protection products,[36] which means that in the topical treatment PFAS are replaced by other chemicals.

Some PFAS-free carpets can also be found under the "Blue Angel" certificate. The certificates Blue Angel,[37] Nordic Swan and Cradle-to-Cradle[38] ban halogenated organic compounds (including all PFAS) from their labeled products. GUT (Association for Environmentally Friendly Carpets) lists 33 single PFAS that are not allowed in products with their certificate[39] and Oeko-Tex 100 bans PFOA-related substances.[40] In response to our information request, Blue Angel replied that PFAS-free polyamide carpets have been registered by the Condor Group.[41]

Alternatives Assessment. Limited information about alternatives is publicly available.[32] Some information on chemical synthesis processes and ingredients can be found in patents, as listed in the SI-1. However, no information is available on the specific properties of the materials or on any results from toxicity or degradability tests. According to the manufacturers contacted, this is confidential business information.

Conclusion. It is possible and economically feasible to produce synthetic carpets without PFAS-based impregnation. PFAS in carpets are therefore substitutable. More information on the alternatives should be made publicly available so that their impacts can be evaluated transparently.

3.3. Cleaning Products. *Uses.* PFAS lower the surface tension and improve wetting and rinse-off in a variety of industrial and household cleaning products. Examples are car wash products, floor cleaning products and floor polish, carpet spot cleaner, cleaning solutions for optical devices, and dishwashing liquids in which, for example, PFOA has been detected.[42,43]

Availability of Alternatives. Alternative household cleaning products are based on ingredients that are biodegradable, in some cases readily biodegradable. These products are available on the market. Examples for surfactants other than PFAS used in dish soap include for example sodium lauryl sulfate and lauryl glucoside.[44] Surfactants used in laundry detergent are for example C12−C16 pareth-7, potassium cocoate, decyl glucoside[45] or sophorolipids.[46] Examples for floor polish and carpet spot cleaner are provided in the SI-1.

Alternatives Assessment. The list of ingredients of a dish soap (Ecover Zero dish soap)[44] was used for the assessment of alternatives. No indication of carcinogenic, mutagenic, or reproductive hazards was found for any of the ingredients. The environmental hazards were also lower: all substances in the dishwashing liquid have calculated degradation half-lives of 4−37 days, with biodegradation studies available and in agreement with the estimated values for most of the substances. Regarding bioaccumulation, all logarithmic octanol−water partition coefficients (log K_{OW}) are below 3, and all bioconcentration factors (BCFs) are below 20. Not all ingredients are listed in the REACH database, but data on the BCF for those available agreed with the estimated values. The use of these substances represents therefore a reduced human-health and environmental hazard when compared to the PFAS used in cleaning products. However, for some surfactants used in floor polish and carpet spot cleaner, the data in the C&L inventory indicate that they are toxic to aquatic organisms.

Conclusion. PFAS in household cleaning products are not technically needed; many alternatives are available and PFAS uses are non-essential. For industrial cleaning products, it would be necessary to look at each case individually in order to evaluate what level of performance is needed, and why, and if alternatives to PFAS are available.

3.4. Chrome Plating. *Uses.* PFAS are used in chrome plating as wetting agents in the pretreatment (etching) of plastic and as mist suppressing agents in the electroplating process. In electroplating (often referred to as chrome plating), fluorosurfactants reduce the exposure to toxic hexavalent chromium aerosols from the plating baths by (i) reducing the size of the bubbles formed and (ii) forming a barrier over the electrolyte solution. More information about PFAS uses in both processes is provided in the SI-1.

Fluorinated surfactants have been used previously for both decorative chrome plating and hard chrome plating. Hard chrome plating provides resistance against corrosion and abrasion to various items such as hydraulic cylinders and rods or railroad wheel bearings and couplers.[47] Decorative chrome plating is mainly used for plated parts, for example in the automotive industry (including car and truck bumpers), but also in the sanitary, medicine, cosmetic, and furniture sectors.[47,48]

Availability of Alternatives. Tests showed that chromium(VI) emissions can be reduced substantially by avoiding air convection.[49] Some companies use closed systems with underpressure and found almost no chromic-acid aerosols. No PFAS are therefore necessary as mist suppressants.[50]

Another reason why the use of chromium(VI) is not essential for all types of decorative chrome plating is that trivalent chromium can be used instead.[47,51] One disadvantage is that trivalent chromium cannot achieve the silvery-bluish color of chromium(VI).[51,52] However, trivalent chromium is much less toxic than chromium(VI) and mist-suppressing PFAS are therefore not needed in processes with trivalent chromium.[42,47,53] A different technology for decorative chrome plating includes processes based on physical vapor deposition (PVD), where PFAS are also not needed.[52] However, the quality of the coating produced by PVD may not be sufficient for materials used for drinking water contact.[54] Also, as of 2016, PVD-based processes did not fulfill the requirements of the German automotive industry in terms of quality, aesthetic value and functionality of the parts.[55]

For hard metal plating, it has been suggested that trivalent chromium could also be used in some applications.[47] Atotech launched a hard-chrome plating process with trivalent chromium and stated that the process exhibits the same benefits as hexavalent-chromium processes.[56] This includes high plating speed, bath stability, and high hardness deposits and wear resistance. However, the technology requires a nickel underlayer to meet the corrosion resistance requirements and is therefore not a drop-in replacement. Besides Atotech, Faraday Technology is also working on a trivalent chromium plating process for functional applications. They stated to us that the trivalent chromium plating process has already passed the tests specified for aerospace applications. They are currently further optimizing the process such that the coating microstructure and appearance is equivalent to that of hexavalent-chromium coatings. More information on chrome plating with trivalent chromium is provided in the SI-1.

Alternatives Assessment. The use of closed systems with underpressure reduces the reproductive hazard of chromium(VI) from the level of "Repr. 1B/H360D" (may damage the unborn child) to "Repr. 2/H361f" (suspected of damaging fertility). It also reduces the environmental hazard as no PFAS or other hazardous substances are needed in this process.

The use of chromium(III) instead of chromium(VI) in electroplating constitutes a shift to a less hazardous substance without the carcinogenic, mutagenic and reproductive toxicity properties of chromium(VI).[57] Atotech and Faraday Technology (the latter from 2015 on) use no boric acid in their processes, which was for a long time a serious drawback of the chromium(III) process.[56,58]

Processes based on PVD use UV-lacquer and, according to Gerhardi Kunststofftechnik (2016a),[52] some of the substances in the application in UV-lacquers are listed as Substances of Very High Concern in the EU. However, no further details are available.

Conclusion. PFAS have been technically important in both decorative and hard chrome plating. For many decorative chrome plating processes, trivalent chromium can be used. For hard chrome plating, there are two ways in which the use of PFAS in the electroplating step may be avoided: either by switching to a closed system in a process still using hexavalent chromium or by switching to trivalent chromium, which removes the need for a mist-suppressing surfactant. The first approach has already been used for 10 years and is feasible, although initially more expensive due to the costs for modifications of the plant. The second approach is not yet used at large scale and might require more research and time for implementation. The use of PFAS in chrome plating (electroplating) is substitutable. Whether or not PFAS can be replaced in the etching pretreatment process is unclear.

3.5. Chemical-Driven Oil Production.

Uses. The production of crude oil and gas generally occurs in three steps: (i) primary oil recovery (providing 12−15% of the oil),[59] (ii) secondary oil recovery (or "water flooding", providing an additional 15−20% of the oil); (iii) enhanced oil recovery (EOR), aiming to collect some of the remaining 60−70% of the oil.[59] EOR techniques are classified in thermal processes, gas injection, and chemical flooding.[59]

Fluorinated surfactants are used during water flooding (secondary oil recovery) and in EOR.[60] When used in water and chemical flooding, fluorinated surfactants increase the permeability of the formation by reducing the interfacial tension between the reservoir surface and the aqueous phases.[61] Fluorinated surfactants also increase the wettability of the rock.[62] In chemical flooding, fluorinated surfactants are used to render the surfaces of the oil reservoirs hydrophobic and oleophobic. This supports the displacement of the oil from the sand and rock formations.[63] Fluorinated surfactants are also used in fracturing rock formations penetrated by the wellbore, where they act as part of a foaming agent that initiates and extends the fractures in the formation.[64] It has also been described that fluorinated surfactants are used to generate foam that is stable in contact with the crude oil, while imbibing and transporting the oil through the subterranean formation.[61]

Overall, PFAS are used for several different functions in chemical-driven oil production. Generally, they are used because they have a very low surface tension (between 17 and 24 mN/m) and are chemically and thermally stable.[61]

Availability of Alternatives. Multiple efforts have been made to synthesize alternative surfactants with the same physicochemical properties as PFAS.[62] Branched hydrocarbon surfactants are an alternative which could replace fluorinated surfactants in EOR. Kiani et al. (2019)[62] studied a non-fluorinated anionic surfactant, iC18S(FO-180), CAS No. 181355−81−7, see structure in Figure 1A. C18S(FO-180) has a surface tension of around 25 nM/m and can enhance the oil recovery up to 72%.[62]

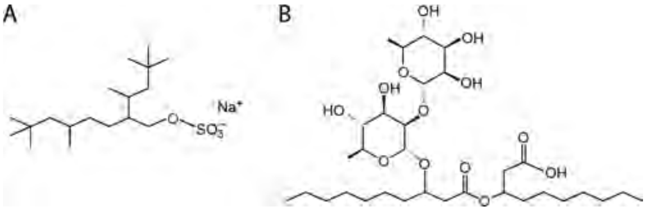

Figure 1. A: surfactant iC18S(FO-180), according to Alexander et al. (2014),[65] Kiani et al. (2019);[62] B: a rhamnolipid (CAS 4348−76−9) as an example of glycolipids used as biosurfactants.

Another potential additive in EOR is hydrophobin-II (HFBII).[59] HFBII is a small cysteine-rich amphiphilic protein from the hydrophobin family (HFBs). HFBs are naturally produced by fungi and comprise about 100 amino acids. HFBs can self-assemble at hydrophilic−hydrophobic interfaces into an amphipathic film. This protein film renders hydrophobic surfaces of gas bubbles, liquids, or solid materials wettable, while hydrophilic surfaces can be turned hydrophobic.[66] The ability of HFBs to self-assemble at oil−water interfaces and stabilize oil droplets makes them candidates for a PFAS-free EOR process. The company BASF has filed a patent for extracting hydrocarbons from oil sand with water and a hydrophobin.[67] Another patent from BASF claims the use of hydrophobins as auxiliary-emulsifying agents for a drilling fluid.[68] However, HFBII can only lower the air/water surface tension to 35 mN/m, which is still too high for EOR.[59] Blesic et al. (2018)[59] concluded that HFBII is not promising for EOR but also noted that an appropriate cosurfactant (e.g., medium-chain alcohols) may improve the performance of HFBII.

Beside hydrophobins there are other biosurfactants that have been used in microbial-enhanced oil recovery (MEOR). These include glycolipids (see Figure 1B), lipoproteins or lipopeptides, phospholipids, fatty acids or natural lipids, and particulate and polymeric biosurfactants. Examples for each group are given in the SI-1, Section 2.6. According to Varjani

(2017),[69] oil release from porous media may involve processes such as (a) dissolution of inorganic carbonates by bacterial metabolites, (b) production of bacterial gases that decrease the viscosity of oil, (c) generation of surface-active substances or wetting agents by some bacteria, and (d) high affinity of bacteria for solids, displacing oil by growing between oil and rock.

There is not much information about how well MEOR works in comparison to EOR with chemicals. However, MEOR has already been applied in the field. For example, in India the Oil and Natural Gas Corporation Limited have developed a technology for MEOC.[70] The technology has been implemented in 130 oil wells and an encouraging success rate has been reported.[70]

In the U.S., 27% of the oil reservoirs and 40% of the oil-producing carbonate reservoirs may be suitable for MEOR.[71] However, effective MEOR application may require substantial research on a case-by-case basis, because the environment will be unique with respect to soil and rock formation characteristics as well as physical and chemical conditions.[71]

Alternatives Assessment. Chemical identification was possible for surfactant iC18S. However, the substance does not have C&L notifications or a REACH registration, which precluded an assessment of human-health hazards. Regarding environmental hazards of iC18S, EPI Suite estimates a low BCF (below 100) and a degradation half-life in water of 81 days. Whereas this half-life exceeds the EU's criteria for persistent substances (40 days in freshwater; 60 days in marine water), it is still much lower than the environmental degradation half-lives of PFAS.

Different amounts of data were found for different biosurfactants as identified by Varjani (2017).[69] According to Banat (1995)[72] and Lazar et al. (2007),[73] biosurfactants are biodegradable and have low toxicity, but data are scarce. There are studies available where no mutagenic effects and no reproductive toxicity were observed or expected for rhamnolipids,[74] sophorolipids,[75] and surfactin.[76] Carcinogenicity data are lacking. Where biodegradation and toxicity data are available, they show that biosurfactants are readily biodegradable,[74,75] or at least not persistent,[77] with low aquatic toxicity.[74−76] There are limited data on bioaccumulation, but sophorolipids have a log K_{OW} < 4.5,[75] suggesting that bioaccumulation is unlikely. For hydrophobin-II, no sufficient data for an assessment were found.

Conclusion. PFAS have been technically important in oil recovery. Alternatives are being explored and in some cases already in use. Therefore, PFAS can be replaced in the oil industry, but not equally well in all types of reservoirs and probably with research and development needed on a case-by-case basis. At least some of the PFAS uses are substitutable.

3.6. Processing Aids for Aqueous Emulsion Polymerization of Fluoropolymers.

Uses. Fluoropolymers can be produced by several methods, including suspension polymerization, aqueous emulsion polymerization, solution polymerization, polymerization using supercritical CO_2, and polymerization in the gas phase. The manufacturing process applied also depends on the commercial grade of the fluoropolymer that is manufactured (e.g., granular versus fine-powder PTFE).[78] Patents for each of the main manufacturing processes are provided in the SI-1.

The most commonly employed polymerization methods include suspension polymerization and aqueous emulsion polymerization. Suspension polymerization generally does not involve (fluorinated) surfactants; it results in larger polymer particles than aqueous emulsion polymerization[79] and is used, for example, for granular PTFE.[78] Aqueous emulsion polymerization has traditionally involved the presence of a fluorinated surfactant, which is used to stabilize the polymer particles formed.[79] Aqueous emulsion polymerization is used to produce fine-powder and dispersion products.[78,80]

Availability of Alternatives. Fluoropolymer manufacturers are exploring novel processes to eliminate the use of PFAS in aqueous emulsion polymerization. For the production of polyvinylidene fluoride (PVDF), processes with fluorine-free emulsifiers have been implemented by multiple manufacturers.[81,82] One manufacturer has made this transition since 2008,[81] and its patents disclose varied processes that use fluorine-free alternative emulsifiers including blocks of polyethylene glycol, polypropylene glycol and/or polytetramethylene glycol,[83−87] alkyl phosphonate,[88] vinyl/acrylic acids,[89] polyvinyl/acrylic acids,[90] alkanesulfonates,[91] siloxanes,[92] and 3-allyloxy-2-hydroxy-1-propanesulfonic acid salts.[93] More information on the specific substances is provided in Section S2.7 in the SI-1. The same section in the SI-1 also includes patents from several other manufacturers on fluorine-free emulsifiers in the polymerization of PVDF, but it is unclear whether or not they are actually in use.

Fluorine-free emulsifier-based processes for manufacturing other fluoropolymers, including fine-powder and dispersion PTFE, have been patented,[94−98] but, to the best of our knowledge, are not yet implemented.

Alternatives Assessment. Some of the patents by Arkema from 2006 to 2020[83−87] use multiple combinations of 14 glycol-based polymers as emulsifiers. The hazards of these emulsifiers would depend on which of the substances are used. As these are all polymers, EPI Suite could not be run and hazard data were collected from CLP and REACH registrations only. Of the seven substances with available data in CLP and REACH, four would constitute a reduction of hazards. However, there is also one substance that is on the REACH Authorization list because of endocrine-disrupting properties, one that is toxic to aquatic life with long-lasting effects and one that may damage fertility or the unborn child (for more information see SI-1 and SI-2).

All five patents from Arkema[83−87] state that the invention "is generally practiced" with PEG, PPG, and/or PTMG as the sole emulsifiers. PPG and PEG have REACH registrations that provide evidence that the substances are not mutagenic, toxic to reproduction, toxic to the aquatic environment, persistent, or bioaccumulative. PPG also has evidence that it is not carcinogenic, whereas PEG has no evidence for this endpoint. PPG and PEG would be clear improvements in both human-health and environmental hazards. For PTMG there are insufficient data for an assessment. Overall, the use of a polyolefin glycol emulsifier most likely constitutes a reduction in human-health and environmental hazard. However, the patent mentions a variety of terminal groups that may be used in the polyolefin glycols. Because biodegradation of PEG and PPG needs alcoholic end groups,[99] some of these end groups may impair the degradability of the substances.

The alternatives assessment of the 26 other emulsifiers patented by Arkema[88−93] shows again that most of them would most likely constitute a reduction in human-health and environmental hazard. However, there are also substances among them that are very toxic to aquatic life with long-lasting

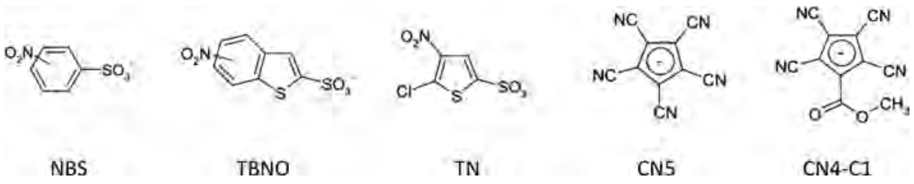

Figure 2. Fluorine-free PAGs proposed by Glodde et al. (2010)[101] and Liu et al. (2010).[102]

effects and one substance that is suspected of damaging fertility or the unborn child (for more information see SI-1 and SI-2). Again, it very much depends on which of the emulsifiers are actually used as patents tend to cover the broadest scope of possibilities.

Conclusion. PFAS emulsifiers have been technically important in aqueous emulsion polymerization. Alternatives have been developed for PVDF, but not yet for other fluoropolymers. The alternatives found for PVDF show that manufacturers need to carefully evaluate and manage their alternatives as some of the patented substances are toxic to aquatic life or toxic for reproduction. According to Arkema, during nearly 15 years of research, many alternatives have been studied; some only enabled a good polymerization process but were not able to meet the risk objectives and some were able to meet both, which proves that it is possible to produce PVDF with alternative emulsifiers exhibiting a good ecotoxicological profile. Beyond the question of PFAS emulsifiers, the essentiality of using fluoropolymers would also have to be assessed.

3.7. Semiconductor Industry.

Overview. Semiconductor manufacturing is a multistep sequence of photolithography and chemical processing steps, comprising over 500 steps in total.[47] Photolithography is the process by which the circuits are created on the semiconductor wafers.[100] Here, a thin film of a photoresist (light-sensitive polymer) is first applied to a substrate, such as silicon-based wafers. Then, light is used to transfer a geometric pattern from a photomask to the photoresist on the wafer. The photoresist is altered when exposed to light, and this allows structures to be built up on the wafer.[100] Photoresists require the presence of (fluorinated) photoacid generators (PAGs) that enable the etching of images smaller than the wavelength of visible light.[47] Other uses of PFAS in the semiconductor industry include, e.g., developer and rinse solutions. More information is provided in the SI-1.

3.7.1. Photoacid Generators (PAGs).

Uses. PAGs are components of a photoresist formulation that are able to generate strong acids under light irradiation. PAGs based on perfluorooctanesulfonic acid (PFOS) were used for a long time and then replaced by PAGs based on perfluorobutanesulfonic acid (PFBS) or PAGs based on functionalized fluoroethanesulfonates.[101] However, these alternative substances are also PFAS, so there is still a need for fluorine-free alternatives.

Availability of Alternatives. One of several requirements in the design of a substance that can form a strong acid is the ability to delocalize the negative charge of the resulting anion. This can be achieved, for example, through the π-system of a benzene ring. The isomers of nitrobenzenesulfonate (NBS) are an example of such PAGs.[101] Preliminary work has also shown that acceptor-substituted thiosulfonate anions exhibit good performances as strong acid generators. Specific examples include benzo[b]thiophene-2-sulfonic acid, 4(or 7)-nitro-, ion(1-) (TBNO) or 2-thiophenesulfonic acid, 5-chloro-4-nitro-, ion(1-) (TN). Another possibility for strong acid generation are PAGs based on acceptor-substituted aromatic anions, such as pentacyanocyclopentiadienide (CN5) or methoxycarbonyl-tetracyanocyclopentadienide (CN4-C1)[102] (Figure 2).

Glodde et al. (2010)[101] and Liu et al. (2010)[102] evaluated some basic performance metrics of the five nonfluorinated PAG anions in photoresist formulations with triphenylsulfonium (TPS) and compared the results to photoresist formulations of perfluorobutanesulfonate as anion with TPS (TPS PFBS). The fluorine-free formulations showed promising results in optical clarity and thermal stability compared to TPS PFBS. However, the fluorine-free PAGs did not perform as well as the TPS PFBS with respect to sensitivity, line-width roughness, and resolution. Fluorine-free PAGs developed by IBM are described in various patents (see SI-1) and have also been officially announced.[103]

Alternatives Assessment. An assessment of alternatives could be carried out for the PAGs where the chemical structures are known. No REACH registrations were found for the corresponding CAS numbers, but C&L notifications were found for two isomers of NBS. C&L data for NBS indicated that this substance has no CMR properties. Environmental hazard data were estimated for NBS, TBNO, TN, and CN5, all of which indicate lower environmental hazard than for PFAS. Calculated degradation half-lives are between 21 and 42 days. All calculated BCF values are below 1.

Conclusion. According to the estimated persistence and bioaccumulation potential of these compounds, the alternatives reviewed seem to be less hazardous than PFOS or PFBS and also seem to be capable of generating strong acids. However, as mentioned above, these fluorine-free PAGs have some technical limitations which are currently prohibitive to high-volume manufacturing. Thus, there is still a need for additional research and development of fluorine-free PAG alternatives. In addition to research focused on the replacement of PFAS with safe and effective nonfluorinated alternatives, research is also needed to develop new technologies for PFAS removal and destruction, as long as PFAS cannot be replaced in these applications. As the viability of photolithography chemicals requires the simultaneous satisfaction of multiple overlapping performance requirements, and the manufacture of semiconductors relies on many interlocking steps, the use of fluorine-free PAGs will require additional technological innovation and process adaptations to ensure viable and effective solutions that can be manufactured reliably.

3.7.2. Immersion Liquid, Developer Solution, and Rinse Solution.

Uses. Besides use in photoresists, PFAS are also used in other parts of immersion lithography. A patent from the Taiwan Semiconductor Manufacturing Company[104] describes the use of fluorinated surfactants as additives to developer and chemical rinse solutions. PFAS are used in these solutions to lower the contact angle of the solutions and, thus, reduce watermark defects after dry spinning. The employment of

PFAS may also help to avoid pattern collapse during spin-drying.[104]

Availability of Alternatives. A patent from BASF[105] refers to the aforementioned patent US20080299487[104] and discloses that a new liquid (and a method of using it) for immersion photolithography of photoresist layers has been developed that allows for a high aspect ratio for line-space dimensions of 20 nm and below without causing pattern collapse, line edge roughness, and watermark defects, without the use of fluorinated surfactants. The patent remains vague regarding the alternative substance/s employed and describes only the possible anionic and cationic functional groups, see SI-1. However, it is mentioned that the newly developed fluorine-free liquid may be used as an immersion liquid for immersing photoresists during irradiation, as developer solution for photoresist layers, and as chemical rinse solution for rinsing the patterned material layers.[105] It is also mentioned that the method does not only work for immersion photoresist layers, but also for extreme UV (EUV) and electron beam (eBeam) photoresist layers. EUV lithography recently became ready for mass production and is the most suitable candidate for the next pattern-feature size (5 nm node).[106,107]

Alternatives Assessment. No information is available on the hazards of the alternatives proposed.

Conclusion. It seems that the alternative described by Klipp et al. (2012)[105] fulfills the technical functions needed and has potential also for future developments in the semiconductor industry. As such, it is a step toward the application of PFAS-free alternatives, which may make PFAS in these uses substitutable. More information would be needed on the physicochemical properties and hazards of these materials.

Conclusion. Even though PFAS may currently be essential in some uses in the semiconductor industry, it has been recognized that PFAS are problematic for the environment and efforts are being made to replace PFAS with fluorine-free alternatives.[108] The Semiconductor Industry Association reported that the semiconductor industry globally has successfully completed the phase-out of PFOS,[47] but PFOS has often been replaced by other shorter-chain PFAS. The two examples above show that fluorine-free alternatives have been patented but that more research is needed to implement them.

4. DISCUSSION

The case studies illustrate the diversity and complexity of the task of a PFAS phase-out. In several cases, the technical function of PFAS directly derives from their water- and oil-repellency and it is relatively clear that PFAS can be replaced by PFAS-free water- or oil-repellent substances (bicycle lubricants, carpets, cleaning products). In chrome plating and fluoropolymer production, the technical function of PFAS is also well-defined, but the conditions and requirements are so demanding that finding alternatives is challenging. Finally, in the semiconductor industry and in oil recovery, PFAS have several different technical functions and/or are used in a multitude of process steps, which makes it more difficult to find suitable alternatives, and many different substances and/or process modifications may be needed.

4.1. Availability of Alternatives. An extensive search of the available literature was conducted. However, the list of identified alternatives is not exhaustive and there might be more (and maybe even better) alternatives. An important point regarding patents is that patents generally reflect an early stage of research and development and cover a broad range of options that might work in processes to be further developed. Therefore, they mostly do not describe solutions that are ready to be implemented, and further research and development over several years may be needed before a viable solution is available.

Alternatives that are already on the market were identified for four of the seven case studies: bicycle lubricants, carpets, household cleaning products, and chrome plating. We did not investigate industrial cleaning products as the specifications for these products might differ substantially between different use areas. The identified alternative products and processes in the four use areas will not be suitable for all specific uses in these areas. However, they show that innovation has happened and that there are feasible options to replace PFAS in these uses. The case of chrome-plating illustrates that sometimes a change in process conditions (underpressure) can be as effective as finding a chemical substitution.

Alternatives for processing aids in aqueous emulsion polymerization have been identified for PVDF but not for other fluoropolymers. However, there are numerous patents that describe fluorosurfactant-free polymerization processes for other fluoropolymers as well, suggesting that it is also possible to make fine-powder PTFE without fluorinated processing aids, but that it is more challenging than for PVDF. Developing PFAS-free emulsifiers requires extensive research and development and a long-term investment (probably more than 5 years). Furthermore, the solution found by one manufacturer will be patent-protected and not directly available for others, which also explains why, for example, in China perfluorooctanoic acid (PFOA) is still used.

The uses of PFAS in chemical-driven oil production and the semiconductor industry and the availability and suitability of alternatives are more difficult to assess. There are alternatives to PFAS also in chemical-driven oil production, but it is unclear how well they work compared to PFAS and what level of performance is necessary in each application. Substantial research might be needed on a case-by-case basis; ultimately, only technical experts in the area of oil drilling might be able to assess the alternatives. A similar situation occurs in the semiconductor industry. PFAS in the semiconductor industry are used in so many different steps and for so many different functions that it is difficult to judge the alternatives, in particular as processes build on each other and are very complex. However, the examples investigated here (PAGs and immersion liquid, developer solution, and rinse solution) show that there is awareness of the PFAS problem in the field and that research into alternatives is ongoing.

4.2. Alternatives Assessment. In the assessment of alternatives, we used a simple and pragmatic approach (information present in the C&L and REACH databases, estimates from EPI Suite, where possible). A more detailed assessment would not have been feasible because of the large number of substances to be assessed and the lack of information about many of the substances. For an initial comparison for the purposes of illustrating the process and the data needs, the approach is sufficient.

The lack of publicly accessible information about many of the alternatives limits the scope of alternative assessments. For many substances, even the chemical identity was not known (and not revealed by the manufacturers contacted) and basic physicochemical properties and results from degradation and toxicity tests were lacking. In several cases, some qualitative information was available ("plant-based"; list of substance groups used such as polyolefin glycols or possible anionic and cationic groups), and for some substances, the chemical identity and structure were available so that some basic properties could be estimated.

Several alternatives were sufficiently characterized so that at least a partial comparison of their properties with those of the PFAS used could be performed. Often, the alternatives offer significant improvements compared to PFAS, at least with respect to persistence. However, it has to be reiterated that more chemical property and toxicity data for the alternatives need to be generated and made available in the public domain.

4.3. Transition to PFAS-Free Alternatives. For the consumer products investigated, the transition to PFAS-free alternatives is feasible without substantial problems. Alternatives are available and labeled and marketed as PFAS free or fluorine free. Regulatory requirements may help to transition to these alternatives. An example is the U.S. State of California, where they request carpet and rug manufacturers whose products contain PFAS to submit a Priority Product Notification (PPN) by August 30, 2021.[109] Within 7 months after submitting the PPN, manufacturers need to remove the PFAS from the products.

In the area of chrome plating, a substantial step forward has been made and even in hard-chrome plating, where use of chromium(VI) was seen as a necessity, processes based on chromium(III) have been developed and are used by two manufacturers,[56,110] and also for the process with chromium(VI), PFAS-free versions exist. However, approximately 22% of the authorizations under REACH are still for chrome plating with hexavalent chromium,[111] which shows that more efforts are needed to support the transition.

In the areas of fluoropolymer production, oil recovery, and the semiconductor industry, the situation is more complex. Because of the demanding and highly diverse conditions or the many interlinked processes with many different PFAS uses, much broader assessments are required. In all three areas, the need for a replacement of PFAS has been recognized and research and development are underway. However, it is not clear to what extent and by how many manufacturers the alternatives are already in use and how much of the market is still based on processes using PFAS. In these areas, it may be desirable to establish technical expert committees that act as an interface between science/engineering and policy making. This would create greater transparency and make it easier for policy makers to follow the process and facilitate next steps. Stronger requirements to reduce emissions of PFAS-containing waste through, for example, stronger regulation and enforcement would increase the need to look for PFAS-free alternatives.

Finally, the transition requires better access to information about both PFAS uses and alternatives and their properties. For a group of chemicals of such high concern to environmental and human health, it is justified to require more transparency and publicly accessible data. What is needed at a minimum is information about the chemical identity and some minimum data on toxicity, degradability, and intended uses. This information should be available to the general public, and also within supply chains. A situation in which a product manufacturer receives a PFAS-free chemical from a chemical manufacturer and uses it in a consumer product without knowing the identity of the chemical, but just relies on the safety-data sheet, is not desirable.

Overall, the phase-out of PFAS may proceed on several different "tracks" with different time scales and priorities. One set of factors that determine these time scales and priorities are, obviously, the amounts of PFAS used and the extent to which the uses are open and dispersive. Another set of factors is the complexity of the assessment tasks and the amount of research and development needed. For a task of such high importance, but also complexity, a roadmap outlining these different tracks and corresponding timelines will be desirable.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c03732.

A list of the manufacturers contacted, additional information on the case studies including information on an eighth case study (climbing ropes) (PDF)

MS Excel document listing data from the alternatives assessments (XLSX)

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Notes

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The Sources and Impacts of Tropospheric Particulate Matter

By: Robert J. Griffin (*Department of Civil and Environmental Engineering, Rice University*) © 2013 Nature Education

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Aerosols vary in composition, size, concentration, and source. They profoundly affect climate, visibility, human health, and biogeochemical cycling.

Aa Aa Aa

Introduction

Aerosol is condensed-phase material suspended as discrete particles in a gas. Atmospheric aerosol, termed particulate matter (PM), is critically important because of its impact on climate, visibility, biogeochemical cycling, atmospheric reactivity, and human health. PM diameter ranges from several nanometers to several micrometers (Willeke & Whitby, 1975; McMurry *et al*., 2000); larger particles settle by gravity too rapidly to be considered aerosol. Smaller groups of molecules are described as gas clusters. PM size is described by a continuum size distribution in which $dN/d(lnD_p)$ (# cm^{-3}) represents the number concentration of particles in a size bin between lnD_p and $lnD_p + dlnD_p$, where D_p is particle diameter (assumed spherical) (Whitby & Sverdrup, 1980).

By adding up the particles in all bins, the total number of particles per cm^3 is found. Number concentrations of particles range from tens of particles (remote) to millions of particles (urban) per cm^3, indicating the importance of proximity to sources in determining particle number concentrations (Pandis *et al.,* 1995).

Particle sizes are determined by the mechanism through which the particles enter the atmosphere. For example, homogeneous nucleation, in which a new particle is formed directly from the gas phase, creates particles on the order of a nanometer in diameter (Hirsikko *et al.,* 2011). These particles grow via coagulation or gas-to-particle conversion to hundreds of nanometers. Nucleation and gas-to-particle conversion of material are examples of secondary aerosol formation processes. In contrast, aerosol material emitted to the atmosphere directly is known as primary. Generally, particles with diameters smaller than 100 nm are known as ultrafine or Aitken-mode particles (Seinfeld & Pandis, 2006). Collectively, all particles smaller than 2.5 micrometers ($PM_{2.5}$) are known as fine aerosols. Particles with diameters between 2.5 and 10 micrometers are correspondingly known as coarse and typically are primary particles generated by physical-mechanical processes (Seinfeld & Pandis, 2006). Aitken-mode particles quickly coagulate and grow due to condensation of vapor species. Because coarse particles settle from the atmosphere relatively rapidly, particles accumulate in the diameter range of hundreds of nanometers and reside in what is known as the accumulation mode (Seinfeld & Pandis, 2006).

Sources of Primary Aerosol

Globally, natural sources of primary aerosol dominate the mass emissions of PM. Because approximately 75% of the Earth's surface is ocean, sea salt is the biggest contributor (Lewis & Schwartz 2004). There are two types of ‘sea salt' particles. Jet drops consist of a brine core (dominated by sodium and chloride) surrounded by an organic film (Lewis & Schwartz 2004). These particles are formed from wave crashing and other mechanical processes. In contrast, film drops are primarily organic and formed from less harsh mechanical processes such as bubble bursting through the sea surface microlayer (Lewis & Schwartz 2004). Another natural source of primary aerosol is soil dust, generated primarily through wind action in arid regions (Mahowald *et al*., 2005). Soil dust particles consist of mineral materials. Primary biological aerosol particles that consist of plant waxes, pollens, spores, and similar material also are natural examples of PM (Despres *et al*. 2012).

Anthropogenic sources of primary PM include industrial and combustion processes. The nature of industrial particles depends on the process, but combustion particles generally are dominated by black or elemental carbon and heavy organic material such as polycyclic aromatic hydrocarbons (Bond *et al.* 2007).

Sources of Secondary Aerosol

Nucleation of new particles is one formation route for secondary particles. It is believed that sulfuric acid (H_2SO_4), ammonia (NH_3) and other amines, and water are involved in this process (Benson *et al*., 2011; Kirkby *et al*. 2011), with speculation that organics also participate (Vaattovaara *et al*. 2006).

Gas-to-particle conversion (partitioning to existing PM via adsorption or absorption) is another pathway through which secondary PM is formed (Pankow, 1994). Species such as H_2SO_4 that have a low vapor pressure can relatively easily undergo such a phase transition. Secondary inorganic PM also can form thermodynamically (salt formation). For example, NH_3 can combine with H_2SO_4, nitric acid (HNO_3), or hydrochloric acid to form ammonium salts when the concentrations of these precursor gases are large enough (Tang & Munkelwitz 1994). Because of the hygroscopicity of many inorganic species, water is often taken up, increasing particle size and mass (Petters & Kreidenweis 2007).

Secondary organic aerosol (SOA) is more complex. It is assumed that a mixture of liquid organics provides a medium into which SOA species are absorbed (Pankow 1994). In general, it is believed that the species that undergo this process are functionalized (e.g., carbonyls, carboxylic acids, alcohols, nitrates) oxidation products of primary volatile organic compounds that are present in the atmosphere as a result of both natural and anthropogenic processes (Hallquist *et al*. 2009). Oligomerization of species in the condensed phase leads to humic-like substances (Kalberer *et al*. 2004). In addition, certain species heterogeneously react at the surface of a particle and are converted into material that remains in the condensed phase (reactive uptake) (Kroll *et al*. 2005).

Secondary PM also forms through cloud processing. Clouds continuously undergo evaporation/condensation cycles. During a period in which clouds have significant water content, (partially) soluble species are absorbed from the gas phase into the droplets. Once there, they can be oxidized into species with decreased volatility, such that they remain as particles once the cloud droplets evaporate. This route is believed to be relevant for SOA (Carlton *et al.* 2006) and secondary sulfate formation, the latter of which is catalyzed by the presence of certain metals in cloud water (Hoffmann & Calvert 1985). An overview of the chemical and physical characteristics, growth and loss mechanisms, and sources of particles in the troposphere is given in Figure 1.

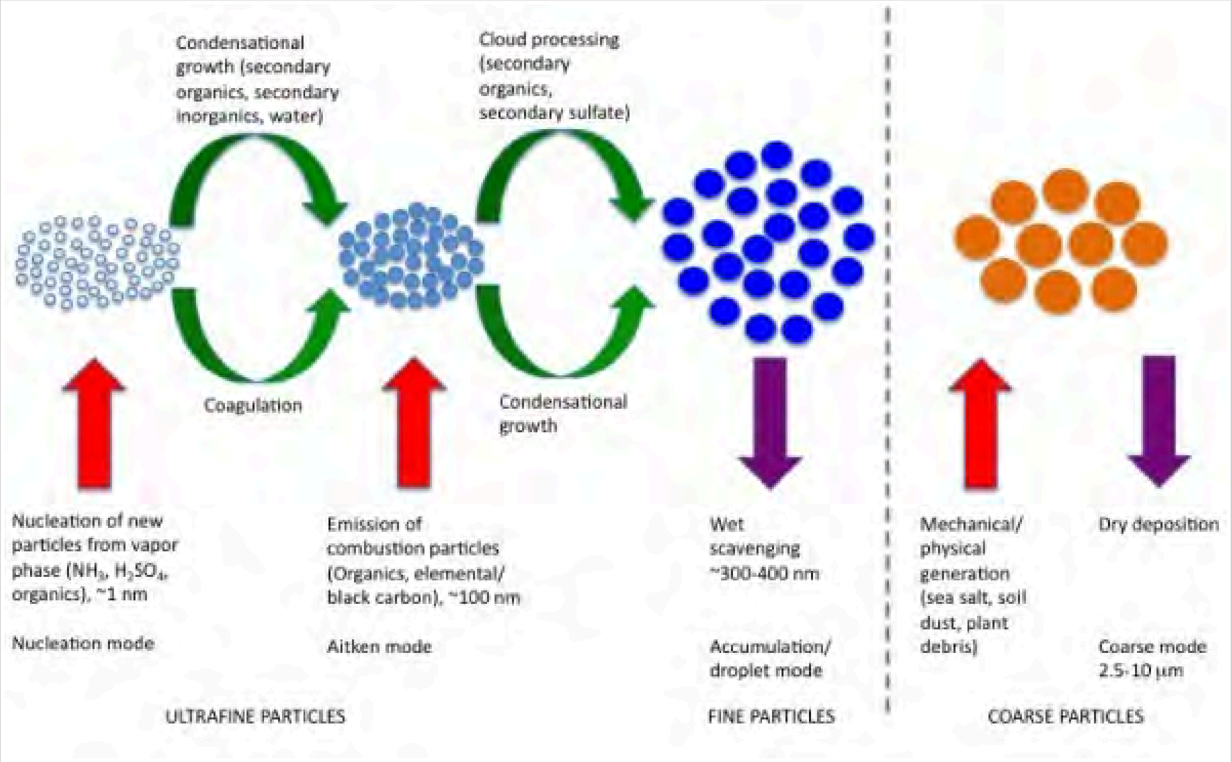

Figure 1

An overview of the chemical and physical characteristics, the growth and loss mechanisms, and the sources of particles in the troposphere. Note the decreasing number of particles as size increases. Red arrows represent particle source pathways, purple arrows represent particle loss pathways, and green arrows represent particle growth mechanisms.

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Impacts of PM

Particles cause direct and indirect climate effects. The direct effect on climate results from altering the global radiation balance through the scattering and absorptive properties of particles in the atmosphere (Charlson *et al*. 1992). PM also influences cloud formation and lifetime. In the upper troposphere, particles serve as ice nuclei (IN) through both homogeneous freezing (direct freezing of a particulate liquid solution) and heterogeneous freezing (freezing caused by the contact of separate liquid and solid phases) mechanisms. Larger, insoluble particles tend to be the most efficient IN, as they provide a lattice upon which ice forms. In the lower troposphere, soluble particles of the appropriate size activate to cloud droplets by behaving as cloud condensation nuclei (CCN) (Twomey 1974; Albrecht 1989; DeMott *et al.*2010). Activation occurs when particles are exposed to supersaturated water vapor (relative humidity in excess of 100%) and take up enough water to grow to a stable cloud droplet. As the number of CCN increases, the size distribution of the cloud droplets shifts to smaller sizes, increasing cloud reflectivity and lifetime. These cloud-particle connections generally increase Earth's albedo, leading to a change in the planetary radiation balance. Although uncertain, it is believed that this overall aerosol indirect effect (~-0.7 W m^{-2}) combined with forcing associated with the direct effect (~-0.5 W m^{-2}) is on the same order of magnitude as, but opposite in sign, to the climate forcing caused by greenhouse gases (~+1.66 W m^{-2}), as shown in Figure 2 (Intergovernmental Panel on Climate Change, 2007).

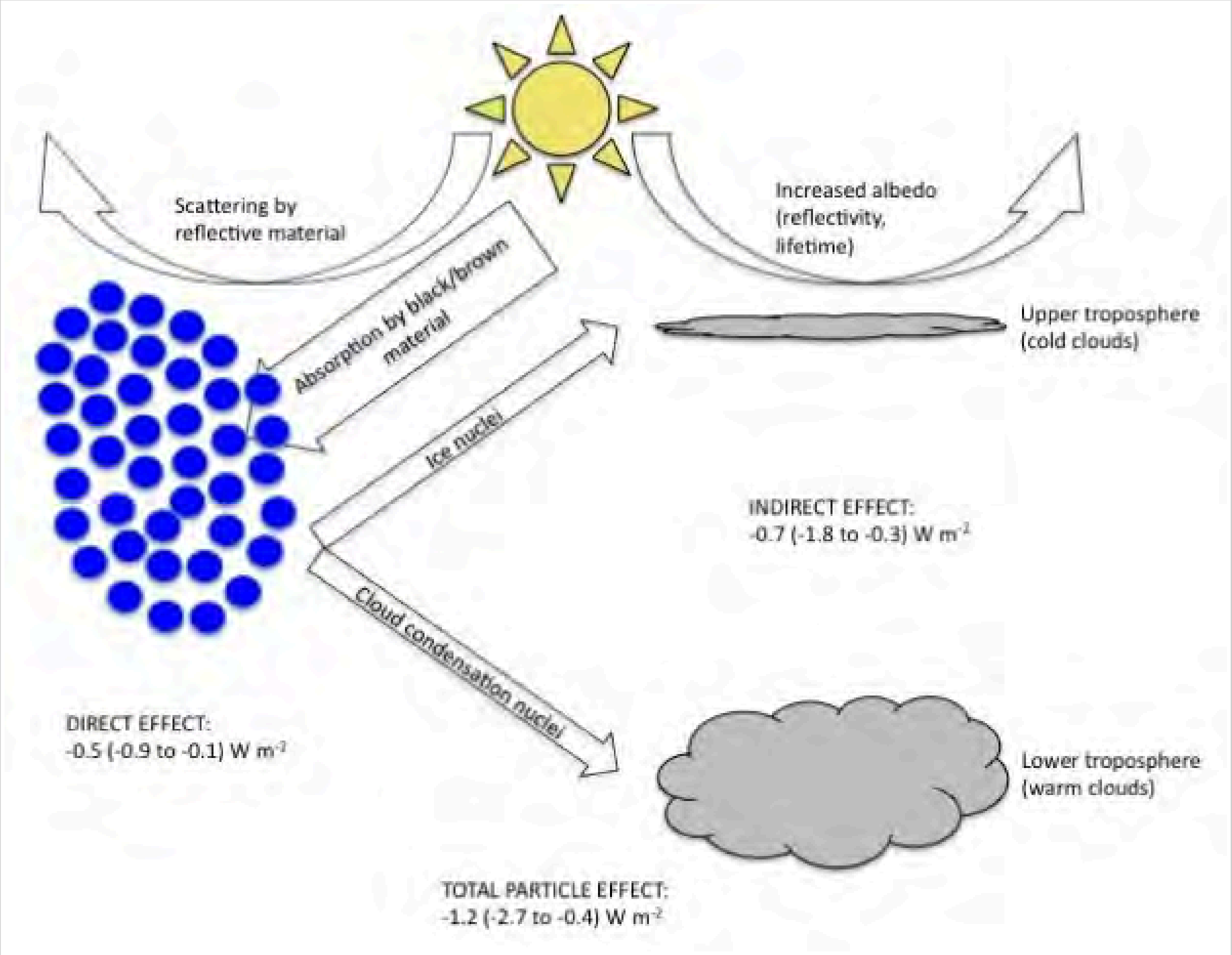

Figure 2

An illustration and description of the relative magnitude of the direct and indirect effect of particles on radiative forcing of climate. For comparison, greenhouse gas radiative forcing is estimated to be +1.66 (+1.49 to +1.83) W m^{-2} (IPCC, 2007).

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Because of their optical properties, particles significantly impair visibility (White & Roberts, 1977). Accumulation mode particles typically reside in a size domain of approximately 300-400 nm. This corresponds to the wavelength of the visible portion of the solar spectrum. According to Mie theory, particle scattering is enhanced when particle size and light wavelength are similar (Bohren & Huffman 1983). Scattering prevents light from reaching an object in the distance and getting reflected back to a viewer's eye, leading to visibility degradation. Visibility degradation is quantified through an extinction coefficient (b_{ext}). In the Beer-Lambert law, b_{ext} and a distance determine the decrease in intensity of light of a given wavelength over that distance.

Because of suspension, transport, deposition, and resuspension, particles provide a mechanism by which material is transported between various environmental media and locations. For example, a small part of the nitrogen cycle includes emission of nitric oxide (NO) from soil (Kulmala & Petaja, 2011). The NO is oxidized in the atmosphere to HNO_3. As described above, HNO_3 can combine with NH_3 to form ammonium nitrate salt. This particle deposits to the surface at some location downwind, completing the cycle between the atmosphere and the Earth's surface.

The presence of particles in the atmosphere also affects chemical processes that can occur. For example, in an urban area into which marine air is transported, HNO_3 displaces chloride from sea salt, leading to the liberation of chlorine and the formation of sodium nitrate (Gard *et al*. 1998). The presence of particles provides a surface upon which heterogeneous reactions occur (George & Abbatt 2010). The curvature of particles also enhances photolytic reactions relative to homogeneous photolysis reactions (Nissenson *et al*. 2006).

The primary motivation behind the establishment by the United States Environmental Protection Agency (USEPA) of National Ambient Air Quality Standards (NAAQS) for both $PM_{2.5}$ and PM_{10} (based on mass of particles per volume of air) is the human health consequences suffered by the exposed population. A positive correlation between statistical rates of morbidity and mortality and ambient PM mass concentrations exists (Schwartz *et al*. 1996).

Inhalation and deposition to the lungs of PM cause or exacerbate cardiovascular issues. Particles that are small enough also cross tissue barriers into the bloodstream and are transported throughout the body. Questions remain regarding the link between human health impacts and specific constituents because of the complex mixture typically associated with PM. It is also possible that the USEPA will move toward a number concentration-based PM NAAQS (Reche *et al*., 2011). The smallest particles dominate the number concentration of particles but contribute very little to the total particle mass concentration. Therefore, any standard based solely on mass concentration may not protect the population from health impacts of the numerous particles that do not contribute significantly to mass concentration.

Conclusion

Significant research over the past decades has elucidated much about the chemistry, physics, and impacts of tropospheric aerosols. However, as the possibility of a number-based NAAQS is considered, it is imperative that processes that greatly influence particle number, such as homogeneous nucleation, continue to be investigated. The probability of more stringent mass-based NAAQS for PM indicates the need to continually focus on emission control of primary PM, the chemistry leading to secondary PM, and best practices for secondary PM precursor control. In addition, it is critical that scientific uncertainty in understanding the roles that aerosols play in climate forcing and human health be reduced.

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Outline | **Keywords** FEEDBACK

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- Conservation of Biodiversity

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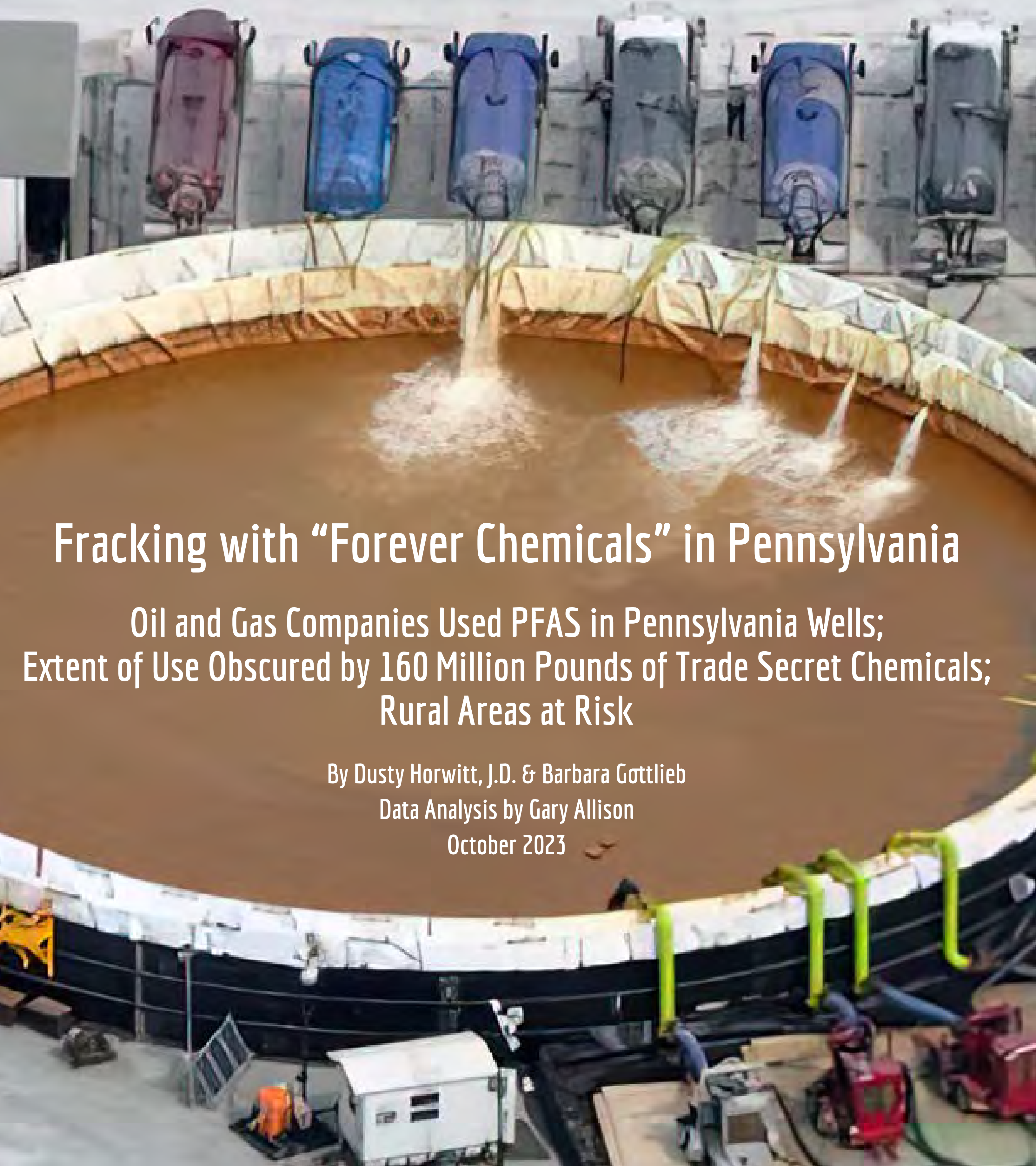

Fracking with “Forever Chemicals” in Pennsylvania

Oil and Gas Companies Used PFAS in Pennsylvania Wells; Extent of Use Obscured by 160 Million Pounds of Trade Secret Chemicals; Rural Areas at Risk

By Dusty Horwitt, J.D. & Barbara Gottlieb
Data Analysis by Gary Allison
October 2023

CONTENTS

Cover photo: Fluids impoundment at Wherry unconventional gas well pad, West Bethlehem Township, Washington County, Pa., April 5, 2021. Photo credit: Courtesy of Marcellus Air.

Maps by Matt Kelso, FracTracker Alliance

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EXECUTIVE SUMMARY

Information unearthed and analyzed by Physicians for Social Responsibility (PSR) shows that since 2012, oil and gas companies* used in Pennsylvania's unconventional or "fracking" gas wells a class of extremely toxic and persistent chemicals known as PFAS. During that same period, the companies used 160 million pounds of unidentified chemicals that could themselves be PFAS. The companies withheld these chemical identities from the public as "trade secrets," a practice allowed by state law.

PFAS are a class of chemicals known for their toxicity at extraordinarily low levels, their multiple negative health effects including cancer, and their persistence in the environment, leading to their nickname, "forever chemicals." Using these chemicals may be particularly risky because PFAS could not only cause contamination near well sites; they could also pollute places where solid waste and enormous volumes of toxic wastewater from oil and gas wells are disposed of, miles from well sites.

Data publicly disclosed by the oil and gas industry indicates that between 2012 and 2022, two oil and gas companies injected the PFAS known as PTFE or Teflon into a total of eight unconventional gas wells in Western Pennsylvania. **However, this number of industry-reported instances may significantly underrepresent the reality of PFAS use in the Keystone State, due to weaknesses in state reporting rules**.

One major hindrance to quantifying the use of PFAS chemicals is the extensive use of trade secret or Confidential Business Information designations. Between 2012 and 2022, oil and gas companies injected more than 5,000 unconventional gas wells with at least one trade secret chemical per well, totaling 160 million pounds. Oil and gas companies injected more than 1,200 wells with incompletely identified chemicals that could be fluorosurfactants, a class of chemical that includes multiple PFAS.

During the same decade-long period, 15 oil and gas companies operating in Pennsylvania injected oil and gas wells in other states with fracking chemicals that are PFAS or potential PFAS, while not reporting that they used these substances in their Pennsylvania wells. These substances include PTFE/Teflon and fluoroalkyl alcohol substituted polyethylene glycol, both of which have been identified as PFAS by EPA. In addition, five companies operating in Pennsylvania disclosed that they injected wells in five other states with nonionic fluorosurfactants, a class of chemicals identified as PFAS, potential PFAS, or precursors that could degrade into PFAS. Yet in Pennsylvania, only two companies reported the use of a single PFAS, PTFE, in eight wells. This raises questions about whether some companies are using PFAS in Pennsylvania on an undisclosed basis.

Should only a fraction of the unidentified chemicals used in Pennsylvania's unconventional gas wells be PFAS, they could pose a significant threat to human health.

It is difficult to access fracking chemical data in Pennsylvania for conventional wells that can be developed without fracking – far more difficult than it is for unconventional gas wells that must typically be hydraulically fractured or "fracked." This difficulty explains why this report focuses on unconventional gas wells. This and other regulatory hurdles prevent the public from knowing how widely PFAS – or other toxic chemicals – have been used in unconventional gas wells or in other types of oil and gas wells. Another potential route of contamination from PFAS is the use in fracking of water already tainted with PFAS. State regulations do not require testing for contaminants in water used for fracking. Our findings, including the gaps in our findings, raise concerns that Pennsylvanians may unknowingly be exposed to highly hazardous PFAS chemicals, particularly in rural areas where most unconventional gas wells are drilled and fracked.

---

* This report refers to "oil and gas companies" or the "oil and gas industry" even when discussing only unconventional gas wells, as some of the companies that operate unconventional gas wells also operate oil wells, whether in Pennsylvania or other states.

An interactive map showing the locations of wells injected with PFAS and trade secret chemicals is available here. Users can zoom in to identify wells near them.

In light of our findings, PSR recommends the following:

- **Halt PFAS use in oil and gas extraction.** Pennsylvania and the U.S. Environmental Protection Agency (EPA) should prohibit PFAS from being used, manufactured, or imported for oil and gas extraction. Many PFAS are replaceable with less-persistent and less-toxic alternatives. In taking this step, Pennsylvania would be following the lead of Colorado, a major oil- and gas-producing state that in June 2022 passed legislation banning the use of PFAS in oil and gas wells.

- **Expand public disclosure.** Pennsylvania should greatly expand its requirements for public disclosure of oil and gas chemicals. The state could again follow the example offered by Colorado by requiring disclosure of all individual chemicals used in oil and gas wells, without exceptions for trade secrets. This action can be done while still protecting product formulas as trade secrets. Pennsylvania should also require disclosure on the part of chemical manufacturers and require chemical disclosure prior to permitting, as have California, West Virginia, and Wyoming.

- **Increase testing and tracking.** Pennsylvania and/or the U.S. EPA should determine where PFAS have been used in oil and gas operations in the state and where related wastes have been deposited. They should test nearby residents, water, soil, flora, and fauna for PFAS, both for the particular type(s) of PFAS used and for organic fluorine to detect the presence of other PFAS and/or their breakdown products. They should use testing equipment sensitive enough to detect PFAS at a level of single-digit parts per trillion or lower.

- **Require funding and cleanup.** Oil and gas and chemical manufacturing firms should be required to fund environmental testing for PFAS in their areas of operation, and should PFAS be found, be required to fund cleanup. If cleanup of water sources is impossible, companies responsible for the use of PFAS should pay for alternative sources of water for homes, schools, hospitals, agriculture and other uses for as long as needed.

- **Remove Pennsylvania's oil and gas hazardous waste exemption.** Pennsylvania exempts oil and gas industry wastes from state hazardous waste rules. Pennsylvania should follow New York's lead and remove its state-level hazardous waste exemption for the oil and gas industry.

- **Reform Pennsylvania's regulations for oil and gas production wells and underground injection disposal wells**. The state should prohibit production wells and underground wastewater disposal wells close to underground sources of drinking water, homes, health care facilities and schools; require groundwater monitoring for contaminants near the wells, and for disposal wells, require full public disclosure of chemicals in the wastewater.

- **Transition to renewable energy and better regulation.** Given the use of highly toxic chemicals in oil and gas extraction, including but not limited to PFAS, as well as climate impacts of oil and gas extraction and use, Pennsylvania should transition away from fracking and move toward renewable energy and energy efficiency while providing economic support for displaced oil and gas workers. As long as drilling and fracking continue, the state should better regulate these practices so that Pennsylvanians are not exposed to toxic substances and should empower local governments also to regulate the industry. When doubt exists as to the existence or danger of contamination, the rule of thumb should be, "First, do no harm."

CH. 1

PFAS: A MANMADE THREAT TO HEALTH AND THE ENVIRONMENT, USED IN PENNSYLVANIA'S OIL AND GAS WELLS

a. PFAS Used in Pennsylvania Wells

Physicians for Social Responsibility (PSR) has identified evidence from publicly reported oil and gas industry[*] records that a highly dangerous class of chemicals, known as per- and polyfluoroalkyl substances (PFAS), has been used for hydraulic fracturing ("fracking") in Pennsylvania's unconventional gas[**] wells and that such use could be much more extensive than reported. PFAS are known for their toxicity at extremely low levels,[1] their multiple negative health effects including cancer,[2] and their persistence in the environment, which has endowed them with their nickname, "forever chemicals."[3] Fracking is the stage of oil and gas operations that typically involves high-pressure injections into oil and gas wells of up to tens of millions of gallons of water, sand, and chemicals to fracture rock formations and free up trapped oil and gas.[4][***] It is possible that PFAS have also been used in additional stages and methods of oil and gas production in Pennsylvania.

The use of PFAS in oil and gas production in Pennsylvania was first exposed in 2021 in an editorial by the Philadelphia Inquirer[5] that was prompted by a report from Physicians for Social Responsibility about the use of PFAS in oil and gas operations in other states.[6] Later in 2021, the nonprofit Public Employees for Environmental Responsibility published a report based on U.S. Environmental Protection Agency data indicating that PFAS had been used in oil and gas operations in Pennsylvania.[7] PSR's findings in this report, however, go even further. Based on fracking chemical disclosures made by oil and gas well operators to the nongovernmental organization FracFocus, PSR is able to identify not only the unconventional gas wells definitively known to have been injected with PFAS between 2012 and 2022, but also the wells injected with trade secret chemicals and, for the first time, the staggering quantities of these unidentified substances.

The wells known to be injected with PFAS consist of eight wells injected with PTFE, also known as Teflon and identified by the U.S. Environmental Protection Agency (EPA) as a PFAS.[8] One of these wells, fracked by Chesapeake Operating Inc. with 18 pounds of PTFE, was located in Beaver County;[9] three wells fracked by Hilcorp Energy Company with 12 pounds of PTFE were located in Lawrence County,[10] and four wells fracked by Chesapeake Operating Inc. with an unknown amount of PTFE were located in Washington County.[11] See Appendix C for more detail about PTFE. PSR was able to identify wells injected with PTFE through disclosure of Chemical Abstract Service (CAS) numbers, unique numeric identifiers assigned to each chemical by the American Chemical Society.[12] Scientists consider CAS numbers the best way to identify chemicals because chemicals can have multiple names or trade names but only one CAS number.[13]

The larger story, however, is the staggering number of wells injected with trade secret chemicals that could be PFAS. PSR found that between 2012 and 2022, oil and gas companies disclosed the use of fracking chemicals in more than 7,200 unconventional gas wells and injected more than 5,000 (70 percent) with at least one trade secret fracking chemical. These chemicals totaled 160 million pounds. In these cases, oil and gas companies did not disclose a CAS number for the chemical, preventing the public from knowing what these chemicals are. Oil and gas companies injected more than 1,000 of the wells with trade secret surfactants, a category of chemical that may be more likely to be PFAS because they include a subcategory known as fluorosurfactants that are often PFAS. According to EPA, surfactants are commonly used in fracking.[14] These substances lower the surface tension of a liquid, the interaction at the surface between two liquids (called interfacial tension), or the interaction between

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[*] This report refers to "oil and gas companies," the "oil and gas industry," etc. even when discussing only unconventional gas wells because at least some of the companies that operate unconventional gas wells also operate oil wells, whether in Pennsylvania or other states.

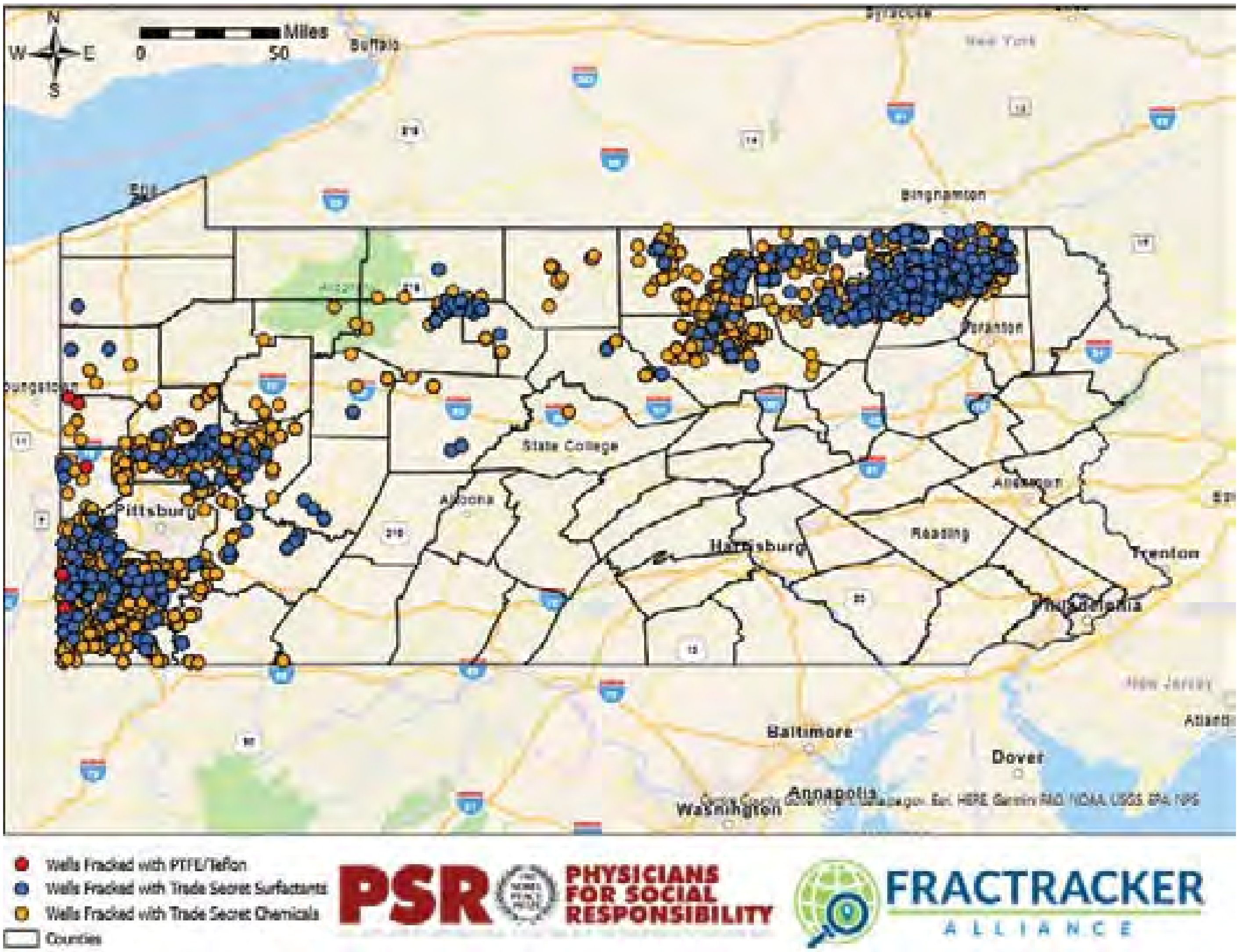
[**] Gas, the principal component of which is methane, is also known as "natural" gas, "fossil" gas and "fracked" gas.

[***] In this report, the term "fracking" is used to discuss a particular stage in oil and/or gas production as distinct from other stages or methods of production such as drilling that precedes fracking. The terms "oil and gas production," "oil and gas extraction," and "oil and gas operations" cover the entire process of producing oil and/or gas.

a liquid and a solid.[15] Compared to other surfactants, fluorosurfactants are said to be "superior in their aqueous surface tension reduction at very low concentrations and are useful as wetting and leveling agents, emulsifiers, foaming agents, or dispersants."[16] At least some fluorosurfactants are PFAS, including the dangerous chemicals PFOA and PFOS[17] and 8:2 fluorotelomer alcohol,[18] a nonionic fluorosurfactant[19] that can break down into PFOA.[20]

The use of PFAS and trade secret chemicals that may be PFAS is particularly alarming as Pennsylvania's gas production has increased by almost 45 times between 2005 and 2021, from 168 billion cubic feet to 7.5 trillion cubic feet.[21] These increases have led to modest gains in jobs in the major gas-producing counties[22] and somewhat more revenue for the state.[23] But they also mean more greenhouse gas emissions[24] and greater risk of pollution from PFAS and other toxic substances associated

Figure 1. Pennsylvania Oil & Gas Wells Fracked with PFAS and Possible PFAS, Including Trade Secret Chemicals, 2012-2022



This map shows the location of oil and gas wells in Pennsylvania known to have been fracked between January 1, 2012 and September 29, 2022 using PTFE/Teflon (a known PFAS), trade secret chemicals, and/or trade secret surfactants. An interactive version of the map is available at https://ft.maps.arcgis.com/apps/webappviewer/index.html?appid=dc81f7ec3af64541a1875e8e6e5add60 where users can zoom in to identify wells near them. For a detailed explanation of data sources, see Appendix A.

with gas extraction, including an increased risk of exposure to naturally occurring carcinogenic radium that emerges from Marcellus Shale wells in millions of gallons of wastewater.[25]

b. Oil and Gas Operations Provide Many Potential Routes of Exposure to PFAS

Oil and gas operations in Pennsylvania deserve scrutiny as a possible source of PFAS contamination, given the documented use of PFAS in the state's oil and gas wells and the potential that people could be exposed to such PFAS via multiple pathways.

EPA in a 2016 national report on fracking and drinking water found that fracking-related pollution could follow a number of pathways that could impact surface water and groundwater. The agency cited the following possible pathways to exposure:

- spills of fracking fluid that seep into groundwater;
- injection of fracking fluid into wells with cracks in the casing or cement, allowing the fluid to migrate into aquifers (see opposite diagram)
- injection of fracking fluids directly into groundwater;
- underground migration of fracking fluids through fracking-related or natural fractures;
- intersection of fracking fluid with nearby oil and gas wells,
- spills of wastewater after the fracking process is completed, and
- inadequate treatment and discharge of fracking wastewater to surface water supplies.[26]

PFAS used in oil and gas extraction could pollute water through any of these pathways, plus other routes discussed in more detail in Chapter 4, including through airborne releases and disposal of oil and gas wastewater in underground injection wells, a pathway that EPA did not examine in its 2016 report.[27]

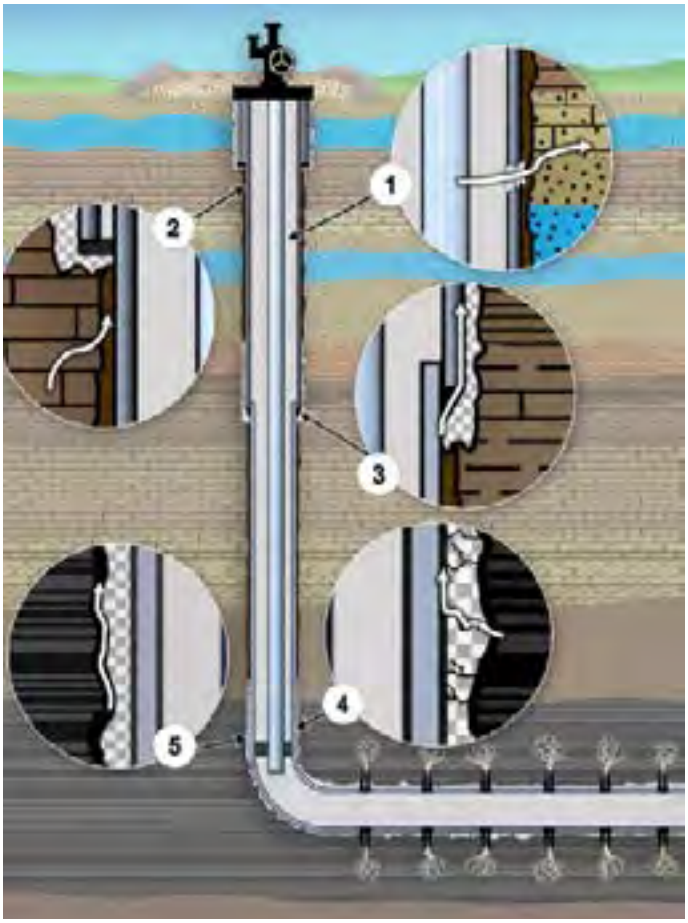


Diagram from U.S. Environmental Protection Agency's 2016 report on fracking and drinking water (p. ES-29) shows the various pathways through which fluid can migrate up an oil or natural gas well and potentially pollute groundwater including through leaks in the steel casing or cement designed to seal off the casing from the groundwater. EPA wrote that "These pathways (represented by the white arrows) include: (1) a casing and tubing leak into the surrounding rock, (2) an uncemented annulus (i.e., the space behind the casing), (3) microannuli between the casing and the cement, (4) gaps in cement due to poor cement quality, and (5) microannuli between the cement and the surrounding rock." EPA noted that the diagram is not to scale.

c. Manmade and Dangerous: PFAS's History and Health Effects

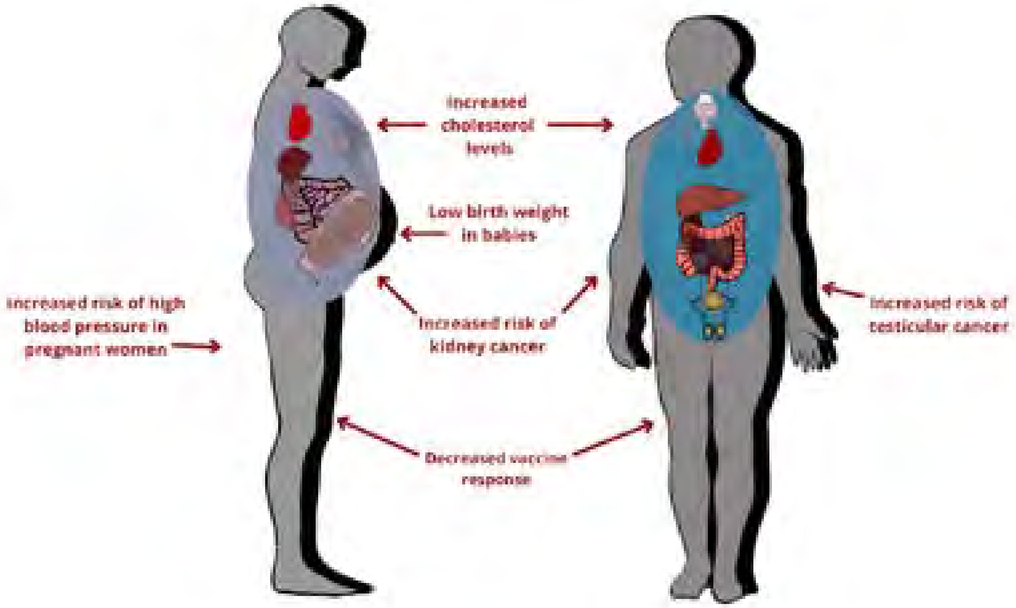
PFAS are a class of thousands of synthetic chemicals manufactured to have properties that are valuable in multiple industrial contexts, such as being slippery, oil- and water-repellant, and able to serve as dispersants or foaming agents.[28] PFAS have been called "perfluorinated chemicals" and "polyfluorinated compounds," or PFCs, though the term currently preferred by EPA is PFAS.[29]

The first PFAS to be sold commercially was created by a chemist at Dupont and was patented as Teflon. Since 1949, it has been used in thousands of products, from nonstick cookware to waterproof clothing to plastics to dental floss.[30] Other PFAS chemicals, the most prominent of which are known as PFOA and PFOS, were used in food packaging, fire-fighting foam, and in 3M's widely used fabric protector, Scotchgard.[31] EPA reported in 2021 that about 650 types of PFAS remained in commerce.[32] Weak chemical disclosure laws make it difficult for the Agency to identify which PFAS chemicals are used, and where.

Between the 1960s and 1990s, researchers inside Dupont and 3M became aware that at least some of the PFAS they were manufacturing or using, particularly PFOA and PFOS, were associated with health problems including cancers and birth defects, had accumulated in people worldwide, and persisted in the environment.[33] Many of these facts, kept internal by the companies, came to light after attorney Rob Bilott filed lawsuits in 1999 and 2001 accusing Dupont of causing pollution in and around Parkersburg, West Virginia with PFOA, a type of PFAS then used in making PTFE (Teflon).[34] In December 2011, as part of Dupont's settlement of the 2001 lawsuit, a team of epidemiologists completed a study of the blood of 70,000 West Virginians and found a probable link between PFOA and kidney cancer, testicular cancer, thyroid disease (over or under-production of hormones by the thyroid gland), high cholesterol, pre-eclampsia (a potentially dangerous complication during pregnancy characterized by high blood pressure and signs of damage to other organ systems, most often the liver and kidneys), and ulcerative colitis (a disease causing inflammation and ulcers in the large intestine or colon).[35]

Current peer-reviewed scientific research on PFAS suggests that exposure to certain levels of some PFAS may lead to adverse health outcomes. Research findings differ, as different studies have examined different PFAS chemicals, different types or levels of exposure, and different exposed populations. However, some findings are more widely endorsed; for example, the U.S. Environmental Protection Agency (EPA)[36] and the Center for Disease Control and Prevention's Agency for Toxic Substances and Disease

POTENTIAL HEALTH EFFECTS OF PFAS EXPOSURE



Exposure to PFAS chemicals can result in a variety of serious health effects including those indicated above. Source: U.S. Environmental Protection Agency, Agency for Toxic Substances and Disease Registry. Graphic by Astra Robles.

Registry (ATSDR)[37] agree that exposure to high levels of certain PFAS may lead to increased risk of high blood pressure in pregnant women; low birth weight in babies; increased risk of kidney or testicular cancer; decreased vaccine response, and increased cholesterol levels. Research is ongoing to determine the health effects of different levels of exposure to different PFAS, including the health effects of long-term, low-level PFAS exposure, especially in children.

PFAS are not only highly toxic; they also demonstrate extreme persistence in the environment. PFAS' nickname "forever chemicals" reflects their chemistry – created by chemical manufacturers – that features a bond between fluorine and carbon atoms that is among the strongest in chemistry and rarely if ever exists in nature. The result: chemicals that are extremely resistant to breaking down.[38] PFAS are also extremely mobile in water,[39] making them able to spread through the environment via groundwater or surface water. Another risk, discussed in Chapter 3, is that PFAS could compound the health effects from other dangerous chemicals associated with oil and gas production.

d. EPA – and Pennsylvania – Recognize Risks of PFAS

EPA has been slow to regulate PFAS, but the agency has taken actions, particularly in recent years, that recognize PFAS's extraordinary risks. In June 2022, reflecting growing public concern about PFAS, EPA significantly lowered its non-binding health advisory level for PFOA and PFOS in drinking water. Previously, EPA had set the combined health advisory level for these two chemicals at 70 parts per trillion.[40]

"**The new published peer-reviewed data and draft EPA analyses [citation omitted] indicate that the levels at which negative health outcomes could occur are much lower than previously understood,**" EPA wrote in June 2022.[41] EPA lowered its new interim health advisory level for PFOA in drinking water to 0.004 parts per trillion and its interim health advisory level for PFOS to 0.02 parts per trillion.[42] EPA also set new final health advisory levels for two other PFAS, known as GenX and PFBS, at 10 parts per trillion and 2,000 parts per trillion, respectively.[43] EPA said that its interim health advisory levels were intended to provide guidance until enforceable drinking water regulations for PFAS take effect.[44] EPA explained that its health advisory level "is designed to be protective of noncancer effects over a lifetime of exposure, including sensitive populations and life stages, and is typically based on data from experimental animal toxicity and/or human studies." The agency wrote that exposure to PFOA, PFOS, and Gen X is associated with cancer. But the agency had not yet developed cancer risk concentrations in water for these substances. EPA added that, at least for PFOA and PFOS, the interim health advisory levels could change following review by its Science Advisory Board.[45]

EPA then in March 2023 released proposed legally enforceable "Maximum Contaminant Levels" for six PFAS in drinking water. These regulations, unlike health advisories, must take into account whether a particular level of protection can be achieved and at what cost.[46] For this reason, they may be much less stringent than the health advisories. The MCLs proposed by EPA included a level of four parts per trillion for both PFOA and PFOS. EPA also proposed an MCL Goal or non-enforceable target of zero for both of these PFAS. The agency proposed that drinking water providers limit the combined levels of four other types of PFAS: PFNA, PFHxS, PFBS, and/or GenX Chemicals.[47] The MCLs would require public water systems to monitor for the six PFAS, notify the public about the levels of these PFAS, and reduce levels of the six PFAS in drinking water if levels exceed the MCLs.[48] The agency said that it expects to finalize the regulations by the end of 2023,[49] though the Pennsylvania Environmental Quality Board has stated that the rules are not expected to take effect until several years after that date.[50]

Even the higher MCL figures demonstrate the extraordinary toxicity of some types of PFAS. At a level of four parts per trillion, a measuring cup of PFOA could contaminate 28 billion gallons of water,[51] more than 90 times the 300 million gallons of drinking water treated each day by Philadelphia.[52]

Pennsylvania has also taken action to identify and regulate PFAS pollution. In March 2021, the Pennsylvania

Department of Environmental Protection (DEP) completed sampling of concentrations for 18 types of PFAS at 372 public water systems and 40 baseline sites.[53] These baseline sites featured at least 75 percent forested land and were located at least five miles from potential sources of contamination such as airports, manufacturing facilities, and military bases.[54] The DEP found PFOA in 112 of the 412 samples at an average concentration of 7.5 parts per trillion and a median concentration of 5.3 parts per trillion.[55] The agency found PFOS in 103 of the 412 samples at an average concentration of 9.9 parts per trillion and a median concentration of 6.5 parts per trillion.[56] All of these average and median concentrations were much higher than EPA's health advisory levels and somewhat higher than EPA's proposed drinking water standard. Environmental Working Group, a nonprofit, has also found elevated levels of PFAS pollution – some staggering high – in public drinking water systems, and at military bases and industrial sites.[57]

Following its sampling program, and before EPA announced its drinking water standards in March 2023, Pennsylvania in January issued drinking water standards for PFOA and PFOS that applied to 3,117 water systems in the state.[58] For PFOA, the state's Environmental Quality Board set an enforceable Maximum Contaminant Level of 14 parts per trillion and a non-enforceable maximum contaminant Goal of 8 parts per trillion.[59] For PFOS, the Board set an enforceable MCL of 18 parts per trillion[60] and a maximum contaminant Goal of 14 parts per trillion.[61] "Although the EPA has started the process of setting more stringent standards for PFOA and PFOS in drinking water," the Board wrote, "that process is expected to take years to complete. For that reason, these more protective standards for this Commonwealth will better protect the health of residents in this Commonwealth."[62]

Several experts told PSR that because of the extreme potency of certain types of PFAS and the fact that chemical makers have created thousands of these forever chemicals, they would recommend particular testing methods to detect PFAS in the environment. The scientists are Linda Birnbaum, Ph.D., D.A.B.T., A.T.S., a board-certified toxicologist and former director of the National Institute of Environmental Health Sciences;[63] Zacariah Hildenbrand Ph.D., research professor in Chemistry and Biochemistry at the University of Texas at El Paso;[64] Kevin Schug Ph.D., Shimadzu Distinguished Professor of Analytical Chemistry at the University of Texas at Arlington,[65] and Wilma Subra, holder of a master's degree in chemistry and recipient of a John D. and Catherine T. MacArthur Foundation "Genius" grant for her work helping to protect communities from toxic pollution.[66] All were in agreement in recommending the use of testing equipment that can detect PFAS in concentrations at least as low as single-digit parts per trillion. They further recommended testing for total organic fluorine in addition to testing for specific types of PFAS. Total organic fluorine is a marker that would indicate the presence of PFAS even if a specific PFAS were not tested for. Testing for specific PFAS might fail to detect other forms of PFAS present in the sample.

e. PFAS in Oil and Gas Operations May Threaten Rural Areas, Add to PFAS from Other Sources

The risk of PFAS pollution from oil and gas operations is likely to be particularly high in rural areas and may add to PFAS pollution from better-studied sources such as military bases. The risk to rural areas is based partly on the fact that most unconventional fracked gas wells, if not other types of wells, are developed in rural areas.[67] In addition, people in rural areas rely on private wells for drinking water that may not be tested for PFAS or other contaminants as frequently as public water supplies.[68] In total, about 2.5 million Pennsylvanians (about 20 percent of the state's population)[69] rely on private water wells.[70] Water wells near oil and gas operations may be at particular risk of contamination from PFAS as a result of leaks, spills, or underground migration of PFAS from the oil and gas wells. However, PSR is aware of only one test for PFAS in a private water well in Pennsylvania near an oil and gas extraction site (see Chapter 3). This lack of testing means that Pennsylvanians living near oil and gas operations may be unknowingly exposed to PFAS through their water wells and other pathways.

A fracking site in Westmoreland County, Pa., Oct. 2022. Photo credit: Ted Auch. Photo courtesy of FracTracker Alliance.

f. PFAS: Among Many Dangerous Chemicals Used in Oil and Gas Extraction

When used in oil and gas operations, PFAS may add to the cumulative human exposure to a host of toxic substances. In fracking, chemicals serve a variety of purposes, including killing bacteria inside the wellbore, reducing friction during high-pressure fracking, and thickening the fluid so that the sand, suspended in the gelled fluid, can travel farther into underground formations.[71]

In its 2016 study of fracking and drinking water, the EPA identified 1,606 chemicals used in fracking fluid and/or found in fracking wastewater. While the agency found high-quality information on health effects for only about 10 percent (173) of these chemicals, that information was troubling. EPA found that health effects associated with chronic oral exposure to these chemicals include carcinogenicity, neurotoxicity, immune system effects, changes in body weight, changes in blood chemistry, liver and kidney toxicity, and reproductive and developmental toxicity.[72]

Chemicals used in the drilling stage that precedes actual fracturing can also pose health risks, including developmental toxicity and the formation of tumors, according to EPA regulators.[73] A disclosure form filed with the state of Ohio, one of only two states to require public disclosure of drilling chemicals (Colorado is the other),[74] shows that Statoil, Norway's state oil company (since renamed Equinor), has used the neurotoxic chemical xylene in drilling.[75] In short, when chemicals used in drilling, fracking or other stages and methods of oil and gas operations come into contact with people or the environment, they can produce serious negative health effects.[76] The use of PFAS in fracking and/or drilling operations would only multiply these health risks.

CH. 2 CHEMICAL DISCLOSURE LAWS SHIELD CHEMICAL IDENTITIES

Due to Pennsylvania's byzantine system of oil and gas chemical disclosure, it is impossible to know how widely PFAS or other toxic chemicals have been used in the state's oil and gas wells. This set of rules features, among other elements that frustrate the public's right to know, opportunities for oil and gas companies to hide fracking chemical identities behind trade secret claims, conceal the identities of chemicals used in other stages and methods of extraction such as the drilling that precedes fracking, and allow chemical manufacturers – the companies who know best what chemicals are being used – to avoid disclosure of chemical ingredients. Pennsylvania also has different standards for fracking chemical disclosure in conventional and unconventional wells, requiring the public to consult multiple repositories in order to secure full information.

Many residents living near oil and gas operations have reported serious health impacts while expressing frustration over the secrecy surrounding chemicals used by the oil and gas industry.[77] In 2020, the Attorney General's criminal grand jury documented these experiences, finding that

> Many of those living in close proximity to a well pad began to become chronically, and inexplicably, sick. Pets died; farm animals that lived outside started miscarrying, or giving birth to deformed offspring. But the worst was the children, who were most susceptible to the effects. Families went to their doctors for answers, but the doctors didn't know what to do. The unconventional oil and gas companies would not even identify the chemicals they were using, so that they could be studied; the companies said the compounds were "trade secrets" and "proprietary information." The absence of information created roadblocks to effective medical treatment. One family was told that doctors would discuss their hypotheses, but only if the information never left the room.[78]

Pennsylvania's rules and laws regarding oil and gas chemical disclosure mean that oil and gas companies could be using PFAS or other toxics much more widely than has been reported, leaving Pennsylvanians at risk of serious health problems.

a. Extensive Use of "Trade Secret" Claims Veils Actual Use

Perhaps the most prominent shortcoming in Pennsylvania law that could conceal wider use of PFAS in oil and gas wells is the ability for oil and gas companies to withhold from the public, though not from regulators, information on their use of fracking chemicals deemed trade secrets, for both unconventional gas wells[79] and conventional oil and gas wells.[80] This provision is an exception to the general requirement that oil and gas well operators are required to publicly disclose their fracking chemicals, whether to FracFocus[81] or to the DEP (see section e pg. 15).[82] According to the DEP, well operators, well service providers, chemical suppliers/vendors, and chemical manufacturers can all declare that a fracking chemical is a trade secret.[83] In these cases, the company declaring the trade secret must submit to the DEP a "Registration of Trade Secret-Confidential Proprietary Stimulation Fluid Chemical Information" form.[84] The submitter must include on the form the CAS Number and/or name of the chemical claimed as a trade secret. The submitter must also assign a code to the chemical in a format designated by the DEP and must include a justification for the trade secret claim.[85] The code is used in place of the chemical name and/or CAS Number in the publicly available Completion Report required to be submitted electronically to the DEP for each oil and gas well.[86] Through this system, the DEP learns the identities of trade secret chemicals, but the public does not. Trade secret claims can thus hide from public view the true identities of dangerous chemicals, including PFAS.

In 2021, the Philadelphia Inquirer reported in an editorial that the state's list of trade secret chemicals contained about 430 substances and that the newspaper had asked the DEP if the agency "would audit the list for 'forever chemicals' — not disclosing the name of the substance or other details." The Inquirer wrote that "a spokesperson wrote that such review is 'possible' but time-consuming as 'staff will need to review approximately 90 individual paper submissions' to identify the chemicals."[87]

Table 1. Disclosed Use of Trade Secret Chemicals in Pennsylvania Oil and Gas Wells, 2012-2022

County Name	Number of wells injected with at least one trade secret chemical	Mass of all trade secret chemicals (lbs.)	Number of wells injected with trade secret surfactants	Mass of trade secret surfactants (lbs.)
Allegheny	107	3,980,000	19	1,860
Armstrong	150	1,160,000	17	1,720
Beaver	79	3,660,000	3	4,280
Bradford	458	14,100,000	168	1,790,000
Butler	219	4,550,000	65	118,000
Cameron	92	937,000	40	77,400
Centre	2	11,300	0	0
Clarion	6	117,000	0	0
Clearfield	7	136,000	2	5,600
Clinton	18	105,000	2	3,260
Crawford	1	60,700	1	918
Elk	154	1,260,000	43	4,360
Fayette	89	2,060,000	3	777
Forest	4	33,000	0	0
Greene	654	22,200,000	40	28,900
Indiana	4	10,400	4	2,350
Jefferson	10	821,000	1	18,900
Lawrence	8	65,300	0	0
Lycoming	290	5,500,000	24	41,900
McKean	80	660,000	15	59,200
Mercer	7	432,000	2	4,850
Potter	16	256,000	0	0
Somerset	5	88,300	0	0
Sullivan	51	1,640,000	10	153,000
Susquehanna	949	21,600,000	443	1,000,000
Tioga	264	5,010,000	55	167,000
Washington	1,082	60,800,000	179	798,000
Westmoreland	63	1,400,000	16	46,100
Wyoming	193	7,660,000	82	463,000
Total	**5,062**	**160,000,000**	**1,234**	**4,790,000**

This table shows by county the number of Pennsylvania wells in which oil and gas companies injected at least one trade secret fracking chemical and/or at least one trade secret surfactant. It also shows the total combined weight of these chemicals by county and statewide. The total weight figures reflect the sum of all records for which we have enough information to calculate a chemical's weight. However, the total weight figures represent an undercount because many fracking chemical disclosures lack sufficient data to perform this calculation. The wells injected with trade secret surfactants are a subset of the wells injected with trade secret chemicals. For a more detailed explanation of data sources, see Appendix A.

Table 2. Oil and Gas Companies that Fracked Unconventional Gas Wells in Pennsylvania Using Trade Secret Chemicals and Trade Secret Surfactants, 2012-2022

Operator	No. of wells injected with at least one trade secret chemical	Mass of all trade secret chemicals (lbs.)	No. of wells injected with at least one trade secret surfactant	Mass of all trade secret chemicals (lbs.)
Range Resources Corporation	816	49,100,000	147	487,000
EQT Production	780	33,700,000	15	25,300
Chesapeake Operating, Inc.	545	25,600,000	224	2,820,000
Cabot Oil & Gas Corp	509	7,220,000	327	356,000
Seneca Resources Corporation	447	3,610,000	128	229,000
Southwestern Energy	343	12,000,000	34	188,000
Chevron USA Inc.	151	2,920,000	3	778
Talisman Energy USA Inc.	140	1,860,000	47	No data available
XTO Energy/ExxonMobil	118	1,380,000	63	133,000
Repsol O&G, LLC.	114	999,000	3	128
Rice Drilling B, LLC	109	1,540,000	31	40
Anadarko Petroleum Corporation	109	86,100	0	0
Shell Oil Company affiliate	107	1,730,000	29	82,100
Snyder Brothers Inc.	99	942,000	9	1,350
PennEnergy Resources, LLC	71	1,470,000	0	0
CONSOL Energy Inc.	69	1,530,000	8	4,970
Carrizo Oil & Gas, Inc.	49	1,050,000	44	19,000
CNX Gas Company LLC	43	734,000	12	301,000
Rex Energy	42	338,000	4	265
Alta Resources	40	3,280,000	0	0
Noble Energy, Inc.	32	2,200,000	12	3,550
EdgeMarc Energy Holdings, LLC	27	1,320,000	0	0
COTERRA ENERGY INC.	27	308,000	14	842
Vantage Energy Appalachia II LLC	27	177,000	0	0
BKV Operating LLC	22	804,000	10	19,700
WPX Energy	20	628,000	14	1,400
Greylock Production LLC	20	518,000	13	3,910
MDS Energy Development LLC	20	54,100	4	364
EOG Resources, Inc.	20	37,200	5	247
Olympus Energy	19	82,600	5	455
Apex Energy LLC	17	560,000	4	41,100
JKLM ENERGY	15	220,000	0	0
MDS Energy, Ltd	12	31,500	1	No data available
Pennsylvania General Energy	11	195,000	0	0
Citrus Energy Corporation	8	43,500	7	41,700
EXCO Resources, Inc.	7	101,000	1	3,260
Rockdale Marcellus, LLC	6	936,000	0	0
Hilcorp Energy Company	6	77,700	0	0
Huntley & Huntley Energy Exploration	6	41,200	6	515
Inflection Energy (PA) LLC	5	69,300	3	11,800
Alpha Shale Resource, LP	5	849	0	0

Table 2. (CONTINUED) Oil and Gas Companies that Fracked Unconventional Gas Wells in Pennsylvania Using Trade Secret Chemicals and Trade Secret Surfactants, 2012-2022

Operator	No. of wells injected with at least one trade secret chemical	Mass of all trade secret chemicals (lbs.)	No. of wells injected with at least one trade secret surfactant	Mass of all trade secret surfactants (lbs.)
Northeast Natural Energy LLC	4	102,000	0	0
LOLA Energy PetroCo	4	56,000	0	0
Chief Oil & Gas	4	38,500	0	0
Halcon Resources Corporation	3	323,000	3	5,770
Campbell Oil & Gas. Inc	3	66,800	2	5,600
Energy Corporation of America	3	8,960	0	0
Warren E&P, Inc.	3	4,910	0	0
INR Operating, LLC	2	125,000	0	0
Clean Energy Exploration and Production	2	21,400	0	0
RMD	2	No data available	0	0
Travis Peak Resources, LLC	1	4,400	0	0
Arrington Oil & Gas Operating LLC	1	2,330	1	2,330
Endeavour Operating Corp	1	No data available	1	No data available
Total	**5,066***	**160,000,000**	**1,234**	**4,790,000**

This table shows the oil and gas companies that fracked unconventional gas wells in Pennsylvania with trade secret chemicals and trade secret surfactants between January 1, 2012 and September 29, 2022. The wells injected with trade secret surfactants are a subset of the wells injected with trade secret chemicals. For a more detailed explanation of data sources, see Appendix A. Please note: separate companies in this table could now be the same company as a result of subsequent mergers and/or name changes.

*In this table, the total number of unconventional gas wells that companies operating in Pennsylvania injected with at least one trade secret chemical (5,066) differs slightly from the total number reported in table 1 (5,062) because a handful of the 5,062 wells were fracked more than once, but by different operators, and those handful of wells are counted more than once in this table.

"Compared with Pennsylvania's important efforts to test water for those substances," the Inquirer commented, "reviewing 90 paper submissions for critical information about potential risk seems a minor cost."[88]

The lack of evidence of additional PFAS use in Pennsylvania's oil and gas wells may reflect extensive use of the trade secret provisions in Pennsylvania's chemical disclosure rules. PSR's data analysis revealed that, between 2012 and 2022, Pennsylvania well operators listed at least one fracking chemical as a trade secret in 5,062 unconventional gas wells located across 29 counties (Table 1). The weight of the trade secret chemicals used in these wells over this roughly 10-year period totaled 160 million pounds.[89] If even a small fraction of this weight were PFAS, that fraction could pose significant health and environmental risks.

In an effort to determine if any of these trade secret chemicals were PFAS, PSR examined whether any were listed as a surfactant. (Surfactants, as noted in chapter 1, encompass dangerous fluorosurfactants, some of which are PFAS.) We found thousands of cases of oil and gas companies using at least one trade secret chemical that they described as a surfactant. These occurred in 1,234 wells, spread across 23 counties.[90] Operators' names for these chemicals were vague, including "proprietary surfactant 00015"[91] and "proprietary surfactant blend."[92] The weight of these trade secret surfactants totaled almost five million pounds. Should even a small percentage of them be fluorosurfactants, they could include PFAS, and pose significant and long-lasting threats to human health and the environment. Yet the public cannot know what these chemicals are, due to the extensive use of trade secret protections.

These data show that multiple oil and gas companies have injected oil and gas wells in Pennsylvania with trade secret

TABLE 3. Examples of Individual Unconventional Gas Wells

Well Operator	Well Number	County	Year Fracking Completed	Chemical used in Well	CAS Number	Trade Name	Mass (lbs.)
Chesapeake Operating, Inc.	3712527156	Washington	2014	PTFE	9002-84-0	ambiguous	non calculable
Chesapeake Operating, Inc.	3700720415	Beaver	2014	PTFE	9002-84-0	ambiguous	19
Cabot Oil & Gas Corp	3711522540	Susquehanna	2020	nonionic surfactants	proprietary	not reported	3,102
Range Resources Corporation	3712527583	Washington	2015	surfactants	proprietary	StimOil ENX	35,179
Seneca Resources Corporation	3711722086	Tioga	2021	proprietary surfactant blend	proprietary	NFR-64	23,892

This table shows a sample of wells injected with the types of fracking chemicals referenced in the larger table above, including trade secret surfactants such as the "nonionic surfactants" and "proprietary surfactant blend" as well as PTFE. The examples cover a range of years and represent wells fracked in several Pennsylvania counties. Even the smallest mass shown for a proprietary chemical (3,102 pounds for nonionic surfactants) could be a highly dangerous amount if this proprietary chemical were PFAS.

chemicals that could be PFAS or other toxic substances. Table 2 identifies the companies responsible for this activity, as well as the quantities of trade secret chemicals and trade secret surfactants they injected.

b. Examples of Individual Wells Injected with PFAS and/or Trade Secret Chemicals

FracFocus data show that in some cases, oil and gas companies have injected hundreds or even thousands of pounds of trade secret chemicals into unconventional gas wells for fracking. If the toxicities of some of these chemicals were similar to those of PFOA or PFOS, these quantities would be enough to contaminate vast amounts of water. Table 3 provides selected examples of the chemicals reported to have been used in several Pennsylvania wells.

c. Lack of Disclosure of Drilling Chemicals Could Also Conceal PFAS Use

Another exemption in Pennsylvania's disclosure rules that prevents the public from knowing the extent of PFAS use in oil and gas wells is that well operators are not required to disclose the chemicals used in the drilling process that precedes fracking. During drilling, companies bore deep holes in the earth. Working in successive stages, companies bore deeper and deeper until the production zone is reached where the oil and/or gas are located.[93] During the first stage of drilling, these holes typically pass directly through groundwater.[94] Chemicals can be injected in this stage of the process to help keep the drill bit cool and to help lift rock cuttings out of the well.[95] EPA has indicated that any chemicals used during this first stage of the drilling process would be highly likely to leach into groundwater, because only after drilling through the groundwater zone is complete do oil and gas companies seal off the well from the groundwater by inserting into the well steel pipe known as casing as well as cement that fills the space between the outside of the pipe and the groundwater and rock formation.[96] Chemicals could infiltrate the groundwater before the casing and cement are in place.

Chemicals used in the drilling stage could include PFAS as well as other substances that can pose health risks. A peer-reviewed scientific paper published in 2020 reported that the PFAS known as fluorosurfactants have at least been proposed for use in drilling.[97] EPA regulators have found that chemicals proposed for use in drilling could lead to developmental harms and the formation of tumors.[98] A disclosure form filed with the state of Ohio shows that Statoil, Norway's state oil company (since renamed Equinor), has used a neurotoxic chemical, xylene, in drilling.[99] If chemicals used in drilling were to come into contact with people or the environment, negative health effects could result. This potential makes it critically important for these chemicals to be disclosed publicly. However, there is no such requirement in Pennsylvania, creating the potential that people could be unknowingly exposed to PFAS and other dangerous chemicals used during the drilling process that precedes fracking.

d. Chemical Manufacturers' Exemption May Also Obscure PFAS Use in Oil & Gas Wells

Pennsylvania rules may obscure the extent of PFAS use in oil and gas wells in an additional respect: The rules for both unconventional gas wells and conventional oil and gas wells clearly exempt chemical manufacturers from having to disclose the ingredients in their fracking chemical products to the well operators who must ultimately disclose the fracking chemicals to the public.[100] As a result, it is likely that well operators are using at least some fracking chemicals unknowingly. Some of these chemicals could be PFAS.

Chemical manufacturers are in the best position to know the identities of individual fracking chemicals, whether these chemicals are used individually or as ingredients in fracking chemical products comprised of more than one chemical. Yet evidence shows manufacturers often withhold chemical identities from other companies in the supply chain. In 2014, four attorneys with years of experience litigating oil and gas-related cases in Pennsylvania filed a petition with the state Commonwealth Court suggesting manufacturers often withhold chemical identities from other companies in the supply chain. The attorneys discussed the use of Material Safety Data Sheets (MSDS) that manufacturers use to communicate the contents of fracking chemical products. The federal Occupational Safety and Health Administration (OSHA) requires chemical manufacturers to prepare MSDS (now called safety data sheets) to order to protect workers using the chemicals from on-the-job hazards.[101] The attorneys wrote that these sheets often omit chemical ingredients.

> Many times, a vendor of a hydraulic fracturing fluid product merely re-labels product manufactured by another company without ever knowing anything about the chemical make-up of the product it has relabeled other than what may be contained in the manufacturer's MSDS. If that MSDS does not list the full chemical content of the product the vendor obtained, the vendor has no way of discerning the full chemical make-up of the hydraulic fracturing fluid. Thus, if a service provider or vendor never had possession of the entire chemical content of hydraulic fracturing fluid, then it is impossible for the vendor or service provider to pass that information along to the operator who then cannot possibly disclose to the Department [of Environmental Protection].[102]

The attorneys provided as support a record filed in a separate case by well operator Range Resources in which Range suggested that it was relying on MSDS from manufacturers to reply to a request for the chemicals used to fracture or stimulate its wells. Range said that the chemical information in these sheets could be incomplete. "The MSDS are often useful for developing some understanding of what is in a particular chemical or product," Range wrote, continuing,

> However, they vary widely in terms of usefulness. Some manufacturers include very little information about the actual components of a particular product. As a result, Range is currently in the process of seeking additional information from manufacturers that have failed to provide enough information about their products in the MSDS.[103]

In one case, Range said that a fracking or stimulation product called "MC SS-5075" was "an Ammonium Bisulfite Solution manufactured by Multi-Chem. The MSDS describes the formula as 45-70% ammonium bisulfite by weight. Range is currently seeking information on the 30-55% missing from the formula."[104] In another case, Range mentioned that a chemical known as "MC S-2510T," also made by Multi-Chem, contained "Ethylene Glycol (30%-60% by weight)" and "Sodium Hydroxide (5% by weight)." Range acknowledged that "we recognize that this formula fails to account for at least 35% of the weight, so we have contacted Multi-Chem for an explanation."[105]

In 2011, the U.S. House of Representatives' Committee on Energy and Commerce minority staff issued a report on hydraulic fracturing chemicals in which they asked the 14 leading oil and gas service companies to "disclose the types and volumes of the hydraulic fracturing products they used in their fluids between 2005 and 2009 and the chemical contents of those products."[106] While the committee staff found, among other things, that the companies used products containing 29 chemicals that are known or possible human carcinogens, they also found that the companies could not completely respond to the committee staff's request because of chemical information withheld by chemical manufacturers.

> In many instances, the oil and gas service companies were unable to provide the Committee with a complete chemical makeup of the hydraulic fracturing fluids they used. Between 2005 and 2009, the companies used 94 million gallons of 279 products that contained at least one chemical or component that the manufacturers deemed proprietary or a trade secret. Committee staff requested that these [service] companies disclose this proprietary information. Although some companies did provide information about these proprietary fluids, in most cases the companies stated that they did not have access to proprietary information about products they purchased "off the shelf" from chemical suppliers. In these cases, the companies are injecting fluids containing chemicals that they themselves cannot identify.[107]

Researchers at Harvard University wrote in 2013 that rules for creating safety data sheets are unlikely to result in complete disclosure of fracking chemicals by chemical manufacturers. The researchers observed that the rules limit disclosure of chemicals to those that are hazardous and have been studied for workplace exposure. Many chemicals used in fracking might not have been studied for workplace exposure, they wrote, and therefore might not be disclosed in safety data sheets. The researchers also wrote that manufacturers might not list at least some substances in safety data sheets because federal regulations provide that substances are deemed hazardous or not due to existing test data; therefore, if no test data shows that a substance is hazardous, it would not have to be listed on a safety data sheet, even if the chemical were, in fact, hazardous. No new testing is required.[108] These chemicals, in turn, would not be disclosed to companies in the fracking chemical supply chain, leaving the companies unable to disclose these chemicals to the public.

A final example of how chemical manufacturers do not or may not disclose all of the chemicals used in fracking or other oil and gas extraction techniques is found in the book *Amity and Prosperity*. In this book, which won the 2019 Pulitzer Prize for general nonfiction, author Eliza Griswold focused on a woman named Stacey Haney, who lived in western Pennsylvania near three hydraulically fractured unconventional gas wells, a drilling waste pit, and a fracking wastewater storage pond. In 2009, after drilling activity began, Haney and her neighbors suffered unexplained illnesses and the deaths of animals. They suspected the illnesses and deaths were caused by air and water contamination from the gas activity.[109] In a lawsuit filed against Range Resources, the well operator that ran the drilling site, Haney sought a full list of chemicals used at the site. This list would have been important to prove that exposure to the chemicals contributed to her family's health problems. The court ordered Range to disclose the substances, but the company said it could not comply because it did not know all of them. "Range wasn't simply being obstructionist," Griswold writes, "it was likely the company didn't know, since some of the products its subcontractors used were proprietary, and their contents were secret."[110] At least some of the secret chemical identities were held by a chemical manufacturer.[111] After years of litigation, Haney and another plaintiff accepted a confidential settlement that "left them feeling angry and defeated."[112] "The company never provided the plaintiffs with a definitive list of all the chemicals used at the site," Griswold wrote, and the court "refused to sanction Range for not complying" with the court order to disclose its chemicals.[113]

Considering these examples, it is important for states to require disclosure of fracking chemicals directly from the chemical manufacturers so that the public can know if dangerous chemicals such as PFAS are being used in oil and gas wells. Yet Pennsylvania's rules not only fail to require such disclosure; they also eliminate incentives for well operators or other companies in the oil and gas chemical supply chain to seek accurate chemical information from the manufacturers so that the information can be publicly disclosed. Pennsylvania's rules for unconventional gas wells provide that "a vendor, service provider or operator shall not be required to do any of the following... Disclose chemicals that are not disclosed to it by the manufacturer, vendor or service provider."[114] A second section of Pennsylvania's rules for unconventional gas wells similarly removes the incentive for other companies in the fracking chemical supply chain to hold accountable the chemical manufacturers for public disclosure of fracking chemicals.[115]

The rules for conventional oil and gas wells also shield chemical manufacturers from fracking chemical disclosure requirements by providing that a well operator must disclose "a list of the chemicals in the Material Safety Data Sheets, by name and chemical abstract service number, corresponding to the appropriate chemical additive."[116] This provision means that disclosure is limited to what is required on the safety data sheets, and therefore well operators are not responsible for compiling chemical information from manufacturers that is not on the sheets. As stated above, manufacturers do not have to include on the sheets chemicals that have not been studied for workplace exposure or those for which there is no data identifying the substances as hazardous. Therefore, the manufacturers do not have to disclose the identities of at least some chemicals, and operators would not have to disclose these chemicals publicly, including, perhaps, PFAS.

e. Pennsylvania's Rules Direct Fracking Chemical Data to Multiple Repositories

Another challenge the public faces in determining what chemicals oil and gas companies have used in Pennsylvania is that the state has two different systems of fracking chemical disclosure, resulting in disclosure of these chemicals to multiple repositories. For so-called "unconventional" wells, the state provides that gas well operators publicly disclose their fracking chemicals to the FracFocus database, an online repository that can be searched and sorted by multiple terms including type of chemical used.[117] The state defines unconventional wells as gas wells in "a geological shale formation existing below the base of the Elk Sandstone or its geologic equivalent stratigraphic interval" from which gas cannot be economically produced unless particular extraction techniques are used including fracking.[118] In the case of conventional wells, which the state defines as oil wells and all other gas wells, Pennsylvania requires oil and gas companies to disclose fracking chemicals to the Pennsylvania Department of Environmental Protection.[119] As of 2018, the records for conventional wells were stored as paper records in offices in Meadville and Pittsburgh[120] and were not accessible remotely.[121] In 2022, the Department of Environmental Protection reported that well operators can disclose fracking chemicals for conventional wells electronically or on paper to the appropriate office (Meadville, Pittsburgh, or Williamsport). The electronic disclosures are available online but are stored in pdf files that must be reviewed individually and cannot be searched and sorted as a group.[122]

Due to the time it would require to access the records for conventional wells from four different sources (online, Meadville, Pittsburgh, and Williamsport), none of which is easily searchable, PSR has limited this report to an analysis of fracking chemicals disclosed as used in unconventional gas wells. On the one hand, this analysis is robust because it covers more than 7,000 wells, and unconventional gas wells have largely accounted for Pennsylvania's boom in gas production over the past two decades.[123] However, this

An oil and gas well site in Westmoreland County, Pa., Sept. 2021. Photo credit: Ted Auch. Photo courtesy of FracTracker Alliance.

analysis is incomplete, because it leaves Pennsylvanians uninformed about the chemicals they might be exposed to through conventional oil and gas wells. As of 2021, there were close to 40,000 conventional oil and gas wells operating in Pennsylvania.[124]

The difficulty of analyzing chemicals used in conventional wells is particularly troubling because in 2022, the DEP published a report surveying operators with 11 or more conventional wells which showed significant problems with regulatory compliance. Among the shortcomings that the DEP highlighted was improper abandonment of wells and a lack of reporting about waste production and the structural integrity of wells:

> Over the past five years, DEP's OOGM [Office of Oil and Gas Management] has identified significant non-compliance with laws and regulations in the conventional oil and gas industry, particularly regarding improper abandonment of oil and gas wells, as well as reporting requirements for hydrocarbon and waste production and mechanical integrity assessments [related to structural soundness of oil and gas wells]... The reporting non-compliance denies DEP and the public critical information about the operating status of individual wells. Overall performance is so poor among operators with 11 or more conventional oil and gas wells that the failure to report seems to be an industry-wide rule rather than the exception.[125]

The lack of reporting suggests that many conventional wells may pose unknown environmental risks to the public – risks that could be intensified if toxic chemicals such as PFAS are being used. But the public will have a difficult time discovering what chemicals may be present, due in part to the state's fracking chemical disclosure records for conventional wells that are difficult and time-consuming to search.

f. Fracking Data, Published Papers Suggest Underreporting of PFAS Use in Pennsylvania

An indication that oil and gas companies operating in Pennsylvania might not have fully disclosed their use of PFAS is evidence that more of them have disclosed use of PFAS in oil and gas wells when they operate in other states then they have in Pennsylvania. Only two oil and gas companies, Chesapeake Operating, Inc. and Hilcorp Energy, reported using PFAS (in this case, PTFE) in a total of eight of Pennsylvania's unconventional gas wells between 2012 and 2022. However, during the same period, fifteen other oil and gas companies that fracked oil and gas wells in Pennsylvania reported using PTFE for fracking in 346 wells across nine other states. Chesapeake Operating and Hilcorp Energy also reported using PTFE in oil and gas wells outside Pennsylvania. One of the 15 companies, EOG Resources, also disclosed using another PFAS, fluoroalkyl alcohol substituted polyethylene glycol, in 86 wells across New Mexico and Texas, and five of the companies disclosed using chemicals that may be PFAS, known as nonionic fluorosurfactants, in Oklahoma, New Mexico, and Texas. The specific identities of the nonionic fluorosurfactants were withheld from the public under trade secret claims, but three chemists and a board-certified toxicologist who examined this chemical name believe that nonionic fluorosurfactants could be PFAS.[126] The disclosed use of PFAS or potential PFAS in hundreds of oil and gas wells in other states by oil and gas companies operating in Pennsylvania raises questions about whether these companies are using these chemicals in Pennsylvania more widely than they have reported.

An additional indication that the use of PFAS in oil and gas wells in Pennsylvania could be more widely used than disclosed are two papers showing that the use of PFAS in oil and gas wells dates back decades and encompasses a variety of extraction techniques. In 2020, several scientists published an article in *Environmental Science: Processes and Impacts* showing that since 1956, PFAS including fluorosurfactants had been used or proposed to be used globally in oil and gas extraction techniques including chemical-driven gas production, chemical flooding, fracking, and the drilling that precedes fracking and other oil and gas production techniques.[127] In 2008, two authors, one of whom was identified as an employee at DuPont, wrote in the peer-reviewed *Open Petroleum Engineering Journal* that the use of fluorosurfactants was relatively common in the oil and gas industry and that their use was about to surge. They referred to fluorosurfactants as an "emerging technology" and stated,

> While fluorosurfactants have been used in gas and oil exploration for four decades, the increased demand for petroleum and the greater understanding of the benefits of fluorosurfactants have led to growing acceptance for fluorosurfactants throughout the petroleum industry.[128]

The authors did not explicitly say that fluorosurfactants used in oil and gas operations were PFAS, but they described the fluorosurfactants in ways that are commonly used to describe PFAS. They wrote that

> The use of fluorosurfactants is a recent but growing trend due to (i) the exceptional hydrophobic [water-repellent] and oleophobic [oil-repellent] nature of the perfluoroalkyl and perfluoroalkyl ether groups... The bond strength of the carbon-fluorine bond in perfluoroalkyl and perfluoroalkyl ether groups has been demonstrated as the key to remarkable overall stability for fluorochemicals and fluoropolymers.[129]

This evidence suggests that any time an unidentified fluorosurfactant or unidentified surfactant is used in oil and gas production, there is a potential that it is a PFAS. Companies operating oil and gas wells in Pennsylvania have used fluorosurfactants for fracking in other states. It is important to know if they have used these substances in Pennsylvania as well.

Table 4. Use of PFAS and Potential PFAS in Other States by Pennsylvania Oil & Gas Companies

Operator Name	Number of Unconventional Wells in Pa. with Fracking Chem. Disclosure of Any Type of Chemical	Disclosure of PTFE/Teflon for Fracking in Other States (no. of wells)	Disclosure of Nonionic Fluorosurfactants for Fracking in Other States (no. of wells)	Disclosure of Fluoroalkyl Alcohol Substituted Polyethylene Glycol for Fracking in Other States (no. of wells)
Cabot Oil & Gas Corp	689	Texas (1)		
Chesapeake Operating, Inc.	583	Texas (86) Ohio (78) Wyoming (12) West Virginia (11) Oklahoma (6) Pennsylvania (5) Louisiana (1)		
Southwestern Energy	536	Colorado (2) West Virginia (1)		
Chevron USA Inc.	246		Texas (26) New Mexico (11)	
XTO Energy/ExxonMobil	186	Texas (32) New Mexico (7) Ohio (4) Oklahoma (4) West Virginia (4)	Texas (67) Oklahoma (6) New Mexico (4)	
Anadarko Petroleum Corporation	112	Colorado (95) Wyoming (38)	Texas (8)	
Hilcorp Energy Company	87	Pennsylvania (3)		
Carrizo Oil & Gas, Inc.	50	Texas (15)		
Noble Energy, Inc.	46	Colorado (30)		
EOG Resources, Inc.	22	Texas (4)	Texas (2)	Texas (65) New Mexico (31)
WPX Energy	20	New Mexico (9)		
EXCO Resources, Inc.	12	Texas (87) Louisiana (1)		
Northeast Natural Energy LLC	4	West Virginia (9)		
Halcon Resources Corporation	3	Texas (2) Mississippi (1)		
Arrington Oil & Gas Operating LLC	1		Texas (3)	

This table shows the companies that disclosed the use of any and all fracking chemicals in Pennsylvania's unconventional gas wells between 2012 and 2022 and also disclosed the use of PFAS or potential PFAS for fracking in other states during the same period. The types of PFAS or potential PFAS disclosed as being used for fracking in other states include PTFE/Teflon, fluoroalkyl alcohol substituted polyethylene glycol, and nonionic fluorosurfactants. The numbers in (parentheses) show how many wells in each state the companies disclosed as being injected with the particular type of chemical. For example, the cell in the top of the table's third column from the left shows that between 2012 and 2022, Cabot Oil & Gas Corp. fractured one well in Texas with PTFE/Teflon. For a more detailed explanation of data sources, see Appendix A.

CH. 3 HEALTH STUDIES LINK OIL AND GAS OPERATIONS TO ILLNESS

a. Oil, Gas Well Proximity Associated with Disease

A robust and reliable body of scientific studies of PFAS in oil and gas operations – both their presence and their health effects – does not yet exist. However, peer-reviewed scientific studies of people living near oil and gas operations have correlated proximity to active well sites with a variety of diseases and other health effects. It is not unreasonable to extrapolate that, should PFAS have been used in those operations, it could be associated with some of those health effects.

A 2021 study comparing health data in Pennsylvania and New York counties atop the Marcellus Shale found that years of exposure to unconventional natural gas operations in Pennsylvania were associated with higher hospitalization and death rates from acute myocardial infarction (heart attack) than what was found in New York, where no unconventional gas operations took place.[130] The study was made possible by the natural experiment created by New York's moratorium and later ban on fracking and Pennsylvania's decision to pursue shale gas extraction.[131] Similarly, researchers from Johns Hopkins University analyzed data on more than 12,000 heart failure patients in Pennsylvania and compared those with and those without hospitalizations. They found that heart failure patients living near unconventional gas extraction sites were significantly more likely to become hospitalized.[132] The authors of both the New York/Pennsylvania study[133] and the study focused solely on Pennsylvania[134] suggested that particulate matter emitted from fracking operations and the stress associated with living nearby might have played a role in the findings. Neither study examined PFAS exposure, but one of the health impacts associated with PFAS exposure is high cholesterol that is, in turn, associated with heart attacks.[135] These associations, and the known use of PFAS in oil and gas operations, point to the need for more study of the use of PFAS in oil and gas operations and associated health effects.

PSR has collaborated with Concerned Health Professionals of New York to compile and summarize the substantial and growing number of scientific studies that have found serious health effects associated with oil and gas operations. At least two of these health effects, low birth weight in babies and heart disease (that can be linked to high cholesterol) are generally associated with exposure to PFAS, though the research to date has not investigated whether these health effects are specifically linked to PFAS used in oil and gas operations. In the eighth edition (2022) of our report, we wrote,

> Public health problems associated with fracking include prenatal harm, respiratory impacts, cancer, heart disease, mental health problems, and premature death… Poor birth outcomes have been linked to fracking activities in multiple studies in multiple locations using a variety of methods. Studies of mothers living near oil and gas extraction operations consistently find impaired infant health, especially elevated risks for low birth weight and preterm birth. As we go to press, a new study in Pennsylvania finds "consistent and robust evidence that drilling shale gas wells negatively impacts both drinking water and quality of infant health."[136]

Low birthweight is a leading contributor to infant death in the United States.[137]

b. Studies Needed on PFAS

PSR is not aware of published studies that have analyzed well sites for PFAS or that have analyzed health effects related to potential use of PFAS at well sites. We are aware of only two studies of PFAS associated with oil and gas operations, both conducted by government agencies, and both focused on Pennsylvania. In 2023, the DEP tested a water well for PFAS at the Washington County home of Bryan Latkanich[138] in response to Latkanich's complaint that nearby oil and gas operations had contaminated his water with PFAS.[139] The DEP reported that it found some PFAS in Latkanich's water (PFOS at 2.3 parts per trillion, as well as PFHxS and PFOSA), but it found no evidence that PFAS was used in the nearby oil and gas operations, specifically a gas well pad operated by Chevron about 500 feet from the Latkanich home that was the site of two unconventional gas wells.[140] The DEP speculated that the source of the PFAS could be, among many potential sources, water that already contained PFAS being used for fracking in the unconventional gas wells. State regulations do not require testing for chemicals contained in water used in fracking.[141]

These testing results are not necessarily reassuring. The PFOS concentration was 115 times higher than EPA's health advisory level of 0.02 parts per trillion, though below the EPA's proposed drinking water standard of four parts per trillion. DEP tested for 36 types of PFAS and found only three types in the Latkanich well, but there are thousands of types of PFAS in use. A test for total organic fluorine, which the DEP did not conduct, might have indicated the presence of additional PFAS. The lack of evidence of PFAS use at nearby oil and gas operations could have been consistent with actual lack of use, or it could have reflected the use of PFAS chemicals for which the DEP did not test and which regulators or even the companies conducting the gas operations may not have known about. For the second study focusing on PFAS associated with oil and gas operations, see Appendix B.

In the bigger picture, the lack of testing for PFAS at oil and gas sites is not surprising; there were few if any grounds to test for PFAS in connection with oil and gas operations prior to July 2021, when PSR first publicized the probable use of these chemicals in oil and gas extraction. Now that we know PFAS have been used in oil and gas operations for years, scientists should determine where this use takes place and whether there are connections between this use and health effects, for PFAS chemicals individually and as a compounding factor in conjunction with exposure to other fracking chemicals.

An oil and gas fluids impoundment near Zelienople, Pennsylvania, 2015. Photo credit: Ted Auch. Photo courtesy of FracTracker Alliance.

CH. 4 EXPOSURE PATHWAYS TO PFAS ASSOCIATED WITH OIL AND GAS OPERATIONS IN PENNSYLVANIA

As indicated by EPA in the agency's 2016 report on fracking and drinking water, there are multiple pathways through which contaminants associated with oil and gas operations in Pennsylvania can jeopardize health and the environment. These include leaks and spills of chemicals at well sites, leaks and spills of wastewater at well sites or disposal sites, underground migration into groundwater from production wells or wastewater disposal wells used as underground repositories for wastewater, spreading of wastewater on roads for dust suppression and deicing, and dumping at landfills of solid waste that could be tainted with toxic substances. All of these concerns would apply to PFAS as well as to other contaminants.

a. Disposal of Waste Intensifies Pollution Concerns

The risk that PFAS and other chemicals associated with oil and gas drilling could pollute the Pennsylvania environment is especially high because of the staggering volumes of wastewater and solid waste generated by oil and gas extraction. The volumes are so high largely because of the scale of many of the unconventional gas wells being drilled in Pennsylvania compared to conventional wells drilled in past decades. Developing each well involves injecting millions of gallons of water, sand and fracking fluid. A portion this mixture returns to the surface in the form of wastewater known as "flowback." In 2016, the EPA reported that flowback *per well* in the Marcellus and Utica shale formations that are exploited for gas in Pennsylvania can total between 300,000 and one million gallons over the first 10 days after fracking.[142] In addition, following flowback, huge volumes of naturally occurring water from underground formations, known as "produced water," flow out of the wells, potentially for years.[143] In 2016, EPA reported that five years after a well was drilled in the Marcellus shale, it would still be producing wastewater at a rate of hundreds of gallons per day.[144]

The wastewater, whether flowback or produced water, can contain chemicals intentionally added to the fracking fluid such as PFAS; naturally occurring contaminants found in underground formations, including radium, which occurs in significant concentrations in wastewater from Pennsylvania;[145] and may contain chemicals that are products of reactions that occur in underground formations such as those between fracking chemicals and naturally occurring compounds in the formation such as methane.[146] Intentionally added drilling fluids, as well as naturally occurring water encountered during drilling, may be part of the wastewater mix.[147] In addition, drilling the wells involves boring into the earth 9,000 feet vertically and 10,000 additional feet or more horizontally.[148] This process produces tons of rock shards known as "drill cuttings" that could be contaminated with human-made or naturally occurring toxics.[149] FracTracker Alliance has found that wastewater and drill cuttings are the two largest waste streams produced by oil and gas operations in Pennsylvania. According to the organization's analysis of Pennsylvania Department of Environmental Protection oil and gas waste reports, in 2022, oil and gas wells in Pennsylvania generated more than 2.6 billion gallons of wastewater. [150] That liquid waste was transported to 598 facilities in Pennsylvania, New York, Ohio, and West Virginia, with almost 90 percent of the wastewater and 80 percent of the solid waste remaining in Pennsylvania. Most of the wastewater went to other well pads where wastewater can be reused to offset the need for fresh water;[151] to residual waste processing facilities that appear to include facilities for wastewater storage and treatment;[152] to injection disposal wells where wastewater is injected underground for supposedly permanent disposal, and to storage facilities pending disposal or reuse.

Pennsylvania's oil and gas wells produced more than 2.1 billion pounds of solid waste, largely consisting of drill cuttings, but also including produced fluids reported in tons, soil contaminated from spills, and synthetic liner material. The solid waste was transported to 53 facilities in the same four states, with most of the waste going to Pennsylvania landfills. Other destinations for solid waste included reuse at other well pads, residual waste processing facilities, and disposal at injection wells. If some of the wastewater or solid waste were tainted with PFAS, it could pose risks to the environment or health, both at the well sites where the waste is generated, and also at waste disposal sites that can be miles away. See the map below and an interactive online version from FracTracker for destinations for this waste.

The reported volumes of waste from oil and gas wells could be even larger than reported. In 2014, the Pittsburgh Post-Gazette reported that nine landfills located in southwestern Pennsylvania reported accepting three to four times the amount of oil and gas waste that operators told the DEP that they sent to the landfills. The DEP told the Post-Gazette that it did not verify reports on the volume of oil and gas wastewater that oil and gas wells operators sent to centralized waste treatment facilities or underground injection wells, but the DEP had no reason to doubt the figures.[153]

The potential for oil and gas waste to contain PFAS is not just hypothetical, according to an analysis of Pennsylvania state records in 2022 by Environmental Health News.[154] The publication found that the eight wells in Pennsylvania injected with PTFE/Teflon produced more than 23 million gallons of liquid waste and 30,390 tons of solid waste between 2012 and 2022.[155] A map developed for the publication by FracTracker Alliance showed that this waste was transported to at least 97 sites for reuse or disposal in Pennsylvania, Ohio, and West Virginia.[156]

Robert Delaney, a retired geologist and Superfund specialist with the Michigan Department of Environmental Quality (now called the Michigan Department of Environment, Great Lakes, and Energy), told Environmental Health News that "If there were PFAS in any of those waste products, it's likely that it would have gotten into the environment in some of those locations." Delaney spent 36 years working in natural resource protection for the state of Michigan and first warned state officials about the looming problem with PFAS in 2012, though unrelated to oil and gas extraction.[157] "The

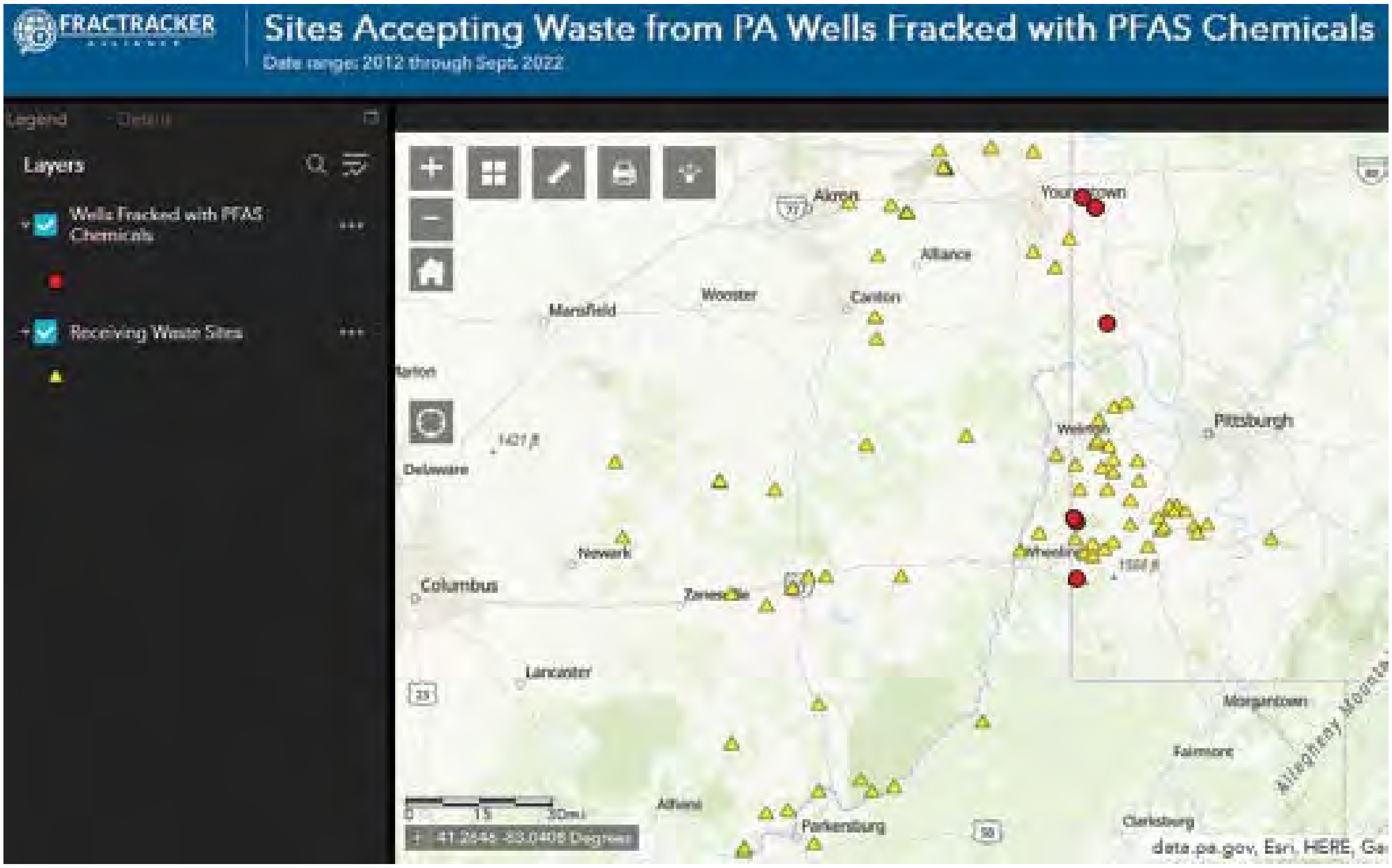
Figure 2. Facilities Accepting Pennsylvania Oil and Gas Waste in 2022

Map courtesy of FracTracker Alliance shows destinations in 2022 for liquid and solid waste generated by oil and gas wells in Pennsylvania. An interactive version of the map is available at https://ft.maps.arcgis.com/apps/webappviewer/index.html?appid=4c61de38fe714bf699349e0c7dbef779.

odds are that just as there were spills at the well pads, there have been spills and leaks at these disposal sites," Delaney told Environmental Health News. "All these places that accepted the waste didn't know that they were dealing with PFAS. And the things you do to treat other chemicals doesn't work on them...these chemicals never go away."[158]

When Environmental Health News first asked the Pennsylvania Department of Environmental Protection to comment on the use of PFAS in oil and gas operations in Pennsylvania, the Department responded that "absent a spill or release on the surface or below surface, there is no reason to conclude that wellsite fluids (whether including PFAS compounds or not) would have reached nearby soils or drinking water."[159] The publication then found evidence that there were two spills at one of the wells, known as Paul Schlinski 8H, in 2017 and 2020, and informed the DEP.[160] DEP spokesperson James Thrasher told the publication, "Given the time period between the use of the PFAS chemicals and the releases, the small amount of the spills, that the spills were contained to the gravel of the well pad, and that they were remediated quickly, DEP does not have current plans to sample for PFAS at this location." Thrasher explained that chemicals used in fracking are likely to be contained in so-called "flowback water" that typically emerges from wells within the first 30 days after fracking. In contrast, the spills occurred four years after fracking and were of produced water that primarily consists of naturally occurring brine from underground formations. His comments implied that the produced water was unlikely to contain chemicals that

Figure 3. Sites Accepting Waste from Pennsylvania Wells Fracked with PFAS Chemicals



Map developed by FracTracker Alliance for Environmental Health News showing destinations for liquid and solid waste from eight Pennsylvania oil and gas wells where oil and gas companies reported using PTFE/Teflon for fracking between 2012 and 2022. An interactive map of these sites is available here: https://www.ehn.org/fracking-pennsylvania-pfas-2658837888.html.

were used in fracking.[161] Delaney, the Superfund specialist, told Environmental Health News that Pennsylvania officials should at least test for PTFE near the well sites where the chemical was used and consider testing at the locations where waste from these wells was disposed of.[162] PTFE, a PFAS, persists, after all, in the environment.

b. Leaks, Spills Raise Pollution Concerns

As indicated by the cases of waste from wells injected with PTFE, one of the major pathways through which PFAS could contaminate water or soil is leaks and spills of drilling fluids, fracking fluids, or wastewater. These leaks and spills are common in oil and gas operations in Pennsylvania, as well as in other states, and they may be more common and serious than publicly reported. In 2017, a team of researchers published a paper in which they found that between 2005 and 2014, unconventional oil and gas well operators in Pennsylvania reported 1,293 spills from drilling through energy production.[163] The researchers calculated that the wells involved had an average spill rate of 4.3 percent during the period; this figure was defined as the total number of spills divided by the number of well-years during the period.[164] The researchers found that the total reported volume of spills in Pennsylvania during the period was 260,000 gallons. However, the authors cautioned that "Pennsylvania may have 'missing' volumes data because reporting of spills has only been required by telephone; agency guidance discouraged written notification." The researchers added that regulations set to take effect in 2016 would require written reports for spills greater than 42 gallons or when a spill may pollute Pennsylvania waters (These regulations for unconventional gas wells are in effect as of 2023).[165]

The freedom of the industry to self-report and the informal reporting of spills by telephone suggest that the number of spills and their volume could have been greater than was reported, increasing the potential for contamination by PFAS and other toxic substances.

Additional evidence from the criminal grand jury investigation conducted by Pennsylvania's Attorney General mentioned in Chapter 2 suggests that oil and gas-related spills and contamination may be more frequent and severe than reported. The grand jury heard testimony about the experience of more than 70 households, a sample size restricted by the Attorney General's limited jurisdiction over environmental crimes in Pennsylvania.[166] The grand jury also heard testimony from dozens of current and former employees of the DEP and Pennsylvania Department of Health.[167] The grand jury was dubious that spills were accurately and comprehensively reported, given that inspectors often relied on industry self-reporting of spills or denials that a spill had occurred and did not visit spill sites. "DEP employees would investigate citizen complaints simply by calling the [oil or gas well] operator and asking him what happened," the grand jury found. "If the operator sent in a photo purporting to show that no spill had occurred, the matter could be closed without ever leaving the office."[168]

The grand jury also found that the DEP used test methods known as a "suite code" to detect water contamination from oil and gas operations that often did not include testing for at least some of the contaminants likely to be associated with oil and gas extraction. The grand jury reported that

> An operator might be using a particular compound on a specific occasion that is not universally present at fracking sites. If DEP did not check the operator's records to see what he was using when a spill occurred (if the chemicals were fully disclosed), the Department would never know what to test for. Reliance on the standard suite code would actually be detrimental, because it would give a clean bill of health to water that might in fact be dangerously contaminated.[169]

PFAS was not one of the contaminants tested for by the DEP,[170] raising the potential that Pennsylvanians could have been unknowingly exposed to dangerous PFAS chemicals through oil and gas-related leaks and spills.

In some cases, authorities have documented water contamination from leaks and spills due to oil and gas operations. In 2018, Pennsylvania's DEP fined a West Virginia company $1.7 million for a host of violations at more than a dozen well sites in Pennsylvania, including a leak of fluid from holes in the liner of a wellsite pit. The release killed nearby vegetation and impacted groundwater and a spring used for drinking water.[171] In a separate incident in 2014, the DEP fined Range Resources a record $4.15 million to settle violations that contaminated soil and groundwater near seven impoundments in Washington County; the impoundments held millions of gallons of fracking wastewater. The DEP reported that the violations included a release of 25 barrels of fracking fluid onto the ground; failure to prevent fracking fluid from flowing from a pipe onto soil and into a tributary of Brush Run, a state-designated High Quality stream, causing harm to aquatic life; and failure to contain about 400 barrels of used fracking fluids, which were released into soil and an adjacent stream.[172] Also in 2014, the Pittsburgh Post-Gazette analyzed DEP records showing that oil and gas operations had contaminated or reduced the flow of 243 private water supplies since the end of 2007. Some of the water supplies were contaminated through spills, the newspaper reported, though the records did not describe in much detail how the water supplies were impacted.[173]

c. Underground Injection Wells, Abandoned Wells Put Drinking Water at Risk

Another major pathway through which PFAS-tainted oil and gas wastewater could contaminate surface or groundwater is through underground injection into disposal wells. Wastewater from the eight unconventional gas wells in Pennsylvania that were injected with PTFE was injected into more than three dozen different underground injection wells in Ohio.[174]

The potential for pollution from oil and gas wastewater is not unfounded. Researchers have known for decades that wastewater from injection disposal wells can contaminate groundwater. In some cases, the wastewater, a mixture of naturally occurring brine and oil and gas waste, has migrated upward from deep underground, moving through nearby oil and gas wells, many of which have ceased operating but have not been properly sealed off from the surrounding underground rock formations.[175] This migrating wastewater can break out of abandoned wells and contaminate groundwater near the earth's surface.[176]

In 1985, the Texas Department of Agriculture quoted the then-existent Congressional Office of Technology Assessment regarding the "insidious" problem of underground injection of oil and gas wastewater. The congressional office had noted that such wastewater is typically injected in exactly the places where prior drilling has created opportunities for the wastewater to migrate through abandoned or closed wells into groundwater.[177] In 1989, Congress' investigative arm, the General Accounting Office (now the Government Accountability Office) reported on almost two dozen incidents of drinking water contamination associated with wastewater disposal wells.[178] Many of these cases involved wastewater migrating up abandoned oil and gas wells.[179]

Pennsylvania's own injection wells are not currently a major destination for wastewater from the state's oil and gas wells. Instead, Pennsylvania trucks far more of its oil and gas wastewater to neighboring Ohio. As of 2023, Pennsylvania had only 12 underground wastewater injection wells,[180] compared to 245 as of 2022 in Ohio, [181] where the geology is more favorable and permitting is easier. However, Inside Climate News reported in 2023 that minutes taken at a DEP Oil and Gas Technical Advisory Board meeting in 2021 alluded to a study from Tetra Tech, a consulting firm, saying that Pennsylvania would need between 17 and 34 extra disposal wells to handle the current amount of oil and gas wastewater produced in the state.

Inside Climate News also reported that a company called Penneco was planning a second injection well near Monroeville in western Pennsylvania. [183] Some local residents were opposing the well, as was the Plum Borough Council, which filed an appeal against its own appointed zoning board after the zoning board approved the well.[184]

Aside from underground injection wells, Pennsylvania is home to thousands of abandoned oil and gas wells, many of them unplugged and in unmarked locations. The world's first commercial oil well was drilled in Titusville, Pennsylvania in 1859,[185] but oil and gas companies were not required to plug non-producing wells until 1984 and were not required to register old wells until 1985. Largely as a result, the state is riddled with old, unplugged or improperly plugged wells. Estimates of the number of these "orphan" wells, as they are known, range in the hundreds of thousands, but the true number may never be known. As noted earlier, the DEP found in 2023 that the practice of abandoning oil and gas wells, at least for conventional wells, has continued into the present day.[186]

Recent history shows that wastewater from injection wells, potentially contaminated with PFAS or other dangerous chemicals, could reach these abandoned wells and migrate up the well shaft. This scenario could occur both in Pennsylvania and across the state line in Ohio where injection disposal wells are more common. Since 2020, two cases – one suspected to have involved an injection well, the other known to have done so – have been documented. In January 2021, more than 1.6 million gallons of what appeared to be fracking wastewater flowed for four days from an unplugged oil and gas well in Noble County, Ohio, idle since 2012.[187] A nearby tributary, Taylor Fork, was impacted by the spill, resulting in a fish kill. The cause of the spill was unclear, but there were six active fracking wastewater injection wells in Noble County, including three within four miles of the leaking oil and gas well. Another example occurred in September 2020 in Washington County, Ohio, when fracking wastewater from a disposal well migrated at least five miles to gas-producing wells, causing state officials to worry about possible groundwater contamination.[188]

Abandoned wells could also be conduits for fracking fluid injected into active oil and gas production wells as opposed to disposal wells – fracking fluid that may be tainted with PFAS or other toxics. In 2022, the Pittsburgh Post-Gazette reported that a man in New Freeport reported that he witnessed "a geyser" of water erupting from the location of an abandoned well on his property. He learned that a Pennsylvania-based oil and gas company, EQT Corp., was simultaneously fracking a horizontal well more than a mile away. The next day, EQT notified DEP about a "well communication" issue, a term that refers to a situation in which one well interacts with another. The company, however, told the Post-Gazette that it did not know if its fracking had caused the geyser. The company and the DEP were investigating. Several neighbors reported that they thought the apparent communication impacted their water.[189]In one case, a person who took a shower on the day of the incident later broke out in hives.[190]

The Post-Gazette's reporting indicated that communication with abandoned wells may be more common than reports reflect because it is likely that no one would be nearby to observe impacts in an abandoned well.[191] Over the previous six years, oil and gas companies had reported to DEP 45 suspected cases of well communication. Most of these suspected cases were discovered by operators of shale gas wells adjacent to the wells that were the apparent source of the communication. These adjacent operators noticed changes in pressure or other impacts in their own wells. But if no one were near an abandoned well with which an active well communicated, the result could be water or soil contamination unknown to the public, whether from PFAS or other toxics.

Compounding these problems is that oil and gas production wells in Pennsylvania can be located as close as 500 feet from a building or water well in the case of unconventional wells, and within 200 feet in the case of conventional wells.[192] This reality means that abandoned wells can be located near people's homes, and communication of toxic fluids from a production well or disposal well nearby could emerge from an abandoned well and pollute well water or soil at a residence. Fluids from the well could also migrate directly into groundwater that feeds a private water well. And airborne pollutants could easily travel such a short distance (see section f below). The Attorney General's grand jury recommended a setback or no-drilling zone of 2,500 feet from homes and 5,000 feet from schools and hospitals. These distances that would be more protective but perhaps not protective enough:[193] In 2012, a New York office of the U.S. Geological Survey warned that if the type of fracking practiced in Pennsylvania were allowed in New York, fracking could jeopardize water supplies within a radius of up to five square miles.[194]

d. Road Spreading

Road spreading -- the practice of spraying oil and gas wastewater on roads for deicing or dust suppression – constitutes another pathway through which PFAS used in oil and gas wells could jeopardize Pennsylvanians' health. Researchers at Penn State University have found salts, metals, and radioactive elements in runoff from road spreading at levels higher than are considered healthy for people and the environment. There is no evidence that they tested for PFAS, but any chemical contained in the wastewater could run off of roads and contaminate water sources. The researchers also found that road spreading is no more effective at controlling dust than rainwater, a conclusion that the oil and gas industry disputes.[195] Two actions have created a partial ban on road spreading in Pennsylvania. In 2016, DEP banned the practice of road spreading with wastewater from unconventional gas wells.[196] In 2018, as a result of a settlement of an Environmental Hearing Board appeal, DEP's Oil and Gas Program halted the practice of approving road spreading of conventional wastewater.[197] However, road spreading with conventional wastewater has continued under a provision of the Solid Waste Management Act called "coproduct determination," in which a company can use industrial waste in place of a commercially available product if the industrial waste does "not present a greater threat of harm to human health and the environment than use of an intentionally manufactured product or produced raw material." The law requires various tests to demonstrate this relative level of safety. However, the tests do not require analysis for PFAS or radium.[198] As indicated earlier, PFAS could be used for drilling in conventional wells, even if the wells are not fracked.

The nonprofit Better Path Coalition found that conventional oil and gas drilling companies spread more than 2.2 million gallons of their wastewater on roads in Pennsylvania between 2018 and the end of 2020,[199] and more than 977,000 additional gallons in 2021,[200] bringing the four-year total to more than 3.1 million gallons. This wastewater could have contained PFAS or other toxics, but it is impossible to know without adequate testing.

e. Landfills

When solid waste from oil and gas operations is taken to landfills, Pennsylvanians could also be impacted by chemicals in that waste, including, potentially, PFAS. Landfills produce their own dangerous wastewater, known as "leachate," when rainwater percolates through the contents of the landfill, comes in contact with buried wastes, and leaches out their chemicals or constituents.[201] Should the rainwater contact oil and gas waste tainted with PFAS and leach out those chemicals, and if that leachate were to escape from the landfill, it could cause contamination.

One case in Fayette County, Pennsylvania demonstrates the potential of leachate from oil and gas waste to cause water pollution, although it is unknown whether PFAS were involved. In 2019, local prosecutors asked the Pennsylvania Attorney General's office to investigate after leachate from a landfill that had accepted drill cuttings was taken to a wastewater treatment plant that discharged into the Monongahela River, a major source of drinking water for Western Pennsylvania.[202] While accepting leachate from the landfill, the plant's discharge of treated water exceeded state and federal pollution standards for several pollutants including ammonia-nitrogen because its treatment system stopped functioning, allowing pollutants to pass through, according to the local prosecutors' complaint.[203] A test of the landfill's leachate in 2019 detected "volatile organic compounds (VOCs), including Xylene, Ethylbenzene, Naphthalene, 1,3, 5 Trimethylbenzene and 1, 2, 4 Trimethylbenzene… All of these contaminates (sic) are constituents of diesel fuel and are associated with waste streams from unconventional wells," an attorney for the wastewater treatment plant wrote in a letter accompanying a consent order prohibiting the landfill from sending its leachate to the treatment plant for 90 days.[204] Oilfield services company Schlumberger[205] and the Oklahoma State

University Extension[206] have stated that diesel fuel has been, or may currently be used, in drilling of oil and gas wells. The treatment plant's superintendent wrote in an affidavit that the plant was able to effectively treat its wastewater during a two-week experiment when it temporarily stopped accepting waste from the landfill – an experiment which showed that the landfill's waste was causing the treatment plant to exceed pollution control standards.[207]

A more recent case involved allegations that leachate from a landfill in Pennsylvania contaminated a creek near York with PFAS, though the source of the PFAS in the landfill was unspecified. In 2023, Lower Susquehanna Riverkeeper Ted Evgeniadis sued Modern Landfill and its owner Republic Services, asking a federal judge to force the company to comply with the Clean Water Act and to impose penalties for alleged violations.[208] Evgeniadis asserted that the landfill was discharging extremely high levels of PFAS into the creek in violation of the law. In his written complaint, he stated that he tested discharges from the landfill into Kreutz Creek as well as areas of the creek downstream from the discharges and found levels of PFOS at 374.3 parts per trillion, levels of PFOA at 847 parts per trillion and added that "25 other PFAS compounds were also measured at very high levels."[209] DEP records show that in April 2019, Modern Landfill received three tons of produced fluid from unconventional gas wells,[210] but it is unclear that this volume of fluid was accurate because records of oil and gas waste shipments and deliveries in Pennsylvania are often inconsistent.[211] Nor is it clear or whether gas-related waste contributed to the high PFAS levels near the landfill.

f. Volatilizing, Flaring Could Pollute Air with PFAS

PFAS used in oil and gas wells could follow airborne exposure routes, according to toxicologist David Brown, former director of environmental epidemiology at the Connecticut Department of Health. Brown, who has investigated health effects associated with unconventional gas drilling for the Southwest Pennsylvania Environmental Health Project, warned that if PFAS were to enter drinking water, it could subsequently volatilize or become airborne inside homes.[212] Brown also added another potential pathway for airborne exposure: PFAS could become airborne when gas is either vented or burned off during flaring at the wellhead.[213]

Bolstering Brown's concern, both the EPA and the Interstate Technology Regulatory Council say that PFAS can be spread through air. Neither source mentions pathways from oil and gas operations, perhaps because such pathways have only recently come to the public's attention. On a webpage devoted to "PFAS Analytical Methods Development and Sampling Research," EPA includes a heading entitled "Source (Air) Emissions." It states under that heading that "There are diverse sources of [air] emissions, including chemical manufacturers, commercial applications, and thermal treatment incineration processes. EPA is developing test methods for measuring PFAS source emissions."[214] The Interstate Technology Regulatory Council (ITRC), a state-led environmental coalition that includes members from state, federal, tribal, and international agencies as well as academia, the private sector and the general public,[215] reported that "Under certain conditions, particularly within industrial stack emissions, or during fire suppression, incineration, or combustion, PFAS can be transported through the atmosphere."[216] The ITRC added that deposition of PFAS could result in pollution of soil, groundwater, or other media:

> Short-range atmospheric transport and deposition can result in PFAS contamination in terrestrial and aquatic systems near points of significant emissions, impacting soil, groundwater, and other media of concern (citation omitted). Evidence of releases has been observed in areas where hydrologic transport could not plausibly explain the presence of PFAS in groundwater, with the extent of contamination reaching several miles from sources and in distribution patterns independent of regional hydrology (citations omitted).[217]

If PFAS are used in oil and gas wells, this information indicates that nearby residents should be concerned about airborne emissions.


John Day unconventional gas well site and fluids impoundment in Amwell Township, Washington County, Pa., June 7, 2021. The Pennsylvania Department of Environmental Protection (DEP) cited discharges from this impoundment as some of the violations and releases that prompted the DEP's $4.15 million fine against Range mentioned on page 25 of this report. Photo credit: Courtesy of Marcellus Air.

CH. 5 OIL & GAS-RELATED CHEMICAL EXPOSURE AS AN ENVIRONMENTAL JUSTICE ISSUE

“Fenceline” communities – people living close to oil and gas operations – often bear a disproportionate risk of exposure to toxic chemicals. Thus, they may be particularly at risk from PFAS used in oil and gas extraction. Although drilling and fracking take place across the U.S., not everyone shares in the risks equally. Rather, oil and gas infrastructure and associated chemicals are frequently located in or adjacent to lower-income, underserved, and marginalized communities, notably Black, Indigenous, and other communities of color, as has been documented in a variety of studies.

A 2019 analysis conducted in Colorado, Oklahoma, Pennsylvania, and Texas found strong evidence that African Americans disproportionately lived near fracking wells in Texas and Oklahoma, while Hispanics disproportionately lived near fracking wells in Texas and urban Colorado. “In Pennsylvania,” the study reported, “where natural gas drilling generally takes place in counties with low shares of minorities, no environmental disparities by race/ethnicity are found, however we do find significantly lower incomes near fracking wells.”[218] Similarly, in 2017, FracTracker Alliance published an analysis that found that out of almost 800 oil and gas wells drilled in Allegheny, Armstrong, and Butler counties between 2010 and 2014, only two were drilled in census tracts where the median home value was $200,000 or greater.[219] A separate study published in 2015 found that census tracts in Pennsylvania with potential exposure to unconventional wells have a higher percentage of lower-income people.[220]

Where a pattern of risks affects people of color and/or lower-income people disproportionately, oil and gas production methods should be viewed and addressed as an Environmental Justice issue. So too should any oil- and gas-related exposure to PFAS.

Unconventional gas well in Union Township, Washington County, Pa., May 19, 2014. Photo credit: Courtesy of Marcellus Air.

CH. 6 POLICY CAN HELP PROTECT PENNSYLVANIANS FROM PFAS IN FRACKING

a. Modest Federal Protections from PFAS Pollution

Governments at all levels will have to do more to protect the public from PFAS, as EPA has taken only modest steps to do so, while Congress and the executive branch have exempted the oil and gas industry from major provisions of multiple federal environmental laws. For example, oil and gas operations are exempt from important permitting and pollution control requirements of the Clean Water Act, including the stormwater runoff permit requirement. [221] Fracking is exempted from the Safe Drinking Water Act pollution control measures unless diesel is used in the fracking process.[222] Oil and gas waste is exempted from the hazardous waste rules that require cradle-to-grave tracking and safe handling of hazardous substances under the Resource Conservation and Recovery Act.[223] These exemptions increase the burden on state governments to address any PFAS pollution associated with oil and gas extraction. [224]

EPA has taken some steps to protect the public from dangerous PFAS. In 2005, EPA reached a then-record $16.5 million settlement with chemical manufacturer Dupont after accusing the company of violating the federal Toxic Substances Control Act (TSCA) by failing to disclose information about PFOA's toxicity and presence in the environment.[225] In 2006, EPA invited Dupont, 3M and six other companies to join a "stewardship" program in which the companies promised to achieve a 95 percent reduction of emissions of PFOA and related chemicals by 2010, compared to a year 2000 baseline. The agreement also required the companies to eliminate such emissions and use of these chemicals by 2015.[226] In 2022, EPA said on its website that the companies reported that they had accomplished those goals, either by exiting the PFAS industry or by transitioning to alternative chemicals.[227] EPA reported in 2022 that the manufacture and use of at least one PFAS, PFOA, had been phased out in the U.S., and that no chemical company had reported making PFOS in the U.S. since 2002. EPA did note that existing stocks of PFOA might still be used, and imported products may contain some PFOA,[228] and a 2020 scientific article reported that PFOA was still used in Asia. EPA stated that limited ongoing uses of PFOS remain. Since the announcement of its PFAS stewardship program in 2006, EPA has allowed nearly unlimited use of closely related "replacement" chemicals in dozens of industries.[231] In response, in 2015 a group of more than 200 scientists raised health and environmental concerns that the new PFAS designed to replace PFOA and PFOS may not be safer for health or the environment.[232]

In October 2021, EPA announced a "strategic roadmap" for regulating PFAS. This plan encompasses a goal of setting federal drinking water standards for several PFAS chemicals by 2023, as well as commitments to "use all available regulatory and permitting authorities to limit emissions and discharges from industrial facilities" and "hold polluters accountable."[233] The plan does not, however, include an examination of PFAS use in the oil and gas industry. (Later that month, 15 members of the U.S. House of Representatives asked EPA to examine this topic.[234] The month before, PSR had asked EPA to collect data on PFAS use in oil and gas extraction, utilizing its authority under TSCA.[235]) As previously stated, in June 2022, EPA announced new health advisory levels for several types of PFAS and in March 2023, announced a plan to regulate six types of PFAS in drinking water. In August 2022, EPA proposed designating PFOA and PFOS as hazardous under Superfund.[236] This designation would enable affected parties to more easily hold oil and gas companies accountable for cleanup costs if PFOA and PFOS were found at oil and gas sites. Under Superfund, liability does not require negligence, and any potentially responsible party (PRP) can be held liable for cleanup of an entire site when it is difficult to distinguish contributions to pollution among several parties. As EPA writes about Superfund, "[i]f a PRP sent some amount of the hazardous waste found at the site, that party is liable."[237]

In acting belatedly to regulate at least some types of PFAS in drinking water, EPA is following the lead of several states, including Pennsylvania. As of 2023 nine states, including at least several with contaminated military sites, had developed enforceable standards for concentrations of several types of PFAS in drinking water.[238]

b. Pennsylvania’s Disclosure Rules: In Need of Sweeping Reform

In Pennsylvania, multiple reforms are needed to protect the public from the use of PFAS in oil and gas operations, including changing the state’s chemical disclosure rules to lift the veil of secrecy that oil and gas companies have used to conceal the use of potentially dangerous chemicals including, perhaps, PFAS. One such change is tighter limits on the use of trade secret provisions.

Oil and gas companies have argued that chemical trade secrets are necessary to protect their intellectual property from competitors. However, this interest does not have to mean a complete withholding of chemical identities from scientists, regulators, and the public. In 2015, California, a major oil-producing state,[239] began requiring full disclosure of the individual chemicals used for well stimulation, including fracking.[240] In June 2022, Colorado, a major producer of oil and gas,[241] followed in California’s footsteps but extended the disclosure requirements to all chemicals used in oil and gas wells, not just fracking or stimulation chemicals.[242]

The methodology utilized in California and Colorado is consistent with a recommendation issued in 2014 by an advisory panel to the U.S. Department of Energy: that companies reveal the fracking chemicals injected into each well, providing that information in a list in which the chemicals are disassociated from the trade name of the commercial products they are part of.[243] This form of disclosure enables the public to know all the chemicals used in fracking without disclosing to rival chemical manufacturers the exact components of proprietary formulas.[244] In a similar way, food producers keep recipes secret while disclosing individual ingredients, enabling the public to know the contents of food products but making it difficult for rival producers to recreate valuable food brands. For unconventional wells, Pennsylvania requires that individual chemicals injected into each well be disclosed, disassociated from chemical products.[245] However, the state’s simultaneous allowance of trade secret claims for individual chemicals, unlike California and Colorado, ensures that Pennsylvania’s disclosure technique results in less than full disclosure.

California, Colorado and other states have additional provisions in their oil and gas chemical disclosure rules that could be models for Pennsylvania. California has a process under which state regulators review secrecy requests from chemical companies to determine whether the information must be kept proprietary,[246] and health and safety data related to fracking fluids are not allowed to be hidden from public view under California law.[247] California also requires disclosure of fracking chemicals before fracking begins,[248] as do West Virginia[249] and Wyoming.[250] Colorado, in its June 2022 legislation, required chemical disclosure from chemical manufacturers.[251] The Pennsylvania Attorney General’s grand jury endorsed many of these measures, recommending full chemical disclosure of all chemicals used in oil and gas wells before they can be used.[252]

These reasonable and feasible reforms are valuable steps to protect the health of people who may be exposed to PFAS and other dangerous oil and gas chemicals, be they industry workers, residents living near well sites, or first responders called to the scene of an accident. They can improve health and potentially save lives. Additional steps to reduce the harms caused by oil and gas extraction are outlined in the recommendations section, including a ban on the use of PFAS in oil and gas operations, an action that Colorado took in 2022.[253] Among the evidence supporting the feasibility of this measure is a peer-reviewed analysis published in 2021 showing that many PFAS are immediately replaceable with less-persistent and less-toxic substances, including for use in the oil and gas industry.[254]

c. Pennsylvania’s Hazardous Waste Rules Also in Need of Reform

Pennsylvania’s state government has recognized the dangers of PFAS but, in doing so, has illuminated another gap in state rules that should be closed to protect the public from PFAS use in oil and gas operations. Subtitle C of RCRA is our nation's law that requires safe management of hazardous waste from "cradle-to-grave."[255] In 2021, in response to a request from New Mexico's Governor Michelle Lujan Grisham to regulate PFAS under Subtitle C, EPA Administrator Michael Regan said that the agency would initiate a rulemaking process to declare four types of PFAS to be "Hazardous Constituents" under RCRA – PFOA, PFOS, PFBS, and GenX – as a step toward listing them under Subtitle C. He also said that EPA would initiate a rulemaking to "clarify that emerging contaminants such as PFAS can be addressed through RCRA corrective action."[256]

Yet under both the federal RCRA[257] and the state's implementation of the federal law in the Solid Waste Management Act,[258] oil and gas wastes are exempt from hazardous waste requirements. This exemption allows drilling companies to take solid oil and gas waste to municipal landfills that have inadequate testing for radioactivity and other toxics, according to Duquesne University microbiologist John Stolz.[259] Similarly, the exemption allows oil and gas companies to inject their liquid waste underground into so-called Class II wells designated for oil and gas waste; these wells have lower standards of environmental protection than Class I wells that are designated for hazardous waste. For example, operators of Class I hazardous waste injection wells must analyze an area of at least two miles' radius from the well to ensure that there are no adjacent wells that could be conduits allowing the oil and gas waste to migrate to the surface.[260] Class II wells can analyze an area as small as within a quarter-mile radius.[261]

Pennsylvania could act to regulate oil and gas waste as hazardous by following the example of New York State, which in 2020 enacted legislation to designate oil and gas waste as hazardous.[262] State Senator Rachel May, one of the bill's sponsors, said in a statement,

> Wastewater from fracking can contain carcinogenic compounds and naturally occurring radioactive materials. The regulatory loophole that allowed waste from fracking and crude oil processing to be treated as standard industrial waste means it enters local sewage treatment facilities, sometimes with radiation levels hundreds of times the safe limit, it then flows directly back into our waterways – the source of drinking water for thousands of New Yorkers.[263]

May issued her statement before it was widely known that PFAS was used in oil and gas operations, but considering the oil and gas industry's record of using PFAS, the statement could apply as well to these dangerous "forever" chemicals. Continuing to exempt oil and gas wastes from hazardous waste treatment means that PFAS in these wastes would be exempt, too, with potentially serious consequences for Pennsylvanians.

RECOMMENDATIONS

In light of the findings shared in this report, PSR recommends the following:

- **Halt PFAS use in oil and gas extraction.** Pennsylvania and the U.S. Environmental Protection Agency (EPA) should prohibit PFAS from being used, manufactured, or imported for oil and gas extraction. Many PFAS are replaceable with less-persistent and less-toxic alternatives. In taking this step, Pennsylvania would be following the lead of Colorado, a major oil- and gas-producing state that in June 2022 passed legislation banning the use of PFAS in oil and gas wells.

- **Expand public disclosure.** Pennsylvania should greatly expand its requirements for public disclosure of oil and gas chemicals. The state could again follow the example offered by Colorado by requiring disclosure of all individual chemicals used in oil and gas wells, without exceptions for trade secrets. This action can be done while still protecting product formulas as trade secrets. Pennsylvania should also require disclosure on the part of chemical manufacturers and require chemical disclosure prior to permitting, as have California, West Virginia, and Wyoming.

- **Increase testing and tracking.** Pennsylvania and/or the U.S. EPA should determine where PFAS have been used in oil and gas operations in the state and where related wastes have been deposited. They should test nearby residents, water, soil, flora, and fauna for PFAS, both for the particular type(s) of PFAS used and for organic fluorine to detect the presence of other PFAS and/or their breakdown products. They should use testing equipment sensitive enough to detect PFAS at a level of single-digit parts per trillion or lower.

- **Require funding and cleanup.** Oil and gas and chemical manufacturing firms should be required to fund environmental testing for PFAS in their areas of operation, and should PFAS be found, be required to fund cleanup. If cleanup of water sources is impossible, companies responsible for the use of PFAS should pay for alternative sources of water for homes, schools, hospitals, agriculture and other uses for as long as needed.

- **Remove Pennsylvania's oil and gas hazardous waste exemption.** Pennsylvania exempts oil and gas industry wastes from state hazardous waste rules. Pennsylvania should follow New York's lead and remove its state-level hazardous waste exemption for the oil and gas industry.

- **Reform Pennsylvania's regulations for oil and gas production wells and underground injection disposal wells.** The state should prohibit production wells and underground wastewater disposal wells close to underground sources of drinking water, homes, health care facilities and schools; require groundwater monitoring for contaminants near the wells, and for disposal wells, require full public disclosure of chemicals in the wastewater.

- **Transition to renewable energy and better regulation.** Given the use of highly toxic chemicals in oil and gas extraction, including but not limited to PFAS, as well as climate impacts of oil and gas extraction and use, Pennsylvania should transition away from fracking and move toward renewable energy and energy efficiency while providing economic support for displaced oil and gas workers. As long as drilling and fracking continue, the state should better regulate these practices so that Pennsylvanians are not exposed to toxic substances and should empower local governments also to regulate the industry. When doubt exists as to the existence or danger of contamination, the rule of thumb should be, "First, do no harm."

APPENDIX A

Data Sources for PFAS Used in Pennsylvania's Oil and Gas Wells

To identify where, and to what extent, PFAS and trade secret chemicals were used at unconventional gas wells in Pennsylvania, PSR analyzed well-by-well reports of fracking chemicals recorded in FracFocus, a database for the oil and gas industry[264] maintained by the Groundwater Protection Council, a nonprofit comprised of regulators from state agencies.[265] The dates of these records extend from January 1, 2012 to September 29, 2022. PSR consulted the open-source version of FracFocus, Open-FF,[266] which is more accurate and informative than the original version of FracFocus. For example, Open-FF corrects for numerous spellings of the same term and consolidates the spellings into a single, corrected term. For more information about the differences between FracFocus and Open-FF, see the link above.

Under Pennsylvania law, well operators must disclose the fracking chemicals used in unconventional gas wells to the FracFocus database. Disclosure must occur within 60 days after hydraulic fracturing treatment.[267] Based on the disclosure forms available on FracFocus' website, operators must list, among other things, each individual chemical injected into the well and each chemical's CAS number, if available.[268] There are, however, significant exceptions to disclosure requirements under Pennsylvania's rules, including an exception for chemicals designated a trade secret[269] as discussed in Chapter 2 and Chapter 6.

APPENDIX B

Government Scientists Investigate Link between Pennsylvania Oil and Gas Wells, PFAS Pollution

In August 2023, as we prepared to go to press, a study conducted by the U.S. Geological Survey (USGS) and the Pennsylvania Department of Environmental Protection (DEP) with implications for PFAS use in oil and gas operations in Pennsylvania was published in a peer-reviewed journal. The study may be the first, or one of the first, by government agencies to recognize oil and gas wells as "facilities that have been documented as potential sources of PFAS."[270] In making this determination, the authors relied on two sources, also cited by PSR in this report, providing evidence of PFAS use in oil and gas operations including a 2008 paper by Murphy and Hewat[271] and a 2020 paper by Glüge.[272] The authors also relied on a paper published in 2022 by Hussain et al.[273]

The study by USGS and DEP detailed testing by scientists of surface water in Pennsylvania from 161 streams for 33 different types of PFAS.[274] The goals of the study included measuring PFAS concentrations, determining the sources of PFAS, and comparing PFAS concentrations to health and environmental standards.[275] The scientists found that 123 of the streams, 76 percent, contained one or more of the 33 types of PFAS.[276] In addition, 16 of the streams contained levels of PFOA that exceeded EPA's proposed drinking water standard for PFOA, and 11 streams had concentrations of PFOS that exceeded EPA's proposed drinking water standard for PFOS.[277]

While the scientists did not report a direct link between oil and gas wells and the types of PFAS for which they tested, they did find concentrations of PFAS in streams located in areas that featured both high levels of oil and gas wells and combined sewer overflow outfalls[278] (pipes that discharge into streams the combination of wastewater from homes and businesses, and runoff from roads, typically during rain storms).[279] The scientists commented that "Research documenting the impacts of OG [oil and gas] development on PFAS contamination in surface waters is limited, but in this study the CSO [combined sewer overflow outfalls] surrounded by OG development in local catchments could be a potential source of PFAS to surrounding streams."[280]

While the study recognized a potential link between oil and gas wells and PFAS pollution in water, the extent of such pollution cannot yet be determined for several reasons. First, the researchers tested for only 33 PFAS out of thousands that have been manufactured. It is possible that oil and gas companies used types of PFAS for which the researchers did not sample. (The researchers stated that future investigation could involve testing for total organic fluorine that could indicate the presence of non-specific PFAS without having to test for individual types.)[281] Second, it is nearly impossible for researchers to test for all the types of PFAS potentially used in oil and gas wells because multiple regulatory gaps allow oil and gas companies and chemical manufacturers to withhold the identities of the chemicals used in oil and gas wells. Third, the researchers did not sample groundwater. PFAS used in oil and gas wells may be especially likely to impact groundwater because PFAS may be used in drilling that precedes fracking,[282] and has been used in fracking fluids.[283] These PFAS could infiltrate groundwater through multiple pathways including during the first stage of drilling when the drill bit passes directly through groundwater before steel casing or cement is placed in the well to separate the well from the groundwater,[284] through leaks and cracks in the casing and/or cement after these protective materials are installed,[285] migration up adjacent faults[286] or adjacent active and abandoned oil and gas wells,[287] and through surface spills.[288] More research and transparency is necessary to fully characterize the extent of PFAS pollution in water supplies located near oil and gas wells or near sites where oil and gas waste is disposed of.

APPENDIX C

Health and Environmental Risks of PTFE/Teflon

Polytetrafluoroethylene (PTFE) is the type of PFAS that oil and gas companies disclosed as being used for fracking in eight unconventional gas wells in Pennsylvania between 2012 and 2022. PTFE is a fluoropolymer, a type of plastic.[289] Scientists'[290] and environmentalists'[291] major concerns about PTFE and other fluoropolymers are related less to these substances themselves, but rather to the associated impacts of their production, use, and disposal. The production of PTFE and other fluoropolymers relies on the use of other, highly toxic PFAS that are used as production aids. As noted in a peer-reviewed study published in 2020, these other PFAS have included fluorosurfactants such as PFOA, whose risks are discussed in the previous chapter, and GenX, which is similarly harmful and has replaced PFOA in fluoropolymer production.[292] PTFE and other fluoropolymers may contain these more toxic PFAS fragments, and those fragments may leach out of the PTFE during use.[293] The authors of the 2020 paper noted that

> The levels of leachables...in individual fluoropolymer substances and products depend on the production process and subsequent treatment processes; a comprehensive global overview is currently lacking.[294] In addition, PTFE may generate other PFAS if the PTFE breaks down under heat.[295]

The 2020 paper authors noted that the persistence in the environment of PTFE and other fluoropolymers could pose problems during disposal, observing that “Landfilling of fluoropolymers leads to contamination of leachates with PFAS and can contribute to release of plastics and microplastics.”[296] One of the authors added in an email to PSR that if PTFE were used in oil and gas wells that have especially high temperatures, defined in publications by oilfield services company, Schlumberger, as 300º-350º F or higher for so-called “high-pressure, high-temperature wells,”[297] the PTFE could undergo a process called “thermolysis” and generate toxic PFAS called perfluoroalkyl carboxylic acids (PFCAs). As a result, he wrote, “there could be some additional problems that need some investigation.”[298] A spokesperson for the Pennsylvania Department of Environmental Protection told PSR in June 2023 that members of the department’s sub-surface team “have found no producing formation in the 300F range or above.”[299]

In 2021, a coalition of national environmental organizations including the Center for Environmental Health, Clean Water Action, Ecology Center, Environmental Working Group, Natural Resources Defense Council, Safer States, and the Sierra Club voiced several environmental and health concerns regarding the risks of fluoropolymers such as PTFE, based on their review of multiple scientific articles. The groups also noted that fluoropolymers are manufactured with chemicals that have an outsized negative effect on climate change.[300]

Public records make it difficult to know for what purpose PTFE was used in Pennsylvania’s unconventional gas wells. For all eight wells in which the substance was injected, multiple purposes were listed for multiple chemical products, and it was unclear which purpose was connected to which product. In addition, the individual chemical components of the products were listed together in a separate portion of each disclosure form, making it impossible to know which components were part of which product or for what purpose the components were used.[301] However, PTFE, which is marketed as Teflon, is known for its slipperiness, suggesting it might have been used as a friction reducer, a common purpose for fracking chemicals.[302]

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[51] EPA's proposed MCL for PFOA and PFOS is four parts per trillion. 88 Fed. Reg. 18638, 18639 (Mar. 29, 2023). Accessed August 7, 2023, at https://www.federalregister.gov/documents/2023/03/29/2023-05471/pfas-national-primary-drinking-water-regulation-rulemaking#addresses. Parts per trillion refers to milligrams per one million liters of water. U.S. Environmental Protection Agency. Environmental Science and Technology Briefs for Citizens. Center for Hazardous Substance Research. Understanding Units of Measurement. Accessed Aug. 7, 2023, at https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.files/fileid/14285. One measuring cup contains approximately 237 milliliters. Exploratorium. Cooking Equivalents and Measures. Accessed Aug. 7, 2023, at https://www.exploratorium.edu/food/measurements. The density of PFOA is 1.8 grams per milliliter. National Institutes of Health. National Library of Medicine. National Center for Biotechnology Information. PubChem. Perfluorooctanoic Acid. Density. Accessed Aug. 7, 2023, at https://pubchem.ncbi.nlm.nih.gov/compound/Perfluorooctanoic-acid. Therefore, the mass of one measuring cup of PFOA is 426.6 grams or 426,600 milligrams. This mass of PFOA is 106,650 times greater than four milligrams (EPA's interim health advisory level per million liters). In order to dilute the mass of the PFOA in an equivalent volume of water, we multiplied 106,650 by 1,000,000. The result is 106,650,000,000 liters of water. There are 3.785 liters of water per gallon. U.S. Environmental Protection Agency. EPA Expo Box Unit Conversion Table. Accessed Aug. 7, 2023, at https://www.epa.gov/expobox/epa-expobox-unit-conversion-table. Therefore, 106,650,000,000 liters of water is equal to a bit more than 28 billion gallons of water.

[52] PSR calculated this figure by starting with 28 trillion gallons, the amount of water that could be contaminated under EPA's Maximum Contaminant Level by one measuring cup of PFOA (see endnote 51) and dividing it by the 300 million gallons of drinking water that the City of Philadelphia treats each day. Philadelphia Drinking Water Department. Drinking Water. Accessed Aug. 7, 2023, at https://water.phila.gov/drinking-water/. The result is that 28 million gallons is 93 times greater than 300 million gallons and therefore, one measuring cup of PFOA could contaminate a volume of water equivalent to what the City of Philadelphia would treat over a span of 93 days.

[53] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 335. Accessed June 6, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

[54] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 334-335. Accessed Aug. 7, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

[55] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 335. Accessed Aug. 7, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

[56] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 335. Accessed Aug. 7, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

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[58] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 333. Accessed Aug. 7, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

[59] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 337-338. Accessed Aug. 7, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

[60] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 339. Accessed Aug. 7, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

[61] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 339. Accessed Aug. 7, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

[62] Pa. Bulletin Doc. No. 23-46 (Jan. 14, 2023), at 345. Accessed June 6, 2023, at https://www.pacodeandbulletin.gov/Display/pabull?file=/secure/pabulletin/data/vol53/53-2/46.html.

[63] Electronic mail communication with Linda Birnbaum (Mar. 10, 2023).

[64] Electronic mail communication with Zacariah Hildenbrand (Mar. 14, 2023).

[65] Electronic mail communication with Kevin Schug (Mar. 14, 2023).

[66] Electronic mail communication with Wilma Subra (Mar. 14, 2023).

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[68] U.S. Census Bureau. Quick Facts. Pennsylvania; United States. Accessed Aug. 7, 2023, at https://www.census.gov/quickfacts/fact/table/PA,US/PST045222.

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[74] Colorado General Assembly. HB22-1348. Senate Amended 3rd Reading (May 11, 2022). Accessed Aug. 7, 2023, at https://leg.colorado.gov/sites/default/files/documents/2022A/bills/2022a_1348_rer.pdf.

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[80] Pa. Rules Title 25 § 78.122(c).

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[82] 58 Pa.C.S. § 3222(b.1)(1)(iii) and Pa. Rules Title 25 § 78.122(b)(6) (conventional wells).

[83] Pennsylvania Department of Environmental Protection. Registration of Trade Secret-Confidential Proprietary Stimulation Fluid Chemical Information Form Instructions for form 8000-FM-OOGM0132, at 1. Accessed Aug. 7, 2023, at https://www.depgreenport.state.pa.us/elibrary/GetFolder?FolderID=3096.

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[86] Pennsylvania Department of Environmental Protection. Registration of Trade Secret-Confidential Proprietary Stimulation Fluid Chemical Information 8000-FM-OOGM0132 Instructions, at 1. Accessed Aug. 7, 2023, at https://www.depgreenport.state.pa.us/elibrary/GetFolder?FolderID=3096. See also 58 Pa.C.S. § 3222.

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[107] United States House of Representatives Committee on Energy and Commerce, Minority Staff. Chemicals Used in Hydraulic Fracturing(April 2011), at 2 (on file with PSR).

[108] Kate Konschnik et al. Legal Fractures in Chemical Disclosure Laws: why the voluntary chemical disclosure registry FracFocus fails as a regulatory compliance tool. Harvard Law School, Environmental Law Program Policy Initiative; 2013, at 5. Accessed Aug. 7, 2023, at https://blogs.harvard.edu/environmentallawprogram/files/2013/04/4-23-2013-LEGAL-FRACTURES.pdf.pdf. 29 CFR § 1910.1200; 2023.

[109] Eliza Griswold. Amity and Prosperity (2018), at 12-13, 41, 50-51, 53.

[110] Eliza Griswold. Amity and Prosperity (2018), at 259.

[111] Eliza Griswold. Amity and Prosperity (2018), at 260-261.

[112] Eliza Griswold. Amity and Prosperity (2018), at 304.

[113] Eliza Griswold. Amity and Prosperity (2018), at 302.

[114] 58 Pa.C.S. § 3222.1(c), (c)(1).

[115] 58 Pa.C.S. § 3222.1(b)(7-9).

[116] 25 Pa. Code § 78.122(b)(6)(iii).

[117] 58 Pa.C.S. § 3222.1(b)(2) and Pa. Rules Title 25 § 78a.122 (unconventional wells).

[118] Pa. Rules Title 25 § 78a.1. Definitions ("unconventional formation" and "unconventional well").

[119] 58 Pa.C.S. § 3222(a-b).

[120] Dusty Horwitt. Keystone Secrets. Partnership for Policy Integrity (Sept. 11, 2018), at 9. Accessed Aug. 7, 2023, at https://www.pfpi.net/wp-content/uploads/2018/09/PASecretFrackingChemicalsReportPFPI9.10.2018.pdf.

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[142] U.S. Environmental Protection Agency. Hydraulic fracturing for oil and gas: impacts from the hydraulic fracturing water cycle on drinking water resources in the United States. Washington, DC: Office of Research and Development; 2016, at 7-6. Accessed Aug. 7, 2023, at https://www.epa.gov/hfstudy.

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[148] Penn State Marcellus Center for Outreach and Research. Cross-Section of Typical Horizontal Marcellus Well (2023). Accessed Aug. 7, 2023, at https://marcellus.psu.edu/resources/maps-graphics-and-videos/.

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McIntyre Wild Area, Lycoming County, Pa., April 2021. Photo credit: Rebecca Johnson. Photo courtesy of FracTracker Alliance.

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Historical Perspective

Fluorinated surfactants: A review on recent progress on synthesis and oilfield applications

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ABSTRACT

The selection of appropriate chemicals and the synthetic method plays an important role in oilfield application. The objectives of this study are to describe the various synthetic route for the preparation of fluorinated surfactants and highlight their oilfield applications. Fluorinated surfactants are the type of surfactants where the hydrophobic tail is either partially fluorinated or replaced totally with fluorine molecules. Fluorinated surfactants have distinct properties compared to corresponding hydrocarbon surfactants such as lower surface tension, better efficiency in lowering the interfacial tension, both oleophobic and hydrophobic nature, high thermal stability, and better chemical tolerance. These properties make them a material of choice for several applications which include but are not limited to fire-fighting, household items, foaming, coating, and paints. Despite these attractive properties, environmental concerns associated with fluorinated surfactants is a major hurdle in extending the application of such surfactants. This review discusses the various synthetic routes for the synthesis of different classes of surfactants such as cationic, anionic, non-ionic, and zwitterionic surfactants. The fundamental surface/interface properties of the synthesized surfactants are also highlighted. In addition, the review highlights the application of fluorinated surfactants in the oil & gas industry.

1. Introduction

Surfactants are the type of organic molecules that contain a hydrophobic tail and a hydrophilic head. Fluorinated (or fluoro) surfactants are a special type of surfactants where the hydrophobic tail is partially or completely fluorinated. In the fluorinated surfactant tail, at least one hydrogen in the tail has been substituted with the fluorine atom [1–4]. The fluorinated tail exhibit both water and oil repellency, and due to this, fluorinated surfactants exhibit outstanding physicochemical properties than the surfactants containing hydrocarbon-based surfactant tail. According to literature, the -CF_2 unit is almost 1.5 times more efficient than the -CH_2 unit in the formation of micelle [5]. Fluorinated surfactants have unique properties that make them a suitable choice for several applications. The potential of fluorinated products was discovered in the early 1950s and has now become an important class with a diverse range of applications such as in fire-fighting, household items, foaming, coating, and paints [6].

The fluorocarbon chain has very high thermal and chemical stability. The decomposition temperature of the perfluoroalkanecarboxylic acids is more than 400 °C [7]. The carbon-fluorine bond is one of the most stable known covalent bonds. The heat of formation of the C—F bond is about 486 kJ/mol in CF_4 [7]. Carbon and fluorine bond is one of the strongest bonds in chemistry due to the great match between the 2s and 2p atomic orbitals of a fluorine atom and the analogous atomic orbitals of carbon. The atomic radius of the fluorine atom is 0.072 nm which is best in terms of size to shield the atoms of carbon with no steric hindrance. The chemical stability of the fluorinated surfactant compared to hydrocarbon surfactant is associated with the high electronegativity of fluorine. The electronegative induction due to the bond between fluorine and acidic group results in strong acid resistance. The dissociation constant of carboxylic acids with a fluorine atom is significantly higher compared to the dissociation constant of carboxylic acid without fluorine. The melting point of linear perfluoroalkanes is also high compared to hydrogenated alkanes.

The critical micelle concentration (cmc) and surface tension corresponding to cmc (γ_{cmc}) are two important parameters to evaluate the performance of surfactant. The critical micelle concentration is a minimum concentration at which surfactants form micelles. Fluorinated

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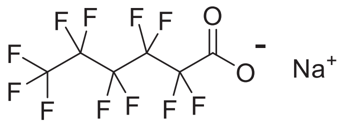
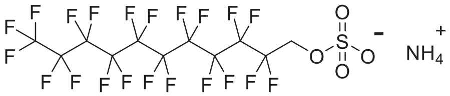
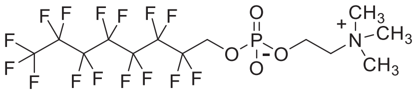
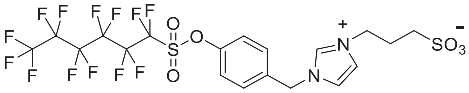
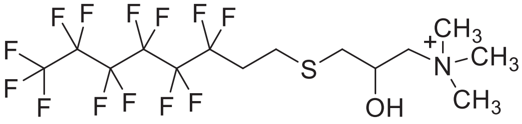
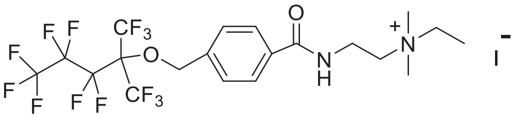
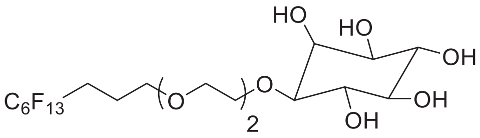
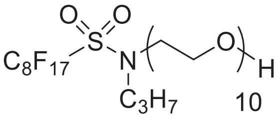
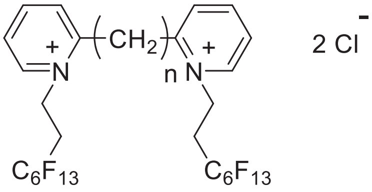
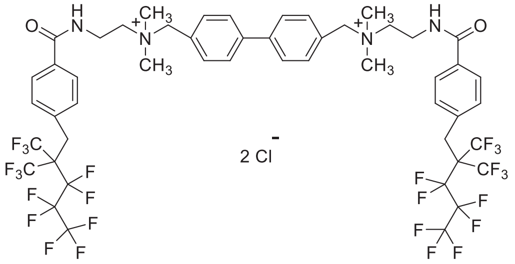
surfactants are more effective in reducing surface tension compared to hydrocarbon surfactants with similar hydrophobic tail lengths.

Surfactants have a range of applications in the oil and gas industry such as in chemically enhanced oil recovery (cEOR), drilling, conformance control, gas injection, stimulation, and hydrate inhibition [8–15]. The surfactants for oilfield applications should have high chemical and thermal stability. In addition, the surfactants for oilfield application must have high salt tolerance. It is because reservoirs conditions are extremely harsh where temperature can reach 150 °C and the salt level could be 200,000 ppm. Some other mechanisms need to be considered when designing surfactants for oilfields such as low/high permeability reservoir, type of clay minerals, pore throat structure, connectivity, capillary resistance, heterogeneity of reservoir rocks, and rock components, etc. The synthesis and development of surfactants to handle such harsh conditions is a significant challenge. Due to high thermal and chemical stability, fluorinated surfactants are the best

Table 1
Representative chemical structures of different classes of fluorinated surfactants.

No.	Surfactant chemical structure	Common Name	Class	cmc (mmol/L)	γ_{cmc} (mN/m)	Ref.
1		Sodium perfluorohexanoate	Anionic	–	–	[18]
2		Perfluoroundecylsulfate ammonium	Anionic	0.02	32.5	[19]
3		Pentadecafluorooctyl-phosphocholin	Zwitterionic	0.58	22.1	[20]
4		Perfluorohexanesulfonylsulfopropylbenzylimidazole	Zwitterionic	0.18	18.5	[21]
5		Perfluoroalkylammonium chloride	Cationic	0.30	20.0	[22]
6		Perfluoroalkylammonium iodide	Cationic	0.83	19.9	[23]
7		Tridecafluorononyl)oxy]ethoxy]ethyl]-myo-inositol	Non-ionic	0.39	17.4	[24]
8		Perfluoroalkyl sulfonamide ethoxylate	Non-ionic	0.005	21.0	[25]
9		Bis-perfluoromethylenepyridinium dichloride	Gemini	0.28	27.7	[26]
10		Bis-perfluorobenzoylammonium dichloride	Gemini	0.34	22.4	[27]

choice to use in harsh conditions such as high pH, high salinity, and high temperature. Almost half of the world's oil reserves exist in carbonate reservoirs and the primary and secondary oil recovery methods face some issues due to heterogeneity and complex fracture network of carbonate rocks. The fluorinated surfactant with a tendency to form stable foam and stability under harsh conditions (high temperature, high salinity) mark them as potential EOR agents in carbonate reservoirs.

One of the major concerns of fluorinated surfactants is their persistence in the water and soil environment. Persistent organic pollutants are those materials that don't degrade in the environment from naturally occurring materials or due to biological processes. The persistence of fluorinated surfactants in the soil is associated with their adsorption on mineral surfaces [16]. From waste disposal and other places, fluorinated products can make their way towards lakes, rivers, and oceans [17].

This review covers the synthesis methodologies of several fluorinated surfactants. The fluorinated surfactants are very attractive to oilfield industries due to their distinct surface/interface properties and excellent thermal/chemical stabilities. These superior properties mark them a material of choice under high pressure, high temperature, and high salinity conditions. This review is important because it covers the synthesis part covers the different routes of the synthesis for anionic, cationic, nonionic, zwitterionic, and gemini fluorinated surfactants. The second part of the review discusses the oilfield applications of fluorinated surfactants. Finally, the last section discusses several challenges and prospects of fluorinated surfactants.

2. Synthesis methodologies

The synthetic method of fluorinated surfactant plays a significant role in obtaining unique surface/interface properties. For instance, long-chain (≥C6) fluorinated surfactants exhibit environmental issues due to stable fluorinated tails with poor biodegradability. Therefore, the research is more focused on the synthesis of fluorinated surfactants that exhibit good biodegradability. This section discusses the various strategies for the synthesis of fluorinated nonionic, anionic, cationic, zwitterionic, and gemini surfactants. Representative chemical structures of different classes of gemini surfactants are also given in Table 1.

2.1. *Fluorinated nonionic surfactants*

Nonionic surfactants contain no charge on their headgroup. Zhang et al. reported the synthesis of a new class of fluorinated surfactants having small and branched fluorinated tails. The yield of the reaction was very low using Wittig reaction conditions due to the low activity of Wittig reagent ethyl(triphenylphosphoranylidene)-acetate. Therefore, fluorinated surfactants were prepared by applying more feasible Wittig-Horner reaction conditions using Wittig-Horner reagent triethyl phosphonoacetate. The maximum isolated yield of the reaction (38%) was obtained (Scheme 1) [28].

In continuation of the synthesis of new fluorinated surfactants with shorter fluorinated tails, Debbabi et al. elaborated two synthetic pathways for the preparation of non-ionic fluorinated sulfamates containing different hydrocarbon spacer and fluorinated tail. Path A consists of addition and rearrangement reactions followed by hydrolysis leading to the formation of sulfamates with high yield. The process was feasible for the preparation of fluorinated surfactants containing 1 or 2 methylene spacers. However, fluorinated surfactants having more than two methylene spacers were prepared by using Path B in which an SN2 type reaction was used leading to the formation of corresponding sulfamates (Scheme 2). The significance of the reaction was the easy synthesis using comparatively non-toxic starting material compared to other classical non-ionic fluorinated surfactants [29].

It was understood that the surfactants with the longer fluorinated tail are not suitable for environmental safety and human health. Therefore, several efforts have been made to develop a suitable alternative for long fluoroalkyl chain surfactants. However, most of the synthetic methods suffer due to low water solubility, a complex method of preparation, and poor surface activity. Shen et al. attempted to prepare non-ionic urethane fluorinated surfactants containing short fluoroalkyl tail as an alternative product to conventional long fluoroalkyl tail surfactants. The non-ionic urethane fluorinated surfactants were prepared by treating an equimolar amount of Isophorone diisocyanate (IPDI) and fluoroalkyl alcohol followed by the addition of polyethylene glycol (PEG) to achieve the final product as a yellow viscous liquid (Scheme 3) [30].

Another effort regarding the preparation of short-chain (≤C6) fluorinated surfactants, Song et al. recently developed new comb-like fluorinated surfactants using free-radical copolymerization reaction. The synthesis was done in a single-step reaction by treating methacrylates with poly(ethylene glycol) methyl ether methacrylates in the presence of 2,2-azobis(2-methylpropionitrile) as an initiator. The authors claimed that the surface properties of the resulting short-tail fluorinated surfactants were found to be superior to the long-tail fluorinated surfactants (Scheme 4) [5].

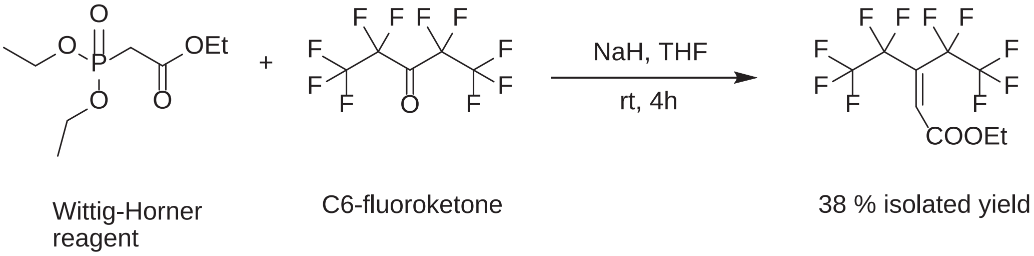
The degradability of fluorinated surfactants can be achieved by introducing the "weak points" such as methine (CH) or methylene (CH_2) units in the tail group which may undergo biodegradation or enzymatic degradation (Fig. 1) [31].

Boutevin et al. synthesized two fluorinated surfactants containing vinylidene fluoride (VDF) telomers. The authors claimed that the surface tension value of VDF-based carboxylic acid (19.8 mN/m) was quite similar to toxic and bioaccumulative perfluorooctanoic acid, $C_7F_{15}CO_2H$ (PFOA) and VDF-based carboxylic acid can be used as an alternative to PFOA (Scheme 5) [32].

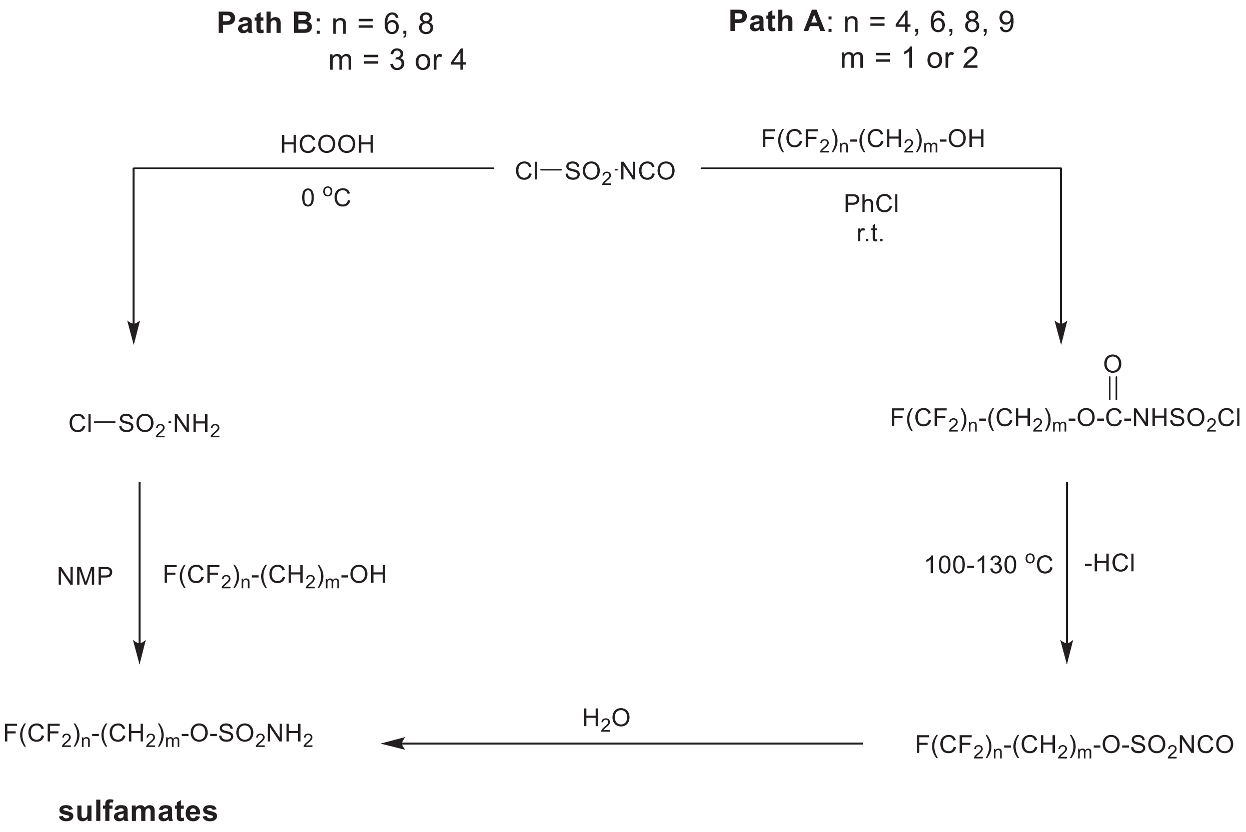
In brief, the alternative routes must be considered to avoid the harmful nature of non-biodegradable long fluorinated tails. For example, the aggregation behavior of fluorinated tails could be controlled by replacing linear tails with brach tails without compromising surfactant properties. In addition, the surface/interface study of fluorinated surfactants in various solutions could allow the replacement of a long fluorinated tail with a bioaccumulative short fluorinated tail.

2.2. *Fluorinated anionic surfactants*

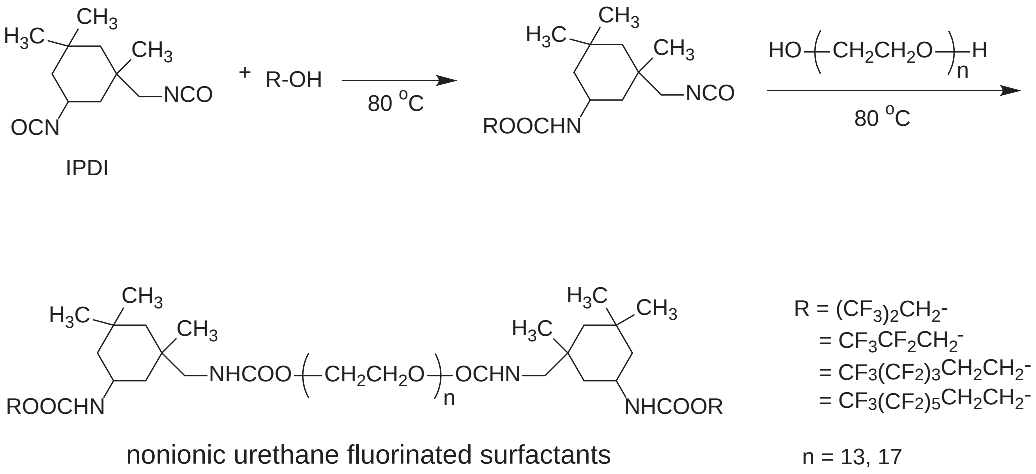
Anionic surfactants are the class of surfactants that carry a negatively charged headgroup. Fluorinated anionic surfactants containing sulphonate headgroup are mostly synthesized and studied such as



Scheme 1. Synthesis of fluorinated surfactants using Wittig-Horner reaction.



Scheme 2. Synthetic pathways A and B of fluorinated sulfamates.

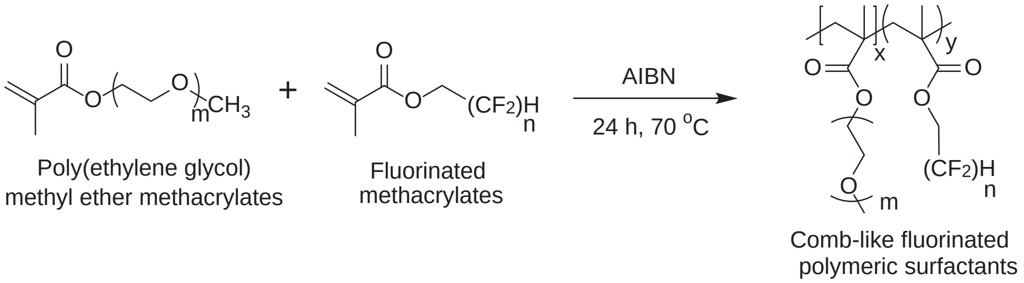


Scheme 3. Synthesis of nonionic urethane fluorinated surfactants.

perfluorooctane sulphonate (PFOS). However, PFOS had been discovered as a nondegradative organic pollutant and can be harmful to the environment as well as human life. To avoid, environmental and human life concerns about the anionic fluorinated surfactants, Chen et al. synthesized sodium *p*-perfluorononenyloxy benzene sulphonate (SPBS) as a new fluorinated anionic surfactant which is different than PFOS [33]. The surfactants were prepared by adding phenol and perfluoro nonene in a three-necked flask connected to a condenser followed by the addition of trimethylamine. The resulting crude product was purified by NaOH (5%) and distilled water and then dried with sodium sulfate (Na_2SO_4) to achieve the product (Scheme 6a).

After preparation of PPE, the reaction flask was charged with PPE and 1,2-dichloroethane followed by dropwise addition of sulfur trioxide (SO_3). The resulting crude product was purified by recrystallization and neutralization using NaOH(aq) and petroleum ether (Scheme 6b).

In hydrocarbon-based anionic surfactants such as sodium dodecyl sulfate (SDS), the cmc decreases below 25 °C and then increases when temperature increase from 25 °C to 55 °C. However, anionic surfactants containing fluorinated tails showed a reverse effect of temperature at 25–55 °C [34]. Zong et al. synthesized a novel hybrid fluorinated surfactant via SN2 type reaction. The surfactants were synthesized by mixing sodium (Na) and THF in a round bottom flask followed by



Scheme 4. Synthesis of comb-like fluorinated surfactants.

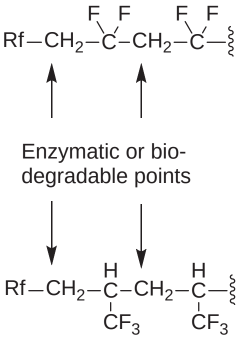
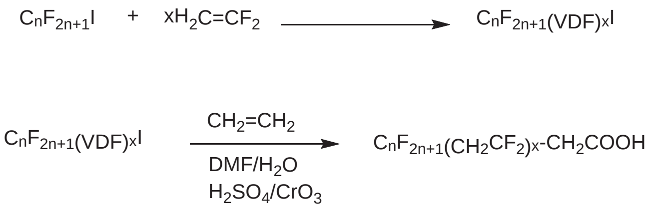


Fig. 1. Potential degradable points of fluorinated surfactants.



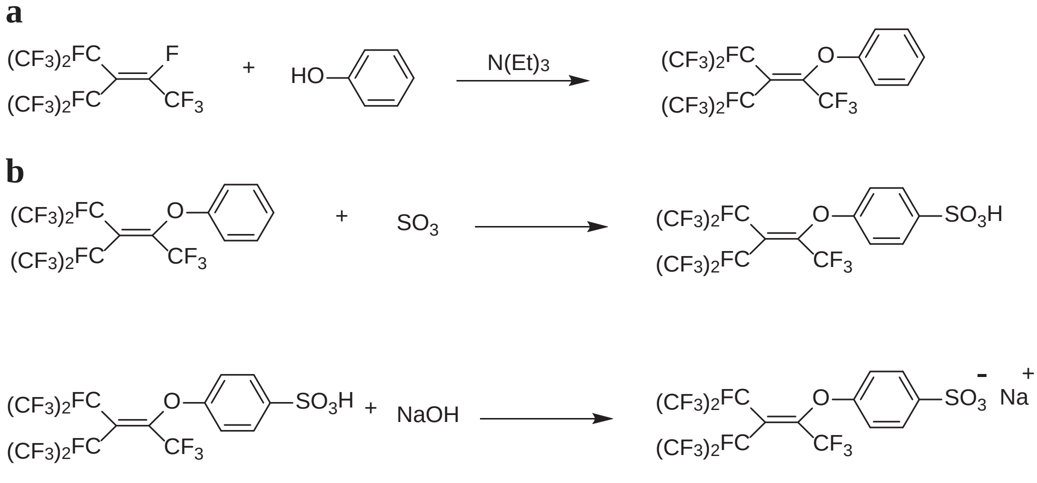
Scheme 5. Synthesis of comb-like fluorinated surfactants.

dropwise addition of perfluorooctyl ethanol (FOE) and THF in the reaction flask. Consequently, sodium 2-chloroethanesulphonate (SCE) in THF was introduced and the mixture was refluxed. After that, the solvent was evaporated and the crude product was purified by column chromatography to achieve targeted anionic surfactant, sodium 2-[2-(perfluorooctyl)] acetoxy ethanesulfonate (HFS8) (Scheme 7) [34].

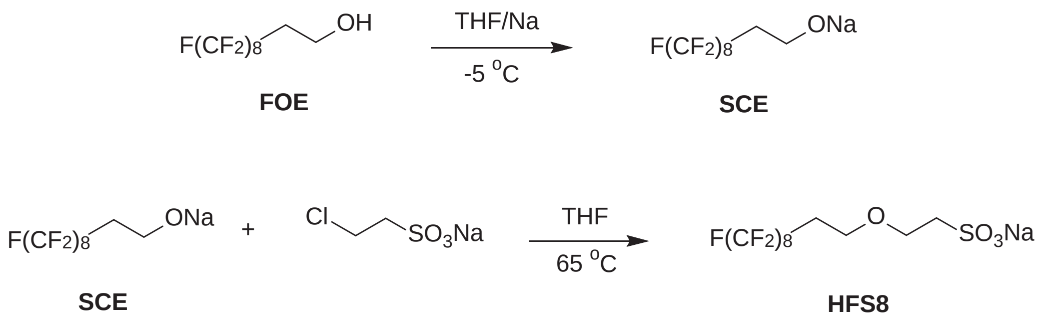
It is understood that fluorinated surfactants show greater efficiency in surface tension reduction, high thermal stability, and improved surface properties when compared to hydrocarbon-based amphiphiles. However, the fluorinated surfactants were found to be less hydrophilic than hydrocarbon-based surfactants. This feature has limited the use of fluorinated surfactants in a broader scope. For example, Yoshino et al. synthesized anionic surfactants containing two polyfluoroalkyl chains and studied the redispersion and flocculation properties for dispersed magnetite particles in the aqueous phase. In their work, they observed the low solubility of the synthesized surfactants in water. The surfactants were synthesized by refluxing *1H,1H,2H,2H*-heptadecafluoro-1-decanol, and maleic anhydride using *p*-toluenesulfonic acid monohydrate. The produced water was separated azeotropically and the reaction was continued until ≥90% water was produced. After that, the impurities were removed by washing with water followed by distillation to obtain the final product as a white solid (Scheme 8) [35].

After almost 7 years, the same group reported the modified chemical structure of the anionic surfactants by incorporating ethoxy groups within the chemical structure to increase the hydrophilicity of the surfactants. According to the revised synthetic method, 2-(perfluorobutyl) ethanol was refluxed with ethylene carbonate in the presence of the catalytic amount of *n*-butylammonium iodide. Additional ethylene carbonate was poured into the reaction flask. After that, an equal amount of water and diethyl ether was injected. The crude product was washed with NaCl (*aq.*) followed by distillation to achieve the ethoxylated product as a colorless liquid (Scheme 9) [36].

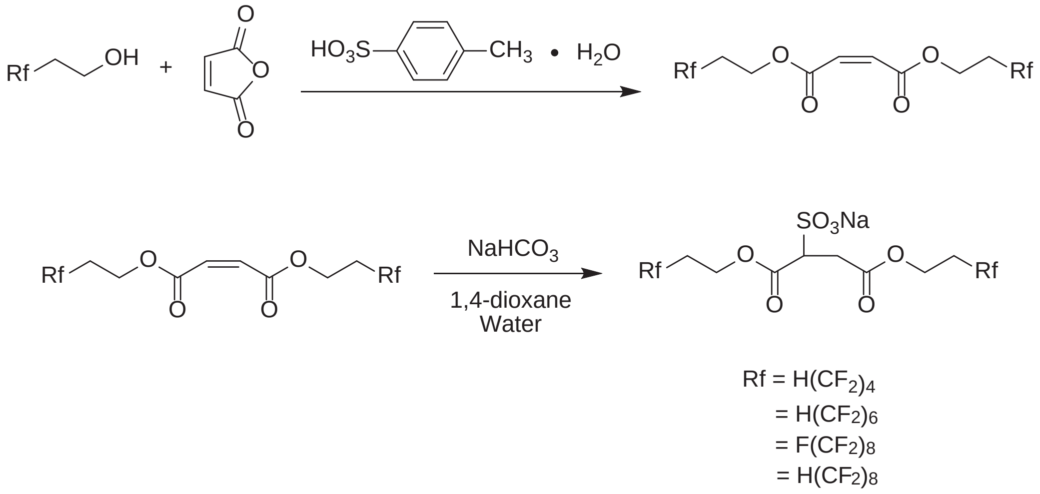
Overall, there is a need to explore better alternative routes for the preparation of environmentally friendly fluorinated surfactants. The incorporation of heteroatoms such as oxygen or nitrogen within the fluorinated tail could lead to the formation of fluorinated surfactants



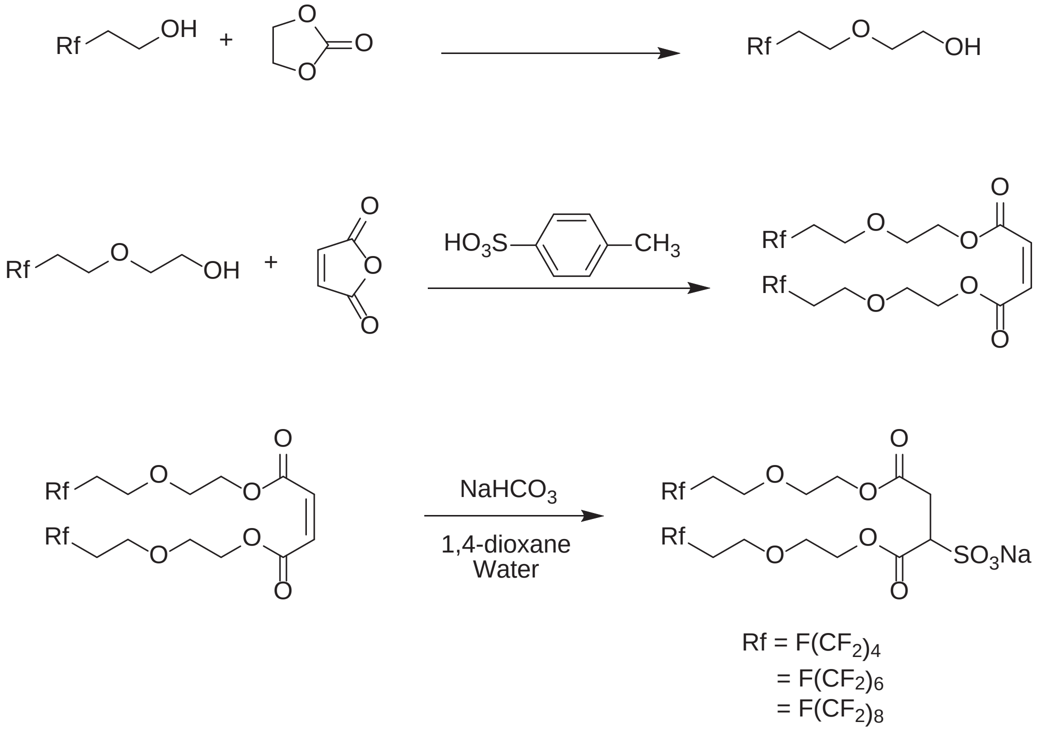
Scheme 6. a. Synthetic method of *p*-perfluorononenyl phenyl ether (PPE). b. Synthetic method of sodium *p*-perfluorononenyloxy benzene sulphonate (SPBS).



Scheme 7. Synthetic method of sodium 2-[2-(perfluorooctyl)] acetoxy ethanesulfonate (HFS8).



Scheme 8. Synthetic method of anionic surfactants containing two polyfluoroalkyl chains.



Scheme 9. Synthetic method of anionic surfactants containing ethoxy groups.

which are more easily degraded compared to simple fluorocarbon tail [31]. Moreover, the addition of heteroatom enhances the solubility of fluorinated surfactants in normal and high salinity brine.

2.3. Fluorinated cationic surfactants

The class of surfactants that possess a positively charged headgroup is known as cationic surfactants. Such kinds of surfactants are selected for positively charged surfaces such as carbonate rocks to decrease adsorption and increase oil/gas production. Yake et al. reported the synthesis of fluorinated cationic surfactants using alkylation and quaternization reactions. The fluoroalkyl ethylene iodides were refluxed with pyridine and the resulting intermediate was treated with *p*-toluene sulfonic acid using methanol as a solvent (Scheme 10) [37].

It is highly desirable to decrease the chain length of fluorinated surfactants or even decrease the number of atoms of fluorine in a partially fluorinated tail while acquiring high surface activities. To achieve this task, Wu et al. synthesized branched fluorinated surfactants and studied the surface activities. The cationic fluorinated surfactants were prepared by treating CsF with hexafluoropropylene and the resulting compound was dropwise added to a mixture of phenol and sodium carbonate in dimethyl sulfoxide solvent. The phenolic intermediate was further treated with chlorosulfonic acid and the resulting compound was reacted with *N,N*-dimethylethylenediamine. The final step of the synthesis was the treatment of amine intermediate with iodomethane using acetonitrile as a solvent under nitrogen atmosphere to achieve the targeted fluorinated surfactants (Scheme 11) [38].

Another important aspect to minimize the environmental issues related to fluorinated surfactants is to lower the number of fluorine atoms by introducing a partially fluorinated tail group without compromising the surface/interface properties. Yake et al. studied the surface activities and foaming properties of the synthesized partially fluorinated pyridinium-based and ammonium-based cationic surfactants and compared them to commercially available perfluoroalkyl analogs for oilfield applications. The authors claimed that the synthesized fluorinated surfactants with a fewer number of fluorine atoms were found to be more fluorine efficient than the perfluoroalkyl analogs (Scheme 12) [37].

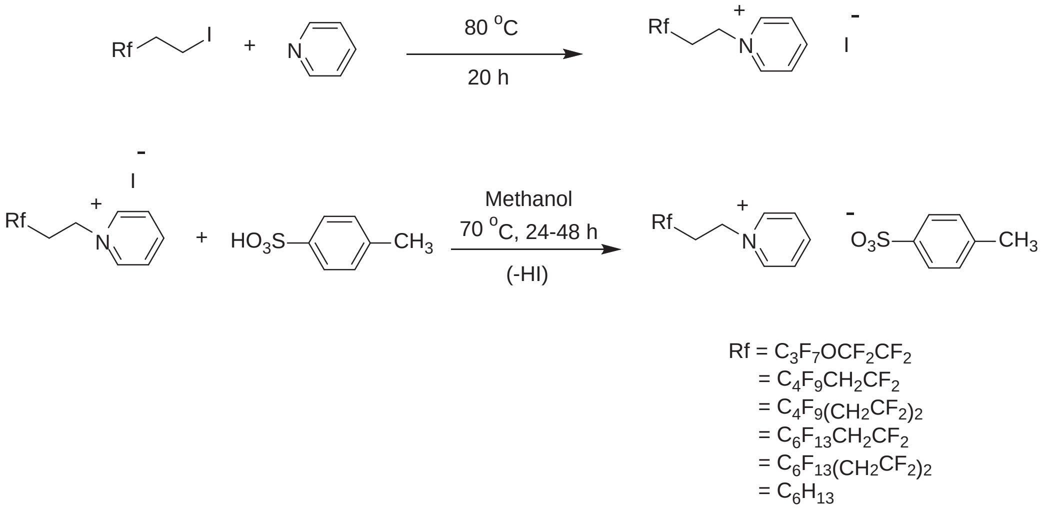
In conclusion, so far, a limited number of counterions were chosen for the synthesis of fluorinated cationic surfactants. However, counterions (F^-, Cl^-, Br^-, I^-) play a significant role in obtaining better physicochemical properties of fluorinated surfactants. For example, the cationic surfactants containing bromide (Br^-) counterion show low cmc and surface tension values compared to cationic surfactants having chloride (Cl^-) counterion. The synthesis of surfactants containing Iodide, bromide, and chloride counterion can readily achieve by reacting amine intermediate with ethyl iodide, ethyl bromide, and ethyl chloride, respectively.

2.4. Fluorinated zwitterionic surfactants

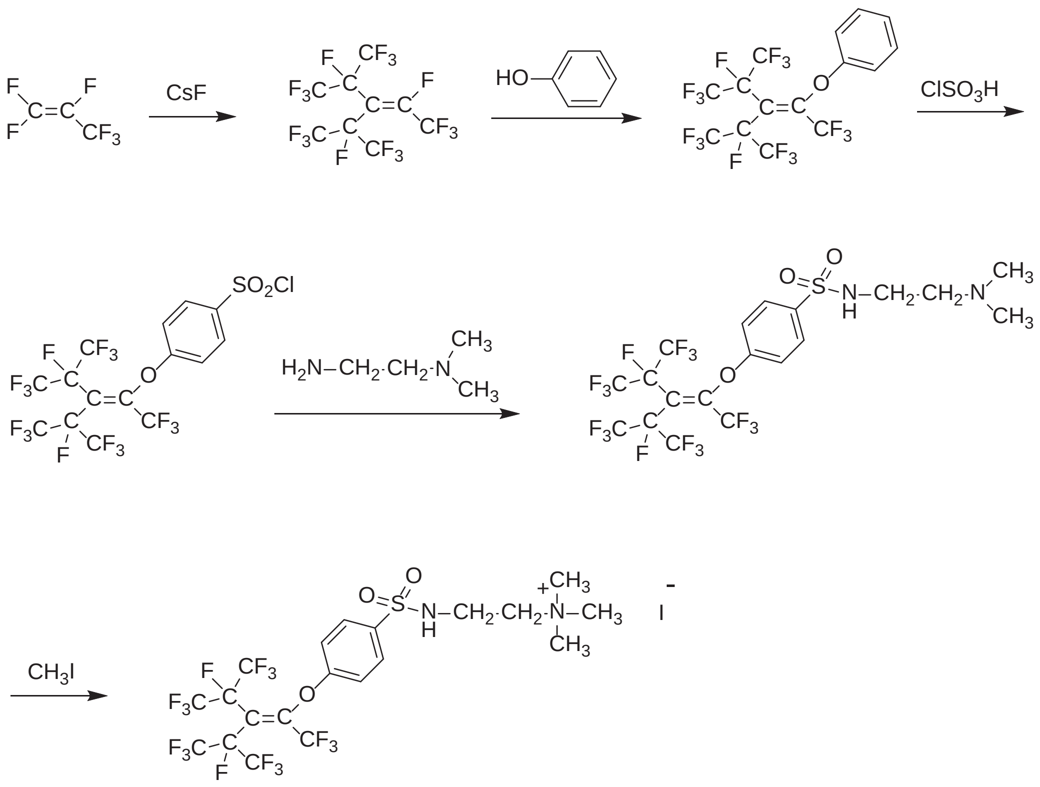
Zwitterionic surfactants are the class of surfactants containing two ionic centers of opposite charges in a single molecule. Zwitterionic surfactants are known to exhibit high thermal stability resistant to mono and divalent reservoir ions. Zwitterionic surfactants are not extensively applied in industries because of the difficult synthesis process. Literature data reveals that the surface tension reduction capability of branched tail fluorinated surfactants with the same number of carbons is comparable to straight-chain fluorinated surfactants at somewhat higher concentrations. However, the cmc values of branched ones are higher than the corresponding straight-chain surfactants. In addition, the interfacial tension values of branched tail fluorinated surfactants with the same number of carbons are lower than the straight-chain fluorinated surfactants [39]. Lin et al. reported the synthesis of new zwitterionic fluorinated surfactants containing branched fluorinated tails. The surfactants were readily prepared by adopting different synthetic routes. For example, Perfluoro-2-methyl-2-pentene was stirred with ethyl bromoacetate in the presence of tetrabutylammonium bromide and potassium fluoride in anhydrous dimethylformamide in an argon atmosphere. The resulting intermediate was stirred with *N,N*-dimethyl-1,2-ethanediamine under argon. The subsequent amido-amine intermediate was reacted with ethyl bromoacetate using dichloromethane as a solvent. The crude product was purified and mixed with the IRA-400 anion-exchange resin (OH^-) in ethanol to achieve branched zwitterionic fluorinated surfactants (Scheme 13) [40].

The solubility of fluorinated surfactants in water and organic solvents can be controlled by a proper balance between hydrophilic and hydrophobic parts of the surfactant molecule [41]. Peresypkin et al. incorporated both fluorinated and hydrocarbon-based surfactant tails in a single molecule and studied the self-assembly properties of the surfactants in both aqueous and organic media. The surfactants were synthesized by treating fluorinated alcohol with 2-chloro-1,3,2-dioxaphospholane 2-oxide in dry THF under an argon atmosphere. The resulting intermediate was further treated with *N,N*-dimethyloctan-1-amine in dry acetonitrile under argon atmosphere to obtain fluorinated zwitterionic surfactants (Scheme 14) [42].

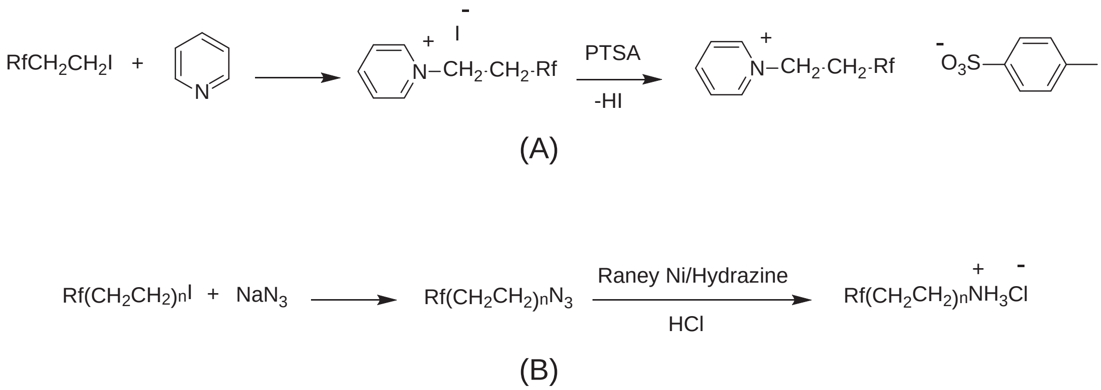
In an attempt to minimize the chain length, Coope et al. examined the surface activities of newly synthesized fluorinated sulfamido betaine



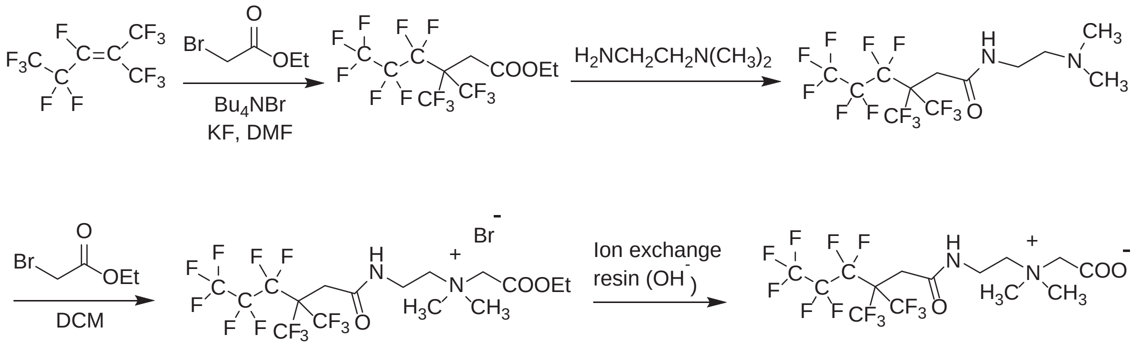
Scheme 10. Synthesis of pyridinium-based fluorinated surfactants.



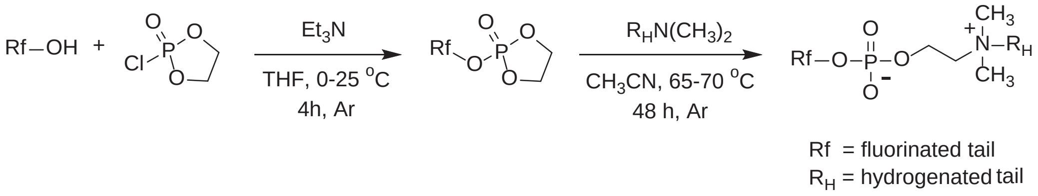
Scheme 11. Synthetic method to produce cationic fluorinated surfactants.



Scheme 12. Synthesis of pyridinium based (A) and ammonium-based cationic surfactants (B).



Scheme 13. Synthetic method to produce zwitterionic fluorinated surfactants.



Scheme 14. The synthetic procedure of zwitterionic fluorinated surfactants.

and fluorinated sulfamido amine N-oxide zwitterionic surfactants and compared them to commercially available perfluoroalkyl analogs for oilfield applications. It was observed that the efficiency of the synthesized zwitterionic fluorinated surfactants with lower fluorine content was comparable or superior to their perfluoroalkyl analogs (Scheme 15) [43].

In general, research more focuses on the synthesis of zwitterionic surfactants containing carboxylate or phosphate headgroups. However, zwitterionic surfactants having sulphonate headgroup is rare in literature. Sulphonate headgroup is known to show better heat stability and salt tolerance capability and it can be synthesized by treating amidoamine intermediate with 1,3-propane sultone [44].

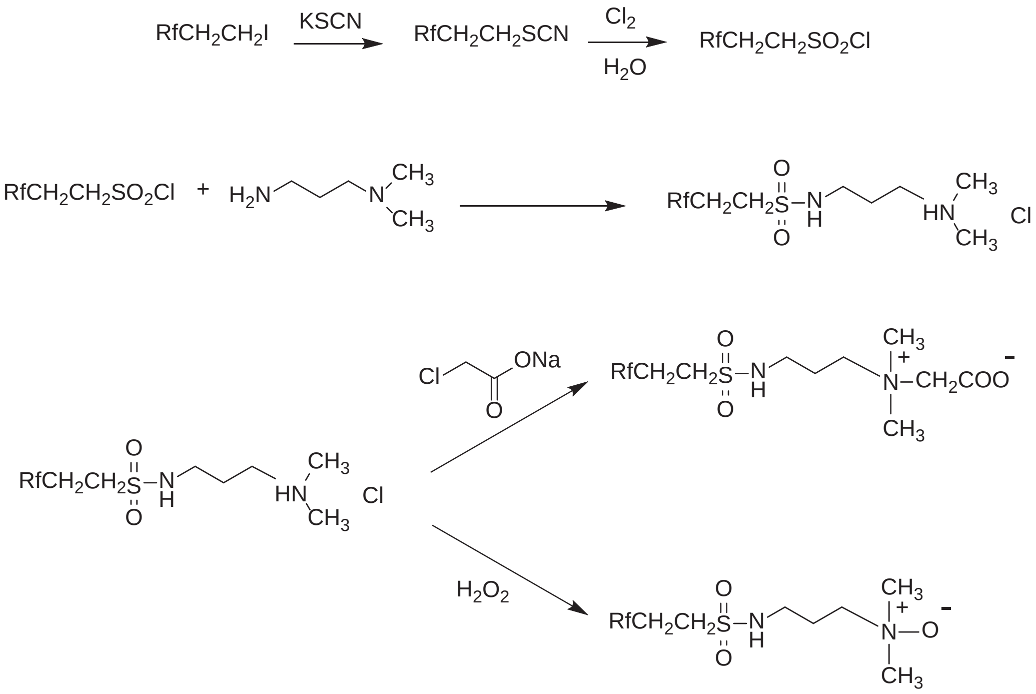
2.5. Fluorinated gemini surfactants

Gemini surfactants have received considerable focus due to their unique chemical structure. A conventional surfactant has a single tail and single head; however, gemini surfactants contain two (or more) tails and two (or more) heads chemically bounded by the spacer. The physicochemical properties of gemini surfactants including lower critical micelle concentration (CMC) and surface property found to be higher than the monomeric (conventional) surfactants. To find the alternatives for long-chain fluorinated surfactants, Du et al. synthesized a series of gemini surfactants containing perfluorinated-ether chains and their surface tension were studied. The gemini surfactants were synthesized in two steps using amidation and quaternization reactions. In the first step, 3-dimethylaminopropylamine was reacted with fluorinated esters, sulfonyl fluoride, or a carbonyl fluoride separately to form the amido-amine product. In the second step, the amido-amine intermediate was quaternized by treating with dibromides to achieve the gemini surfactants (Scheme 16) [45].

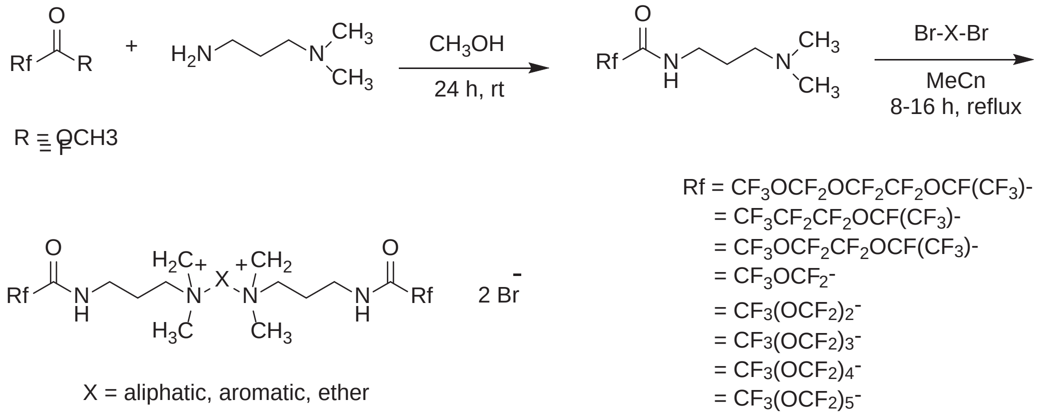
To address the environmental concerns about the fluorocarbon surfactants, Chen et al. synthesized two new gemini surfactants by esterification reaction containing ecofriendly ester bond to increase the biodegradability and aqueous solubility. The surfactants were prepared by refluxing Nonadecafluorodecanoic acid with N-Methyldiethanoamine in toluene. The resulting crude product was vacuum dried and recrystallized using dichloromethane (Scheme 17) [46].

Representative chemical structures of different classes of gemini surfactants are also given in Table 2.

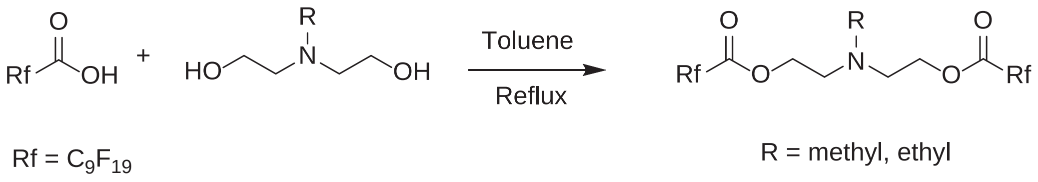
In summary, gemini is a comparatively new class of surfactants that exhibit superior properties compared to conventional surfactants. Gemini surfactants can be nonionic, cationic, anionic, and zwitterionic. However, fluorinated anionic and fluorinated zwitterionic gemini surfactants are very rare in literature. The new strategies for the synthesis of fluorinated anionic and fluorinated zwitterionic gemini surfactants with better surface/interface properties are highly desirable. For example, the treatment of amine intermediate with sultone could lead to the formation of gemini zwitterionic surfactants [47]. The development of a cost-effective procedure for the synthesis of fluorinated surfactants is greatly anticipated. Currently, the synthetic method of most of the fluorinated surfactants is comparatively complicated and limits the possibility of large-scale production. However, the preparation cost can be reduced by simplifying the synthetic method. Chu et al. developed a



Scheme 15. Synthesis of partially fluorinated zwitterionic surfactants.



Scheme 16. Synthetic method of gemini cationic surfactants.



Scheme 17. Synthesis of gemini cationic surfactants containing ether group in spacer.

facile route by solvent-free amidation of fatty acids which can eliminate the cost of reaction solvent [44]. Moreover, the introduction of high salinity conditions can further improve the properties of surfactants. For instance, the surface activity of the fluorinated surfactants can be enhanced at a higher pH level or adding mono/divalent ions which might save the cost [48].

3. Applications of fluorinated surfactants

Surfactants have fascinating and enormous applications in upstream and downstream operations. They serve as significant ingredients in processes like emulsion, acidizing, foaming, cement slurries, drilling, fracturing, and the enhancement of production and recovery of hydrocarbons in the oilfields [49]. Specifically, fluorinated surfactants have distinct properties that make them appropriate for many applications in industrial processes. Their unique features include the ability to lower the surface tension in aqueous solutions, high chemical and thermal stability of their acids and derivatives when used in a very low concentration [50]. Fluorinated surfactants are efficient in numerous enhanced oil recovery (EOR) processes including modification of surface properties of reservoir formation, enhancing the wetting of subterranean, and increasing foams stability [51]. This section discusses the oilfield applications of fluorinated surfactants in different roles.

3.1. *Foaming agent*

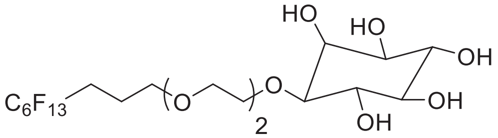
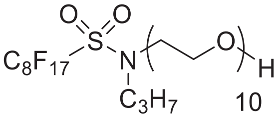
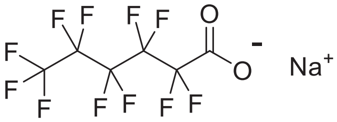
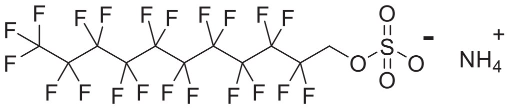
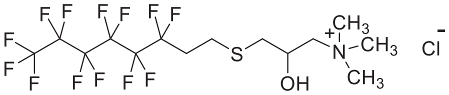
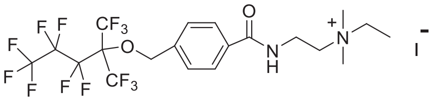
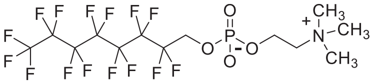
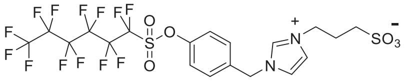
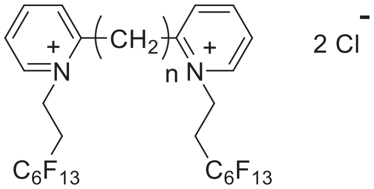
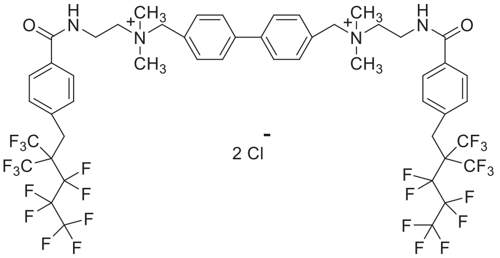
The application of foam is very common in different upstream oilfield applications like CO_2 EOR [52], fracturing and stimulation [53], drilling [54], gas and water shutoff [55], and conformance control [56]. Usually, foam stability is governed by three major factors: (i) gas diffusion through the lamellae, (ii) rupture of the liquid lamellae, and (iii) eventual coalescence of gas bubbles. Most foams generated with carbon dioxide dry quickly after production is stopped, causing foam instability. Systematic inclusion of fluorinated surfactant at a moderate concentration in the liquid and blowing of appropriate gas could rearrange the liquid lamellae and lead to the generation of more foams exhibiting stability longevity [57]. The ability to produce stable foams using fluorinated surfactants in methanol was first demonstrated in 1979 [51]. An example of stabilization of the foam generated by using SDS with a fluorosurfactant (FC1157) combined with xanthan gum has been discussed by Xiaoyang Yu et al. 2020 [58] (Fig. 2).

CO_2 foaming or Surfactant-Alternating-Gas (SAG) is an alternative to simple CO_2 flooding that not only provides miscible flooding but also prevents channeling due to gravity segregation, reduces IFT, reaches smaller pores, and displays a good sweep efficiency. However, at high pressures and temperatures when CO_2 is supercritical, foam generated with conventional surfactants does not remain stable for a longer time. Fluorinated surfactant when used with supercritical CO_2 at high pressure high temperature (HPHT) conditions not only reduces the IFT [59] but also generates a stable foam [60]. Adding of N_2 in supercritical CO_2 for foamed fluorinated surfactant flooding increases foam stability by strengthening the foam and delays the time to breakthrough but reduces the displacement efficiency of CO_2 [61]. While most other surfactants do not generate foam with CO_2 at reservoir conditions [62] due to the presence of oil [63,64], high temperature [65], highly saline environment [66], and/or low surfactant concentration [67], fluorinated surfactants show signs of stable foam and therefore result in high oil recovery [68].

Foamed alcohol-based fluids have been used in the past for stimulation of formations that are sensitive to water, but they still contained 50% water which damaged the formations [69]. The first system containing 80–90% of methanol with fluorinated surfactant [70] proved to be effective however its application was limited due to the high cost of additives. Crema et al. devised a formulation using fluorinated surfactant (Fluorad FC-742) with a non-ionic surfactant (Pluradyne SF-1042) as an additive which reduced the additive cost by about 60% [71].

The use of foam to prevent gas coning in thin reservoirs is quite an old idea [72] and the first field application proved to be successful in stopping the gas-channeling and reducing water-oil ratio WOR [73]. Since then, there have been several successful field projects of foam treatments [55,74–84]. Fig. 3 shows an example of foam treatment for gas-coning. But foams produced with conventional surfactants do not hold their location inside the pores for blocking gas for a longer duration when they encounter oil. Fluorinated alkyl chains being both

Table 2
Representative chemical structures of different classes of fluorinated gemini surfactants.

No.	Surfactant chemical structure	Common Name	Class	cmc (mmol/L)	γ_{cmc} (mN/m)	Ref.
1		Tridecafluorononyl)oxy]ethoxy]ethyl]-myo-inositol	Non-ionic	0.39	17.4	[24]
2		Perfluoroalkyl sulfonamide ethoxylate	Non-ionic	0.005	21.0	[25]
3		Sodium perfluorohexanoate	Anionic	–	–	[18]
4		Perfluoroundecylsulfate ammonium	Anionic	0.02	32.5	[19]
5		Perfluoroalkylammonium chloride	Cationic	0.30	20.0	[22]
6		Perfluoroalkylammonium iodide	Cationic	0.83	19.9	[23]
7		Pentadecafluorooctyl-phosphocholin	Zwitterionic	0.58	22.1	[20]
8		Perfluorohexanesulfonylsulfopropylbenzylimidazole	Zwitterionic	0.18	18.5	[21]
9		Bis-perfluoromethylenepyridinium dichloride	Gemini	0.28	27.7	[26]
10		Bis-perfluorobenzoylammonium dichloride	Gemini	0.34	22.4	[27]

hydrophobic as well as oleophobic do not interact with oil and therefore the bulk foam remains as a blocker in the pores [85].

In Summary, the use of fluorinated surfactants as foaming agents helps in stabilizing the foam, provides low IFT with CO_2, and sustains contact with oil.

3.2. Emulsifier/ IFT modifier

Emulsification is another area of interest where fluorinated surfactants can serve in restructuring the morphology and stability of emulsions. Surfactant EOR is based on interfacial tension (IFT) reduction [5,51,87–90], wettability alteration [5,51,91–94] and emulsification [51,95–97]. Until now, designing qualitative surfactants that could produce low IFT at hydrocarbon-water molecules interface is very rare. The use of emulsifiers in emulsification is a crucial and significant mechanistic process for enhancing oil recovery, whereas, high IFT is a persistence challenge, consequently affecting oil recovery. Appropriate emulsifier (or surfactant) selection could reduce IFT via adsorption at the interface of oil and aqueous phase, while also enhancing the formation and stability of the emulsion. Fluorinated surfactants have played a key role in the stability and reconfiguration of complex emulsions. Fig. 4 illustrates the effect of how a non-ionic fluorosurfactant F

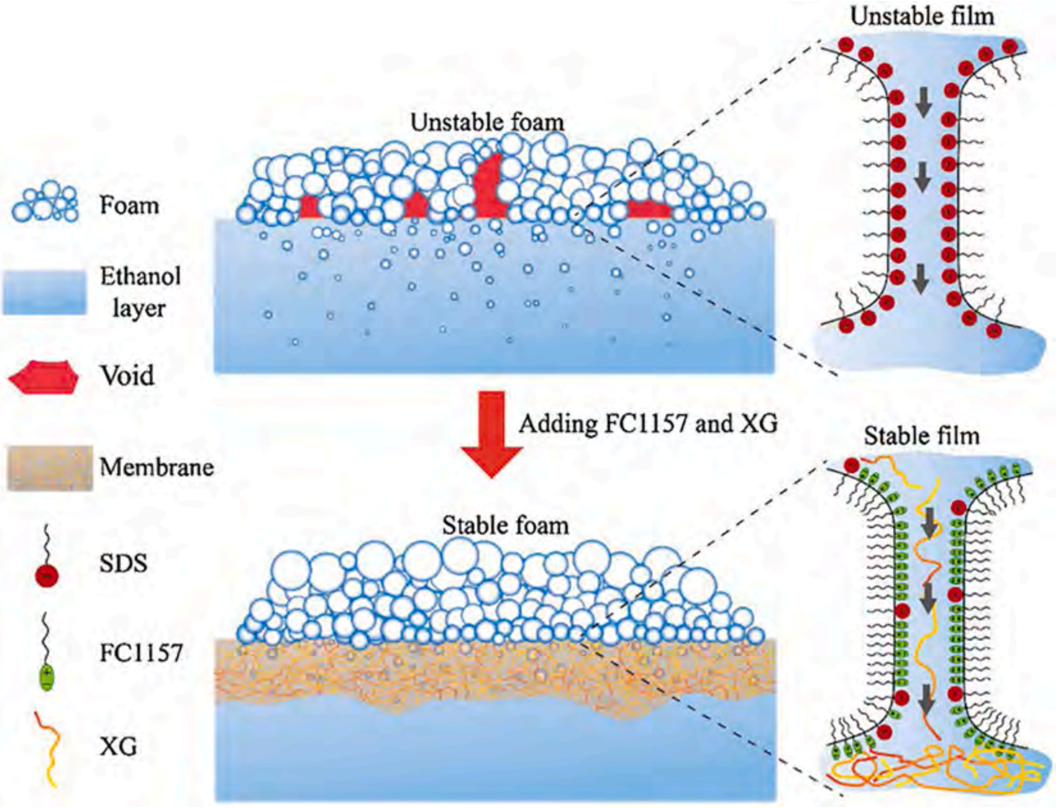


Fig. 2. Stable foam generation using fluorinated surfactant and xanthan gum with SDS [58].

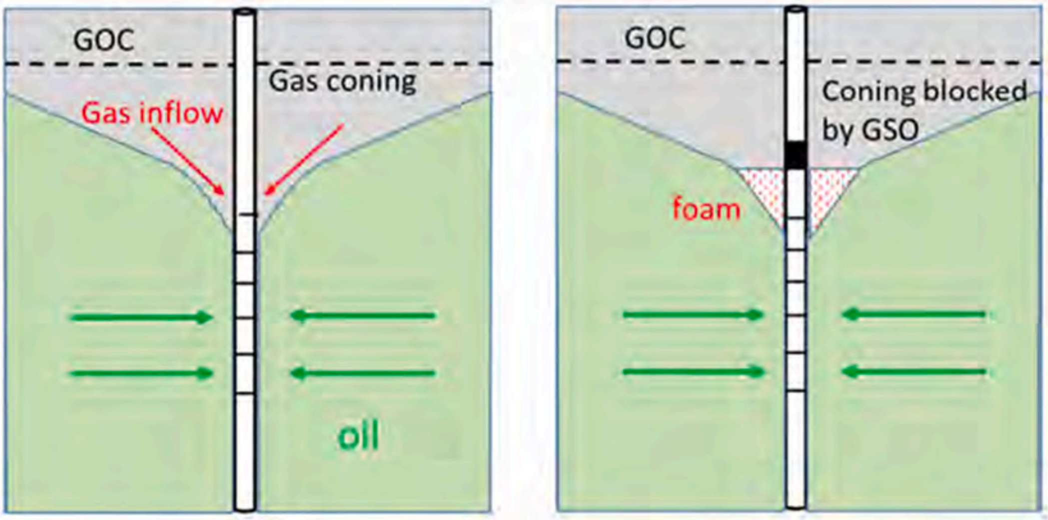


Fig. 3. Gas-coning prevented by foam in a vertical well [86].

$(CF_2)xCH_2CH_2O(CH_2CH_2O)yH$ (called Zonyl) impacted emulsion formation as described in Fig. 4(a) [98]. Above the consolute temperature (Tc), investigators showed that hexane and perfluorohexane became miscible in the presence of about 0.1% Zonyl (Fig. 4 (b)) while below Tc, hexane and perfluorohexane separated into phases to create a hexane-in-perfluorohexane-in- water double emulsion (Fig. 4(c-d)). Likewise, Etienne et al. [99] synthesized a notable number of fluorinated surfactants (Fig. 5 (a-e)) and investigated how they influence the IFT. They established that nearly all of these nonionic diblock and triblock copolymer fluorinated surfactants stabilized water drops dispersed in fluorinated oils and they prevented quick coalescence. In particular, the influence of the length of their hydrophilic poly (ethylene glycol) (PEG) blocks on interfacial tension was investigated. Accordingly, the IFT decreased with increased PEG molecular weight until it reaches a minimum of 4.3 mN m^{-1} (Fig. 6) for surfactants containing Jeffamine900, which contained PEG with a molecular weight of 550 Da. The inference from the study is that the choice and selection of most appropriate surfactant would largely depend on the fluid's composition. By and large, fluorinated surfactants are promising candidates for producing high quality emulsions with tendency of lowing the IFT when synergized with suitable copolymers.

In order to sustain the quality of emulsion injection into the target

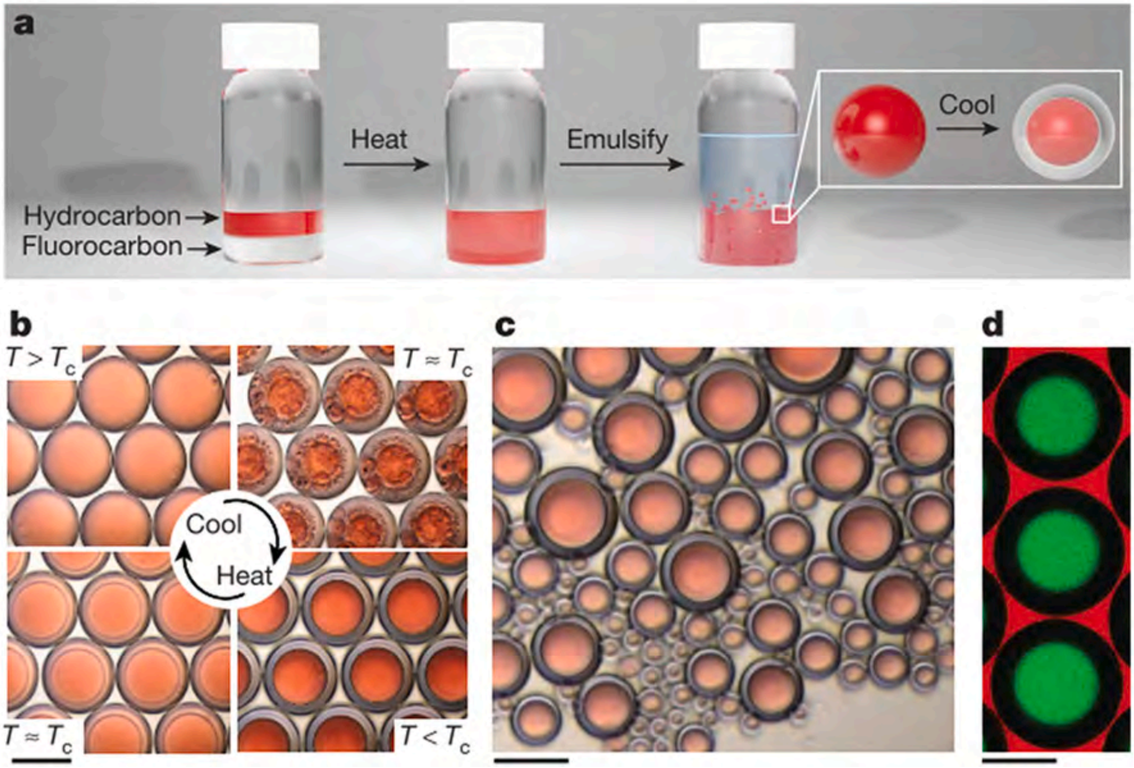


Fig. 4. Producing complex emulsion via the temperature-controlled phase separation of hydrocarbon and fluorinated liquids [98].

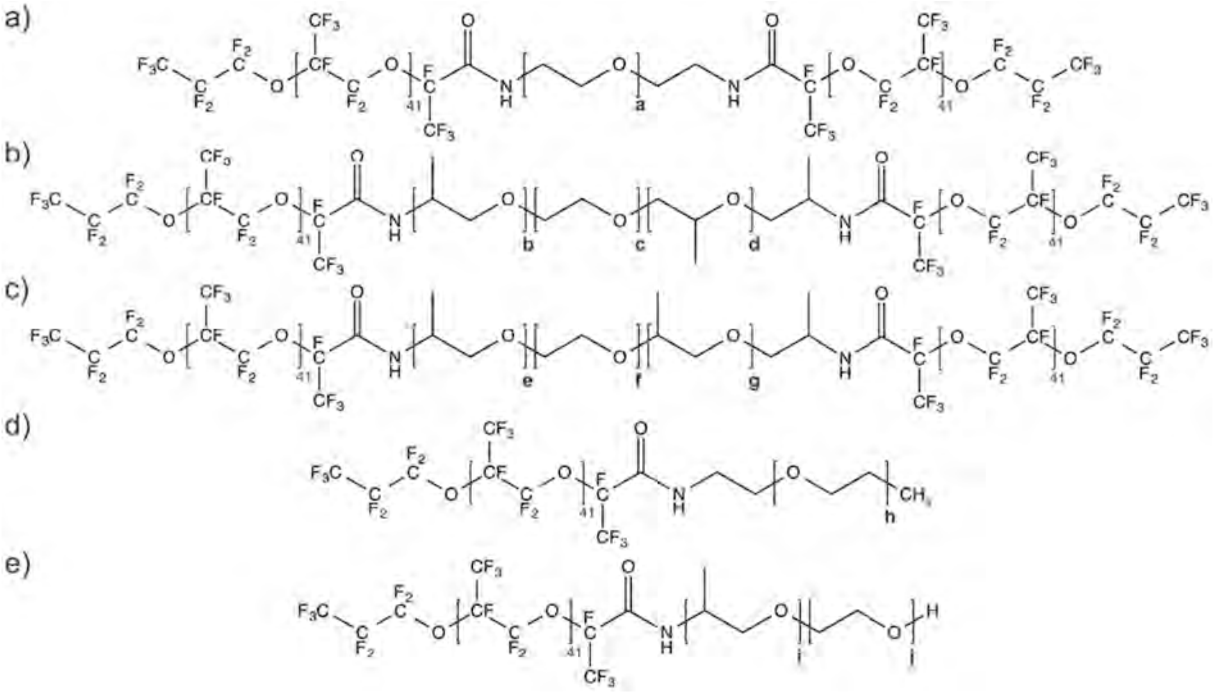


Fig. 5. The chemical structure of (a) FSH2-PEG308 and FSH2–594, (b) FSH2-Jeffamine600 and FSH2-Jeffamine900, (c) FSH2-Jeffamine2000, (d) FSH-PEG220, and (e) FSH-Jeffamine600, FSH-Jeffamine1000, and FSH-Jeffamine2000.

reservoir zone and aid the macroscopic sweep efficiency and microscopic displacement of the reservoir, it is necessary to ensure that the emulsion generated is stable enough and does not separate quickly before reaching the target zone. Elevated reservoir temperature can cause splitting of the emulsion into various phases during the injection which can subsequently retards its functionality for an effective oil recovery application. To mitigate a quick emulsion separation scenario, it is incumbent that a suitable and thermal resistant surfactant is selected. Fluorinated surfactants are promising candidates for producing stable emulsion [93]. Besides, fluorinated surfactants have demonstrated good tolerance for salts and minimal adsorption on carbonates rocks. It should however be noted that the persistence of fluorinated

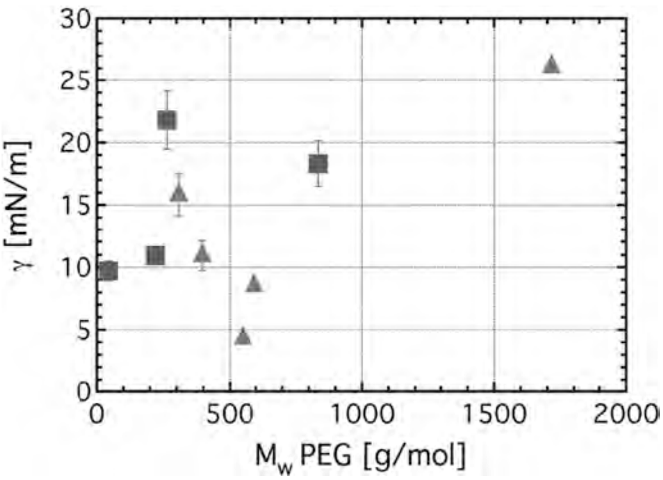


Fig. 6. Impact of the PEG molecular weight on the interfacial tension (γ)). The interfacial tensions between the fluorinated oil (called-HFE-7500) and drops containing pure water stabilized with triblock and diblock fluorinated surfactants are shown as a function of the molecular weight of PEG contained in the surfactants [99].

surfactants in soil and water environment contributed immensely to their regular adsorption onto the solid surfaces and by doing so, the underlying mechanisms responsible for the adsorption of fluorinated surfactants are better understood via thorough kinetics and thermodynamics studies [100,101]. It is evident that the varying salt concentrations, aqueous pH, and chemistry can grossly impact the adsorption of fluorinated surfactants on mineral surfaces [16]. The adsorption of fluorinated surfactants could be better elucidated by hydrogen bonding, hydrophobic interactions, ion exchange, electrostatic interactions, and ligands. Currently, adsorption studies that discussed the influence of fluorinated surfactants on solid or mineral surfaces appear to be limited [16,100,101] and further research investigations are therefore recommended to get more insight into these surfactants and solid surfaces interactions and the underlying chemistry.

In a typical oil-water-surfactant system, when fluorinated surfactant molecules replace the oil-water molecules at the interface, this new reorganization involves interaction between the hydrophobic component of fluorinated surfactant and oil as well as the hydrophilic part of this fluorinated surfactant and water. This new rearrangement can reduce the IFT depending on the molecular structure of the surfactant. By and large, achieving a low IFT in a system comprising fluorinated surfactants is challenging and demanding. To achieve an ultra-low IFT in the presence of fluorinated surfactants would require a thorough understanding and manipulation of their molecular structures and optimizing the composition of the fluid system by adding an appropriate cosurfactant or cosolvent. Again, it is necessary to point out that the ability of several surfactants, including the fluorinated surfactants to reduce the IFT between brine and crude oil is grossly sensitive to the type and concentration of ions in the brine [102]. As such, the concentration and various types of salts applied to formulate brine can be systematically assessed to achieve the targeted IFT values, otherwise, the presence of different ions in brine can trigger a change in surfactant's behavior in the form of IFT alteration.

During heavy oil recovery, a mixture of hydrocarbon (as a mutual solvent) with fluorinated surfactant can not only increase the sweep efficiency, by diverting flow from high-permeability to low-permeability channels, but also reduce the oil viscosity to make it easily recoverable [103].

3.3. Wettability modifiers

Rock wettability has a crucial impact on oil recovery and modifying rock wettability from oil-wetting to intermediate-wetting to water-wetting can enhance oil production [104]. Sandstones mostly demonstrate water-wet to intermediate-wet characteristics, while carbonates usually exhibit intermediate-wet to oil-wet properties. Now, surfactant injection is among the notable methods for rock wettability alteration and transition into the water-wet stage which increases the oil recovery significantly. In the selection of a suitable surfactant for any EOR application, a criterion for economic success is mitigating the surfactant loss due to adsorption. Among the factors affecting surfactant adsorption include pH, temperature, salinity, types of rocks existing in the reservoir, and type of surfactant used. From these aforementioned factors, only surfactant type can be manipulated for EOR use while other factors are grossly influenced by the reservoir condition. Even though surfactants can be fine-tuned to serve the intended EOR purposes, literature studies have demonstrated that many surfactants like anionic and cationic surfactants were incompatible and thermally unstable at reservoir conditions [93], whereas, fluorinated amphoteric surfactants have indeed displayed excellent thermal stability, qualitative synergistic viscosity enhancement in the presence of polymer and lowering adsorption [105]. Additionally, tolerance for salts is a great challenge for several surfactants. In a way, the proportionate and systematic blending of fluorinated surfactants with either anionic or cationic surfactants could produce new surfactant systems with improved properties for upstream applications. Li et al. used a cationic (SDCSA-1)/nonionic (FC-0) fluorinated surfactant system at different concentrations and mole ratios. The authors observed wettability alteration of sandstone from water-wet to intermediate-wet using an optimal system with 10^{-4} concentration and 1:1 mol ratios [106]. Jin et al. studied the effect of fluorinated surfactant on surface modification of nanosilica. Fig. 7 shows nano-silica modification using a fluorinated surfactant. They concluded that the wettability of sandstone core can be altered from liquid-wet to intermediate-wet by treatment with fluorinated surfactant [107].

Kumar et al. demonstrated with experimental coreflood and simulation data that gas-condensate relative permeability in sandstones can be increased up to 3 times at temperatures between 60 °C to 135 °C using fluorinated polymeric surfactants [108,109]. A fluorinated surfactant “Novec FC4430” mixed in methanol-water proved to be the most effective formulation for wettability alteration near-wellbore from water-wet or oil-wet to intermediate gas-wetting. Methanol has been tested to be a good solvent for fluorinated surfactants and it can also be used to stimulate gas-condensate wells alone, however, when mixed with a specific quantity of water can enhance the solvency. Jin et al., used 40 mm nano silica modified with a fluorinated surfactant (called FG40) shown in Fig. 8 to achieve super gas-wetting cores [110]. Near-wellbore wettability alteration using fluorinated surfactants is one of the most effective methods for gas productivity enhancement in gas-condensate reservoirs [111]. Fluorinated surfactants have also been applied as a stimulating agent in gas-condensate reservoirs. During the production of gas, pressure reduction leads to the loss of gas productivity. Karandish et al. use a new technique for enhancing the gas production by altering the wettability of carbonate rocks from aqueous-wet to intermediate gas-wet in the near well-bore area by injecting anionic fluorinated surfactants. The authors observed the improvement of gas relative permeability by a factor of 1.7 due to the wettability alteration [112].

3.4. Swelling inhibitors

Wellbore instability and adhesion of cutting sticking on drill bits are among the challenges of drilling in oilfields. Shales have been the most encountered rock during drilling into the formation. Conveying water-based drilling fluid while drilling usually constitutes swelling of clays and eventual stickiness of the shale [113]. This occurrence can result in a series of problems ranging from bit balling, hole erosion, hole collapse, hole closure, and weak mud formation. To mitigate the problem of bit

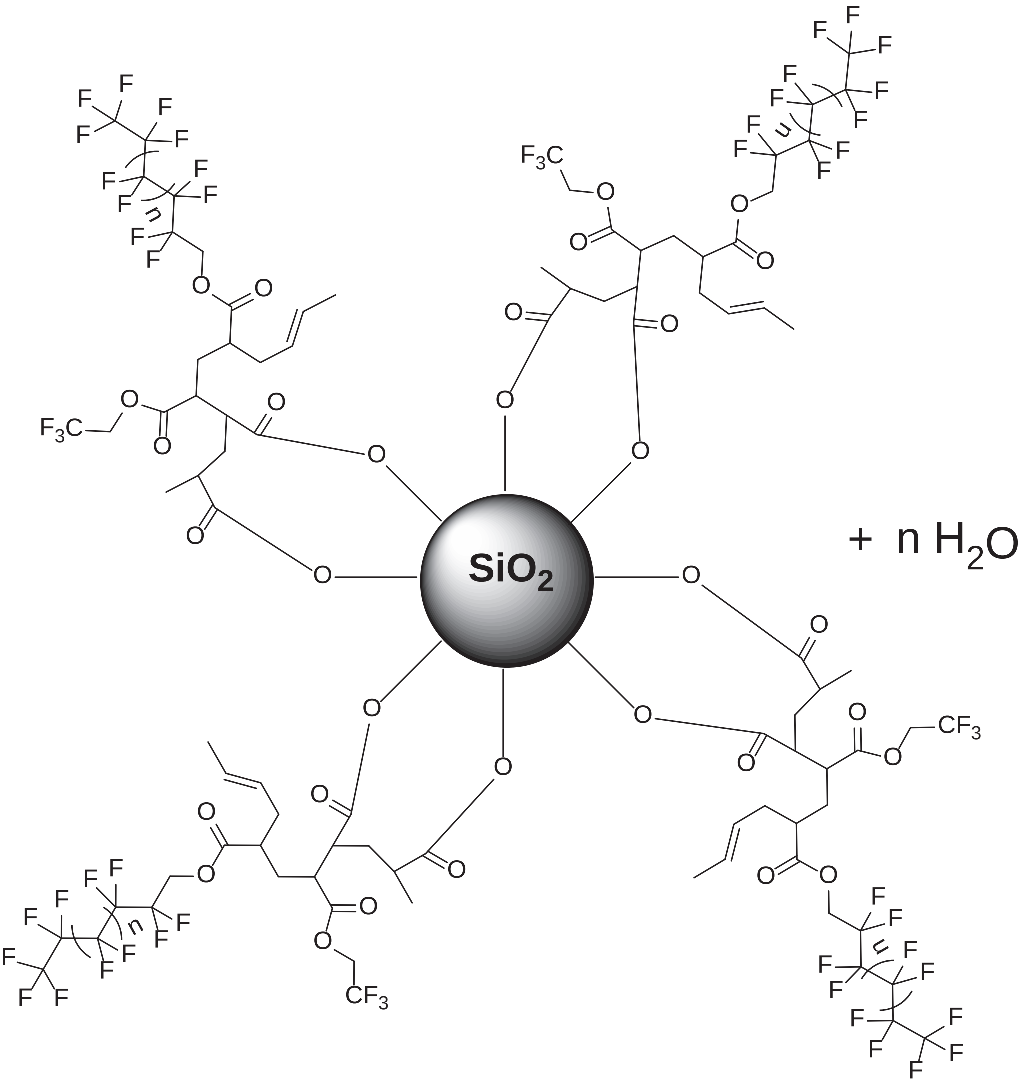


Fig. 7. Modification of Nano-silica using fluorinated surfactant [107].

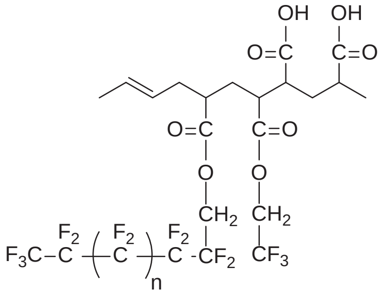


Fig. 8. Fluorinated surfactant (called FG40) is used to modify nanosilica nanoparticles [110].

balling, the inclusion of surfactants as additives in water-based drilling fluids is suggested as surfactants inhibit the clay swelling.

The attachment of fluorinated molecules to hydrophobic parts of surfactant and its careful introduction into the water-based drilling fluids can control swelling when in contact with clay surfaces and consequently reduce the adverse effect of bit balling on drill bits [100,114]. However, fluorinated surfactants have not been evaluated for clay swelling inhibition. Interactions of fluorinated surfactant with different types of clay need further investigation.

Because of the high temperature and salinity tolerance of fluorinated surfactants, a mixture of perfluoropolyether, brine, and barite has been used to develop fluorous-external invert emulsion fluid (F-IEF) to be used for high temperature applications of drilling mud. PTFE is a common perfluorinated polymer compatible with fluorous media and can therefore be used as a lost circulation material [115].

By and large, fluorinated surfactants are a new class of special surfactants that would serve enormous purposes in gas EOR, chemical EOR, drilling, fracturing, and stimulation in different roles, if properly applied. Fluorinated surfactants can be a material of choice in high temperature carbonate reservoirs where the temperature reaches up to 150 °C. Due to the strong bonding between carbon and fluorine, fluorinated surfactants exhibit excellent stability against heat and are expected to stay inside the reservoir for several days without any change in chemical structure or decomposition.

4. Concluding remarks and prospects

This review mainly focuses on the synthesis and oilfield applications of fluorinated surfactants. Fluorinated surfactants have unique aggregation properties compared to hydrocarbon surfactants. The incorporation of fluorinated atoms in the hydrophobic surfactant chain makes such surfactants thermally and chemically stable. These surfactants have huge potential in applications in harsh conditions owing to extremely high thermal and chemical stability. This also makes them an ideal candidate for oilfield application as most of the commercial hydrocarbon surfactants are not tolerant to high temperature and high salinity reservoir conditions [14,116]. Although recently several publications report oilfield application of fluorinated surfactants, several aspects still need further investigation to synthesize cost-effective and environment-friendly fluorinated surfactants. Future research should focus on the following points to fully utilize fluorinated surfactants in the oilfield and other applications.

1. The research should be more focused on the synthesis of short-chain fluorinated surfactants to avoid environmental issues associated with the long-chain fluorinated surfactants.
2. Synthesis of fluorinated surfactants using green chemistry is rare in literature. For example, the utilization of synthetic methods that minimize the generation of hazardous by-products or conducting reactions in green solvents can make the synthesis more environmentally friendly.
3. The hazardous nature of long-tail fluorinated surfactants can be minimized by the introduction of labile bonds in the tail using heteroatoms such as oxygen or nitrogen which lead to the formation of degradable fluorinated surfactants.
4. A comprehensive study on the effect of counterions needs to be conducted to identify the role of counterion on the aggregation and morphology of the fluorinated surfactants.
5. Gemini surfactants are the growing class of surfactants with excellent surface/interface properties. However, anionic and zwitterionic gemini surfactants are very rare in literature. The new strategies for the synthesis of anionic and zwitterionic gemini surfactants with better surface/interface properties are highly desirable.
6. Despite the enormous potential of fluorinated surfactants in the petroleum industry, their usage seems to be limited due to environmental concerns. Fluorinated surfactants have environmental concerns due to their bioaccumulation and biomagnification. An easy formation pathway and cost-effective novel fluorinated surfactants are very significant to maximize their usefulness in upstream and downstream operations. More importantly, recovery and recyclability of several fluorinated surfactants during petroleum processes would be of great interest because the majority of them don't degrade easily and this could constitute a serious challenge for aquatic life.

Likewise, it is very glaring that fluorinated surfactants differ significantly from other known conventional surfactants, and owing to this phenomenon, toxicity and environmental impact assessments of these surfactants are worthy of investigation. Realizing the full utilization of fluorinated surfactants in the petroleum industry would depend on finetuning their preparation methods such that a new class of fluorinated surfactants can emerge with unique features and in accordance with environmental regulations and requirements.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Review

Gas-Wetting Alteration by Fluorochemicals and Its Application for Enhancing Gas Recovery in Gas-Condensate Reservoirs: A Review

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Abstract: Gas-wetting alteration is a versatile and effective approach for alleviating liquid-blockage that occurs when the wellbore pressure of a gas-condensate reservoir drops below the dew point. Fluorochemicals are of growing interest in gas-wetting alteration because of their high density of fluorine groups and thermal stability, which can change the reservoir wettability into more favorable conditions for liquids. This review aims to integrate the overlapping research between the current knowledge in organic chemistry and enhanced oil and gas recovery. The difference between wettability alteration and gas-wetting alteration is illustrated, and the methods used to evaluate gas-wetting are summarized. Recent advances in the applications of fluorochemicals for gas-wetting alteration are highlighted. The mechanisms of self-assembling adsorption layers formed by fluorochemicals with different surface morphologies are also reviewed. The factors that affect the gas-wetting performance of fluorochemicals are summarized. Meanwhile, the impacts of gas-wetting alteration on the migration of fluids in the pore throat are elaborated. Furthermore, the Wenzel and Cassie-Baxter theories are often used to describe the wettability model, but they are limited in reflecting the wetting regime of the gas-wetting surface; therefore, a wettability model for gas-wetting is discussed. Considering the promising prospects of gas-wetting alteration, this study is expected to provide insights into the relevance of gas-wetting, surface morphology and fluorochemicals, further exploring the mechanism of flow efficiency improvement of fluids in unconventional oil and gas reservoirs.

Keywords: gas-wetting alteration; liquid-blocking effect; fluorochemical; morphology; flow behavior

1. Introduction

Over 172,700 billion cubic m of proven natural gas reserves worldwide can be found in gas-condensate reservoirs [1–3]. Major gas-condensate reservoirs around the world, such as the Arun gas field (Indonesia), Urengoy gas field (Russia), South Pars gas field (Iran), North Field (Qatar), Cupiagua oilfield (Colombia), Karachaganak oilfield (Kazakhstan), and Tarim oilfield (China), occupy important positions in the global energy supply [4]. Gas in low-permeability condensate reservoirs is mainly recovered by the elastic energy accumulated in rocks and fluids. Primary gas deliverability in gas-condensate reservoirs is promising when the gas channels in porous media are flowable. However, the gas phase tends to condense into a "liquid-ring" or "liquid-bank" region around the gas well once the wellbore pressure drops below the upper dew pressure (point 2 in Figure 1), leading to a sharp decline in gas productivity, known as liquid-blocking effect. Basically, all gas-condensate reservoirs experience the dilemma of severe liquid-blocking effect after long periods of isothermal depletion [5–7], and increasing the gas recovery from mature gas reservoirs has become a major concern [8].

The poor mobility of fluids in liquid-wetting porous media is recognized as one of the major causes of liquid blockage [9]. The migration and allocation of fluids in the pore throat are governed by reservoir wettability; the rock spontaneously imbibes and retains liquid phase due to capillary force, increasing the liquid saturation and decreasing gas permeability [10]. There are multiple approaches for mitigating the impact of the liquid-blocking effect, including the chemical-injection method, the pressure-maintenance method, the horizontal wells strategy, hydraulic fracturing, and the combination of two or more of these methods [7], among which gas-wetting alteration achieved by chemical injection has been arousing wide attention because of its easy operation and permanent effectiveness.

This study elaborates gas-wetting alteration and the mechanism by which it enhances gas recovery, along with a summary of methods for evaluating gas-wetting, the various fluorochemicals used to achieve gas-wetting, and influential factors; the difference between gas-wetting alteration and wettability alteration is explained, and the relationship between surface morphology and gas-wetting is illustrated. Subsequently, the effect of gas-wetting on the flow behaviors of fluids in porous media is summarized, providing a better insight into the behaviors of trapped liquids in gas-condensate reservoirs.

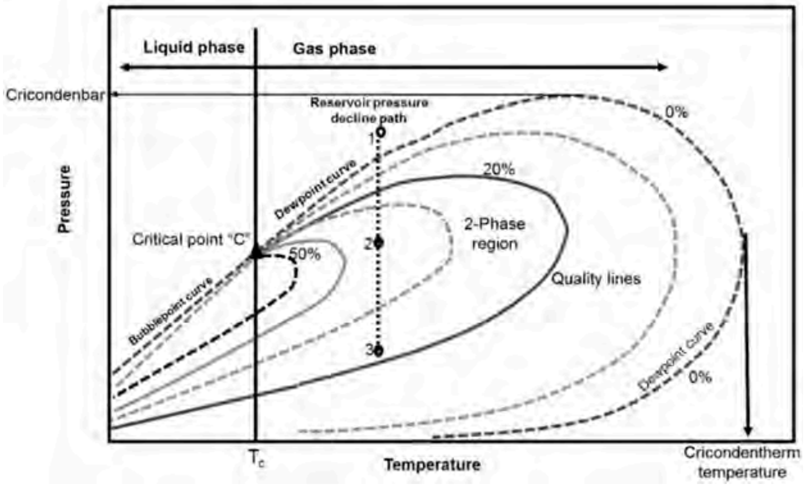

Figure 1. Typical temperature–pressure diagram for a multiphase system. Reproduced with persimission from [11], Copyright © 2010 Elsevier.

2. Gas-Wetting Alteration and Its Effect on EOR

2.1. Gas-Wetting Alteration

In 2000, the gas-wetting alteration technique was first proposed to alleviate the impact of liquid-blockage in gas-condensate reservoirs by altering reservoir wettability [12], which has been proved to be one of the most effective methods for improving the flow efficiency of fluid in the liquid-blocked region. Apart from condensate, another factor that contributes to liquid-blockage and loss of gas productivity is the presence of retained water, including the injected water and the water derived from the water-bearing formation [13]. It is difficult for the retained liquid in the pore throat to flow due to the low permeability and capillary pressure, and the combined effect of condensate and water in the wellbore region exacerbates the decrease in gas deliverability [6]; hence, the key to mitigating the liquid-blocking effect is to enhance the migration efficiency of both water and oil.

The principle of gas-wetting alteration is to change the rock wettability from liquid-wetting to gas-wetting by fluorochemicals; if the liquid saturation in the gas-wetting region is obviously less than that in the untreated region, then gas deliverability can be enhanced after gas-wetting alteration, as shown in Figure 2. It is worth noting that gas relative permeability might be more sensitive to the flow rate of fluids than liquid relative permeability, Li et al. [14] found that gas relative permeability increased as the flow rate increased after gas-wetting alteration, and a sharp decrease in gas relative permeability could be observed when the liquid saturation reached the critical condensate saturation; hence, it is reasonable to conclude that gas relative permeability increases due to the increase in the liquid mobility induced by gas-wetting alteration, leading to a reduction in liquid saturation and an increase in gas saturation. Wu and Firoozabadi [15] found that a cationic fluoropolymer could be applied to change the sandstone wettability to neutral gas-wetting, and the adsorption of the fluorochemicals showed less impact on the gas permeability. The liquid saturation of fluids trapped in porous media could be reduced by more than 25% after gas-wetting alteration under high-temperature and -pressure conditions [16]. Meanwhile, liquid mobility and gas deliverability in a gas-liquid rock system can be enhanced by fluorochemical polymers without core damage, and sand production can also be relieved due to gas-wetting alteration [17]. Subsequently, a novel fluorine-containing acrylate copolymer was synthesized through emulsion polymerization, the imbibition volume and rate of liquids in the rock decreased sharply following gas-wetting alteration, helping to mitigate the water-blockage effect [18]. Sheydaeemehr et al. [19] simulated the effect of gas-wetting alteration on gas production and relative permeability in a Middle East oilfield, and the results indicated that both gas and condensate production could be effectively improved following gas-wetting alteration, and the production plateau of the gas-condensate reservoir could be extended. In China, gas-wetting alteration has been conducted in the central and northwest oilfields, and the results show that the relative permeabilities of gas and liquid were substantially enhanced by gas-wetting alteration [20]. It is worth noting that the desorption of fluorochemicals also influences the permanence of gas-wetting alteration, which is neglected in the current studies.

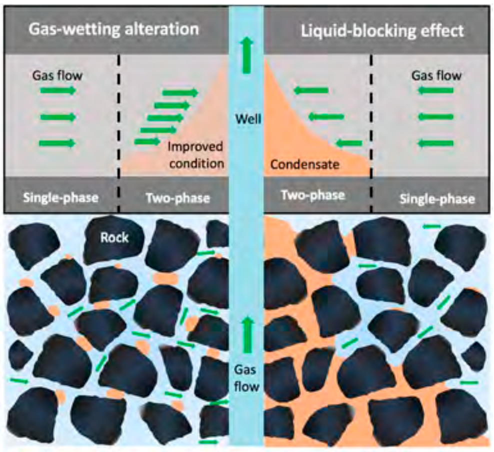

Figure 2. Sketch of mitigation of liquid-blocking effect by gas-wetting alteration in gas condensate reservoir.

In summary, both fluorosurfactants and fluoropolymers can be used to eliminate the liquid-blocking effect by improving liquid mobility, and the carbon–fluorine bond on the molecule plays a vital role in achieving gas-wetting alteration. The relevance between surface wettability and the fluorine content of the fluorochemical molecules has been investigated by experiments and molecular simulation, finding that the fluorine amount of fluorosurfactant molecule is proportional to its hydrophobicity [21].

Additionally, the surface morphology of a solid is also closely associated to its surface wettability, with high surface roughness being one of the prerequisites for fabricating a super gas-wetting surface.

2.2. Wettability Alteration

Wettability is the phenomenon whereby a fluid tends to replace another fluid on a solid surface, and is determined by the balance between adhesive and cohesive forces [22]. For conventional oil reservoirs, rock wettability can be characterized as water-wet, oil-wet, mixed-wet, and intermediate-wet according to the predominance of fluids on the rock surface [23]. Rock can be considered to be liquid-wetting (water-wet or oil-wet) if the liquid can spread on the rock surface, or the contact angles of liquids are lower than 90°; the rock can be regarded to be intermediate-wet if the contact angle of liquid droplet is close to 90°. Additionally, a reservoir might be both water-wet and oil-wet because of the complex structure of the pore throat, and can be denoted as being mixed-wet. Wettability alteration refers to the process of transition between liquid-wetting (water-wet, oil-wet) and intermediate-wet through the use of surfactants or polymers in a liquid–liquid–rock system. Generally, oil recovery can be enhanced following wettability alteration; the rock will spontaneously imbibe water, which will displace out due to the increase in affinity to the water phase, and then the capillary force for the oil phase will transfer from a resistance force into a displacing force under these circumstances [24]. However, conventional surfactants or polymers can only achieve intermediate-wet, and further enhancement of oil/gas recovery through wettability alteration is limited.

Gas-wetting refers to a solid surface with high surface free energy being replaced by a surface with low free energy that has a better affinity for air, but on which it is difficult for water and oil phases to spread, indicating that the contact angles of both water and oil are more than 90°. Gas-wetting alteration through fluorochemicals involves gas–liquid–rock systems, while wettability alteration only occurs in liquid–liquid–rock systems, which is the major difference between gas-wetting alteration and wettability alteration. The Wenzel and Cassie-Baxter models are the classic theories that have been used to describe the wetting regime of liquids on solid surfaces [25], but they are unable to reflect the wetting regime of gas-wetting. Meanwhile, previous studies have shown that the flow in a liquid-wetting reservoir obviously differs from that in gas-wetting reservoirs [12,26–29]; our understanding of the flow behavior of fluids in gas-wetting porous media is still limited. The performance of wettability alteration depends on multiple factors, such as the usage and types of chemicals and reservoir conditions. The performance of gas-wetting alteration is mainly influenced by the fluorine content of the gas-wetting agents, the surface morphology of gas-wetting adsorption, and the reservoir conditions. Considerable work needs to be accomplished in order to better understand the relationship between gas-wetting alteration and wettability alteration.

2.3. Gas-Wetting Measurement

This section discusses the methods for gas-wetting evaluation, including the static contact angle method, the OWRK method, the spontaneous imbibition test, the capillary rise test, the nuclear magnetic resonance technique, and streaming potential measurement. Additionally, the improvements and deficiencies of the current techniques are also described.

2.3.1. Static Contact Angle Measurement

Static contact angle measurement (CA) is one of the principal methods used to quantitatively evaluate rock wettability, and it has the advantages of high accuracy and easy operation [30]. The mechanism of contact angle measurement is to quantify the static contact angles of the liquid phases in an air–liquid–rock system. A gas-condensate reservoir can be regarded as a CH_4–liquid–rock system, while the mobile phases in a conventional reservoir are only composed of water and oil phases; hence, the major limitation of the current method is its inability to be conducted in CH_4–liquid–rock systems. In a CH_4–liquid–rock system, rock can be considered to be liquid-wetting (water-wet or oil-wet) if the liquids spread on the rock surface or the contact angles of the liquid droplets are lower than 90°; the rock can be regarded as intermediate gas-wetting if the contact angles of the liquid droplets are close to 90°; the rock can be considered to be gas-wetting if the contact angles of the liquid droplets are within the range 90~120°; and if the contact angles of water and oil phases are more than 120°, and at least one exceeds 150°, the rock wettability can be recognized to be superhydrophobic or superoleophobic, namely, to be super gas-wetting [31–33]. it is worth noting that static contact angle measurement has limitations under the following circumstances: (1) the measurement error is non-negligible when the contact angle of the liquid droplet is below 20°; (2) the droplet size and the roughness of the solid surface will have an impact on the accuracy. However, the foregoing limitations can be offset by controlling the liquid amount and standardizing the surface treatment of the sample; therefore, static contact angle measurement can still be a reliable and convenient method used to evaluate the rock wettability.

Recently, Tabar et al. proposed a novel contact angle measurement based on the axisymmetric drop shape analysis, and found that there exists a correlation between contact angle, droplet volume, and surface roughness [34]. Moncayo-Riascos et al. [21] used the molecular dynamics model to predict the contact angle of water droplets after gas-wetting alteration, finding that the simulation results matched the measured contact angle well. In consideration of the non-ideality of the solid surface, contact angle hysteresis (CAH) is also a vital parameter for characterizing the wetting state of the solid surface; the smaller the contact angle hysteresis, the weaker the drop adhesion [35,36]. Generally, the definition of a super gas-wetting surface is that the advancing contact angle is larger than 150° and the contact angle hysteresis is less than 10° [37,38].

2.3.2. Owens–Wendt–Rabel–Kaelble Method

The surface free energy (SFE) is derived from the intermolecular interactions after the generation of the new surface, and is a key factor that can be used to predict the wettability regime of a solid surface [39]. Typically, the Owens–Wendt–Rabel–Kaelble (OWRK) method, the Wu method, and the Van Oss–Chaudhury–Good method are employed to quantitatively estimate the change in the free energy of the solid surface before and after wettability alteration [40–42]. The surface free energy consists of polar force and dispersion force, which can be calculated using Young's equation based on the contact angles of liquids with varying polarities on the solid surface. The surface free energy can be calculated using the OWRK method, as described in Equation (1) [42]. The polar (dispersion) force is used to describe the interaction between polar (non-polar) substances and the solid surface, the rock will exhibit different affinities for liquids with varying polarities. The contact angles of both water and oil on a gas-wetting surface are obviously higher than those on a liquid-wetting surface, leading to a major difference in surface free energy. Therefore, the surface free energy can be an effective parameter for reflecting the gas-wetting regime of rock surfaces. Additionally, Gindl et al. compared the methods used to calculate the surface free energy of solid surfaces, including the Zisman method, Berthelot's approximation, the Fowkes method, and the acid-based approach [43]. However, these methods involve more than two liquids, and the calculation results depend heavily on the choice of the liquids. Neumann proposed an "equation of state" theory to determine the solid surface free energy by introducing an empirical constant to the mentioned methods, the calculation results are reasonable, but one major limitation of this method is that only the total surface free energy can be estimated [44,45].

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\left(\sqrt{\gamma_{sv}^{D}\gamma_{lv}^{D}} + \sqrt{\gamma_{sv}^{P}\gamma_{lv}^{P}}\right) \tag{1}$$

where γ_{sl} is the interfacial free energy between the liquid and solid, γ_{sv}^{D} and γ_{lv}^{D} denote the dispersive part, while γ_{sv}^{P} and γ_{lv}^{P} represent polar part of solid surface energy and liquid surface energy, respectively.

2.3.3. Spontaneous Imbibition Test

Spontaneous imbibition refers to the process of absorption in which a wetting fluid can spontaneously be imbibes into the pore throat due to capillary force. As early as 1950, Brownscombe and

Dyes [46] realized the importance of spontaneous imbibition in oil recovery during the waterflooding process of water-wet fractured reservoirs. If the reservoir wettability is water-wet, then an oil-saturated rock will preferentially imbibe water into porous media, displacing the oil out as the rock is immersed in water [47]. However, for gas-condensate reservoirs, the imbibition of water or oil would cause serious formation damage to gas deliverability. The measurement of the spontaneous imbibition rate and the volume of the liquid phase by rock could be a reliable and reproducible method for the quantitative evaluation of gas-wetting. The principle behind the imbibition test is that a wetting phase tends to be spontaneously imbibed into a pore throat occupied by a nonwetting fluid. However, the method also raises the problem of measuring the imbibition volume of a liquid in the core sample with non-negligible errors [48]. Li and Firoozabadi suggested an improved imbibition apparatus by which the average liquid saturation in the sealed rock sample could be calculated [12]. Later on, an improved imbibition test in a CH_4–liquid–solid system was suggested to simulate the imbibition process in gas-condensate reservoir conditions [32].

2.3.4. Capillary Rise Test

The capillary rise test has been studied for several decades, since its first proposal [49]. Compared with contact angle measurement, the capillary rise test has been extensively applied to evaluate the wetting regime of solid particles or powders [50]. Liquid is spontaneously imbibed into untreated capillaries due to capillary force, and then the affinity of the capillary tube towards a certain liquid can be evaluated by a liquid-level according to the Washburn equation [32,50]. The Washburn equation is shown in Equation (2) [51]. The capillary force will be the resistance force for liquids where the rock wettability is gas wetting. Therefore, the capillary can be considered to be gas-wetting when the liquid level in the capillary tube is negative; a theoretical contact angle can be calculated based on the different liquid levels. Obne premise need to first be satisfied before performing this method: total wetting liquid must be used to adjust the geometric factor. However, in practice, it is hard to find an ideal liquid that can totally wet any tube. Moreover, it is noteworthy that the surface physicochemical properties and sizes of tube also have a direct influence on the liquid level in the tube [50,52,53].

$$h^2 = \frac{r\gamma_{lv}\cos\theta}{2\eta}t \tag{2}$$

where h is the liquid level in capillary; r, γ_{lv}, and η denote the capillary radius, surface tenson of liquid, and the viscosity of liquid, respectively; t represents the imbibition time.

2.3.5. Nuclear Magnetic Resonance Technique

Understanding the wetting regime of a rock under reservoir conditions is crucial for choosing optimal development programs. Being different from the above-mentioned methods of wettability measurements, the nuclear magnetic resonance technique (NMR) has the advantage of monitoring the wettability change during the displacement process in situ; it is cost-effective and does not intervene in fluid saturation [54,55]. The principle of this method is to measure the transverse relaxation time of the wetting phase (for example, the water phase) used to reflect the pore size distribution of the water-wet rock; the wetting state of the rock can be determined once the change in the relaxation time of wetting phase has been detected. Currently, the NMR technique is only used to predict water-wet, oil-wet, or mixed-wet, although its application in gas-wetting evaluation can be expected. Moreover, there are other classic methods, such as the Amott test and the USBM index, that are time-consuming, expensive, and are unable to monitor the wettability change in real time.

2.3.6. Streaming Potential Measurement

Streaming potential method (SPM) can be employed to investigate the wetting state of the intact rock sample since there is a close correlation between the surface wettability and the electrical charge of rock [56]. Streaming potential is derived from the charge transportation that occurs when a fluid flows through surface-charged porous media or under an external potential gradient, the excess charge within the double layer would transfer to the fluid, generating a streaming current. SPM is suitable for predicting the wetting regime of porous media by measuring the average value of the zeta potential during the dynamic coreflooding process [57]. Based on the sensitivity and accuracy of the SPM technique, the gas-wetting degree of porous media can be predicted by calculating the streaming potential ratio between liquid and gas.

3. Properties of Fluorochemicals

Fluorine is the most electronegative element in nature, ranked third-highest among all elements in first ionization energy [58]. The C-F bond is the strongest bond, and endows fluorochemicals with the features of high thermal stability, low adhesion, and strong chemical inertness [59]. Since the discovery of poly (tetrafluoroethylene) (PTFE) in the 1930s, fluorochemicals have been widely used in various applications, such as functional and protective coatings [60], optical and electronic devices [61], special sensors [62], and in biotechnology [63]. Its applications in oilfields show that gas-wetting alteration by fluorochemicals can be an effective approach for improving gas deliverability in unconventional reservoirs [9,30]. The molecule structures of conventional surfactants and polymers are more vulnerable and easier to disrupt under high-temperature (120~150 °C) and -pressure (37~111 MPa) conditions. The pressure and temperature of gas-condensate reservoirs increase with depth, and this aggravates the liquid-blocking effect near the wellbore region [64]; fluorochemicals could exhibit excellent hydrophobicity and oleophobicity under harsh environmental conditions, such as ultra-high temperatures and pressures [65,66], and therefore, great interest has been aroused by the use of fluorochemicals as a preferable candidate for improving gas deliverability.

3.1. Fluorosurfactants

Fluorosurfactants are fluorine-containing surfactants that consist of a polar hydrophilic head and a hydrophobic and oleophobic C-F tail, which can achieve gas-wetting alteration and decrease interfacial tension under harsh reservoir conditions because of its strong C-F bond [67]. Fluorosurfactants can be categorized as non-ionic, anionic, and cationic types according to the charge on their polar ends. Given the reality of reservoir rock being negatively charged, non-ionic and anionic fluorosurfactants would be suitable for avoiding excess loss. In 2000, fluorosurfactants were firstly used as a gas-wetting alteration agent for eliminating the liquid-blocking effect in gas-condensate reservoirs; oil and gas recovery was significantly improved after treatment [12]. Fahimpour and Jamiolahmady [68] further investigated the effect of anionic and nonionic fluorosurfactants on gas productivity in a gas-condensate reservoir; their research showed that liquid mobility could be substantially improved after treatment with fluorosurfactants. Gas permeability tends to sharply decline after liquid-blockage, which can be ameliorated after treatment with fluorosurfactant; this can be attributed to the adsorption of fluorosurfactant molecules on the pore throat [16].

Compared with conventional surfactants, such as SDBS and CTAB, fluorosurfactants also possess a better capacity to decrease interfacial tension to an ultra-low level that would be favorable to the improvement of oil and gas production [69]. Kamal et al. [70] studied a non-ionic ethoxylated fluorosurfactant for EOR applications, finding that the fluorosurfactant was thermally stable under conditions of high salinity and high temperature. Foam flooding is a promising EOR technique due to its ability to overcome the problem of gravity segregation and viscous fingering, but the instability of foam under high temperature and pressure hinders its further application. Siddiqui et al. [71] investigated the effect of an amphoteric amine oxide-based fluorosurfactant on foam stability by core flooding experiments; the low interfacial tension of foam system induced by the fluorosurfactant promoted foam stability under high-pressure conditions.

Fluorosurfactant molecules tend to adsorb on a solid surface to form monolayer or multilayer adsorption, which could transfer the surface wettability of rock from liquid-wetting to gas-wetting. The adsorption of fluorosurfactants on reservoir rock is dominated by the chemical composition, charge, and functional groups of the rock; the functional groups and charge on the polar end of fluorosurfactant also affect the adsorption process. Generally, both physical adsorption and chemical adsorption occur on rock surface [72]. The physical adsorption process dominates during the initial stage, and fluorosurfactant molecules scatter on the rock surface when the concentration of fluorosurfactant is low. Monolayer adsorption occurs on the rock surface when the concentration reaches the critical micelle concentration, as shown in Figure 3b. With the increase of concentration, fluorosurfactants tend to form a compact multi-adsorption layer on the rock surface due to the electrostatic force and dispersion force, as shown in Figure 3c; however, the affinity between the first layer of fluorosurfactant and the rock becomes stronger with the increase of temperature and time, and fluorosurfactants can bond with the hydroxyl or carboxyl groups of rock surface to form new bonds [73]. Therefore, the adsorption of fluorosurfactants on the rock surface can be considered to be a combination of physical adsorption and chemical adsorption.

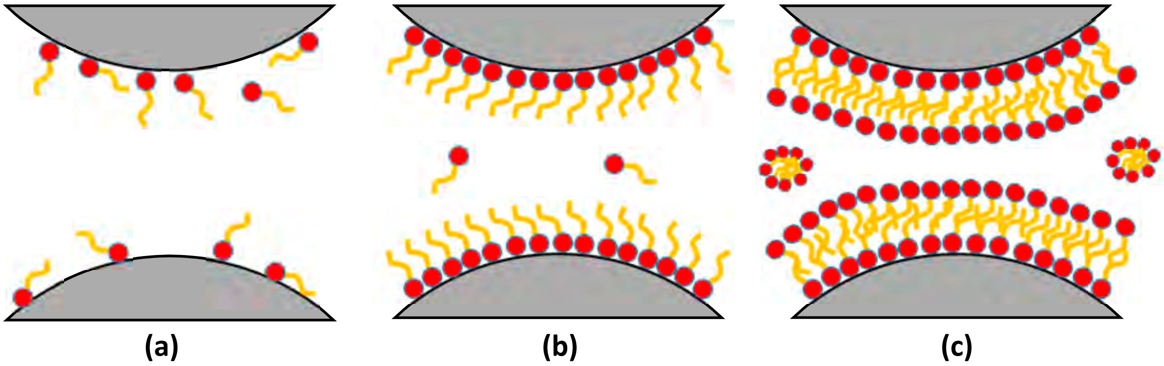

Figure 3. Schematic of fluorosurfactant adsorption on the rock surface: (**a**) low concentration; (**b**) critical micelle concentration; (**c**) high concentration. Reproduced with permission from [74], Copyright © 2002, American Chemical Society

3.2. *Fluoropolymers*

A fluoropolymer is defined as a polymer that consists of carbon and fluorine, which is composed of the C-C backbone and the C-F branches [75]. In 2000, Li and coauthors found that a fluoropolymer named "FC722" could be used to alter rock wettability to gas-wetting, which could effectively mitigate the liquid-blockage phenomenon during the development of gas-condensate reservoir [12]. Subsequently, some commercial fluoropolymer products, such as Zonyl 8740, G06, and Lot 201, were proved to have the capacity to alter the reservoir wettability from water-wet or oil-wet to intermediate gas-wetting, and the flow efficiency of gas could be further promoted after treatment [15,76]. However, the low solubility and high cost of the fluoropolymer impede its large-scale application. To address the above problems, fluoropolymers with varying morphologies have been synthesized by emulsion polymerization, such as core–shell [77], acorn-shape [78], and Janus-shape [79], as shown in Figure 4. The distribution and content of fluorine groups in fluoropolymers can be tuned by adjusting the synthesis process and fluorine-containing monomer usage, which can improve the solubility and reduce the cost of the fluoropolymer.

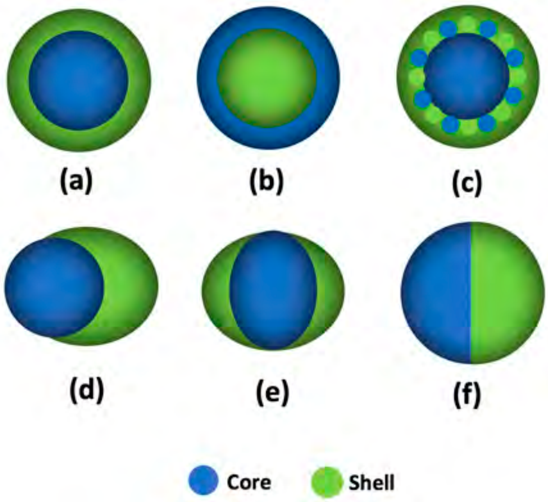

Figure 4. Schematic of fluoropolymer particles: (**a**) core–shell structure; (**b**) inverted core–shell structure; (**c**) triple-layer structure, the middle-layer contains a mixture of core monomer and shell monomer; (**d**) acorn-shaped structure; (**e**) egg-shaped structure; and (**f**) Janus-shaped structure.

The fluoropolymer adsorption layer on a rock surface can not only modify the chemical composition of the rock, but can also change the surface microstructure of the rock [80,81]. In solution, fluoropolymers are normally dispersed as latex particles rather than single polymer chains, and the conformation of fluoropolymer depends on the nature of the monomer and the synthesis procedure. Once adsorbed on the rock surface, the arrangement of these latex particles can synergistically enhance gas-wetting degree by fabricating high surface roughness adsorption. The conformation of fluoropolymer could be dominated by the following elements: (1) the stretching of the hydrophobic group; (2) the repulsive interaction among the stretching groups; and (3) influential factors, for instance, temperature, pH, and salinity [82].

3.3. Fluorochemical-Modified Nanoparticles

Recent advances in nanoparticle modification have attracted wide attention due to their tailored features and huge potential to enhance oil and gas recovery [83]. The primary applications of nanoparticles in the petroleum industry are related to alleviating formation damage and improving oil and gas recovery, such as the liquid-blocking effect, and aqueous phase trapping caused by hydraulic fracture [84]. Inspired by the unique microstructure of the lotus, nanomaterials with liquid-wetting can be decorated by fluorochemicals to prepare super gas-wetting nanoparticles that are of both high surface roughness and low surface free energy. Varying morphologies and chemical compositions of the adsorption layer can be obtained by adjusting the mass ratio between nanoparticles and fluorochemicals. Mousavi et al. [85] proposed a novel and effective approach for altering the wellbore wettability from liquid-wetting to intermediate gas-wetting using fluorochemical-modified nanoparticles, and found that the volume of liquid trapped in the pore throat and the pressure difference between the two sides of the core significantly decreased after gas-wetting alteration. Different morphologies of nanoparticles could also be decorated using fluorochemicals, such as nano-rod and peanut-shaped nanoparticles; gas-wetting degrees could be tuned by changing the morphologies of the nanoparticles [86–88]. Furthermore, varying sizes and kinds of nanomaterials could be modified by fluorochemicals to achieve different purposes, such as fluoropolymer-modified CNT for enhancing gas recovery [89], multi-scale nanoparticle blocking for EOR [90], and switchable superhydrophobic/superhydrophilic surfaces induced by UV light [91].

The surface modification of nanoparticles by fluorochemicals mainly includes chemical treatment, grafting of synthetic polymers, and the ligand exchange technique [92]. Among the above modification techniques, chemical treatment is a versatile and convenient method for improving the dispersibility and functionality of nanoparticles. Generally, the surface of the untreated nanoparticles covers numerous hydroxyl groups that could bond with the polar-end of fluorochemicals molecules to form gas-wetting nanoparticles, while the surface of the modified nanoparticle is covered with fluorochemical molecules. The mechanism for grafting fluorochemical on silica nanoparticles is presented in Figure 5, the spreading C-F bonds endow the modified nanoparticle with the features of hydrophobicity and oleophobicity.

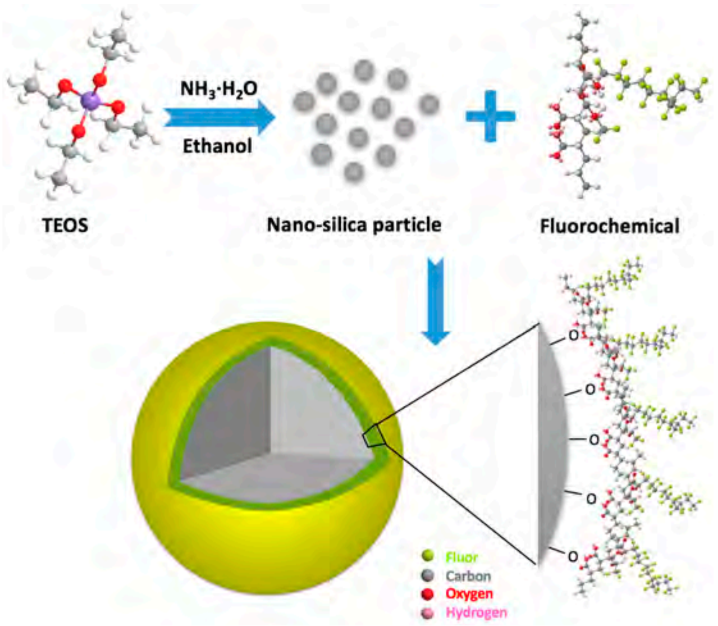

Figure 5. Sketch of the fabrication of nanoparticles with gas-wetting.

Various approaches can be used to investigate the modification mechanism of nanoparticles. The changes in adsorption peaks and newly formed bonds on fluorochemicals modified nanoparticle can be verified by FT-IR and XPS techniques. The morphologies of nanoparticles can be explored by Scanning Electron Microscopy (SEM), High-Resolution Transmission Electron Microscopy (HRTEM), and Confocal Laser Scanning Microscopy (CLSM). The Atomic Force Microscopy technique (AFM) could be employed to quantitatively estimate the roughness of the rock surface, and the relationship between surface roughness and wettability can also be obtained by the AFM technique.

3.4. Morphologies of Fluorochemicals and Modified Nanomaterials

The wettability of rock is closely related to its surface morphology and chemistry. Generally, there are two essential conditions required to achieve super gas-wetting: high surface roughness and low surface free energy. The morphologies of fluorochemicals vary according to their molecule conformations, which range from two-dimensional monolayers to three-dimensional multilayers. Hoseinpour et al. [93] altered the wettability of sandstone from water-wet to intermediate gas-wetting by coating a fluorocarbon surfactant film; the volume of spontaneous imbibition of water and decane significantly decreased after treatment. An obvious difference in the morphologies between fluorosurfactant and fluoropolymer can be observed, with the self-assembly of fluoropolymer latex particles on rock surface contributing to the decrease in surface free energy and increase in surface roughness [87] (Figure 6b). Furthermore, Jin et al. [94] studied the morphology of fluorosurfactant-modified nanoparticles, finding that the modified nanoparticles could adsorb on the rock surface by forming a gas-wetting adsorption layer, which contains numerous air cavities with huge capillary force, preventing liquids (water and oil) from entering the pore throats of the reservoir rock.

It has been found that the adsorption of fluorochemical-modified nanoparticles on rock surface matches the Freundlich model, indicating that the multilayer adsorption formed by modified nanoparticles might be involved in the chemisorption process, which can be verified by FT-IR and XPS techniques [23]. The morphology of rock surfaces treated by fluorosurfactant-modified nanoparticles can be investigated using the SEM and AFM techniques, as shown in Figure 6c,g. In addition to modifying spherical nanoparticles, one-dimensional nanomaterials, such as carbon nanotubes, can also be decorated. The adsorption layer formed by fluoropolymer-modified CNT is rich in air cavities, as shown in Figure 6d. According to the results of AFM analysis, it can be concluded that the surface roughness of solid surfaces increases with the size of the adsorbed substance, as shown in Figure 6e–h. For fluorochemicals, molecules with positive charge tend to self-assemble ahead of the air–solid–liquid interface on negatively charged rock surfaces due to the electrostatic force; then, the non-polar end with the characteristics of hydrophobicity and oleophobicity would be expose to air [95]. With respect to modified nanoparticles, they be adsorbed in multiple layers on the rock surface due to electrostatic force and chemical bonding; meanwhile, nanoparticles in self-assembled multilayers could impose structural disjoining pressure on the liquid–oil–rock boundary, facilitating the spread of nanofluid [96].

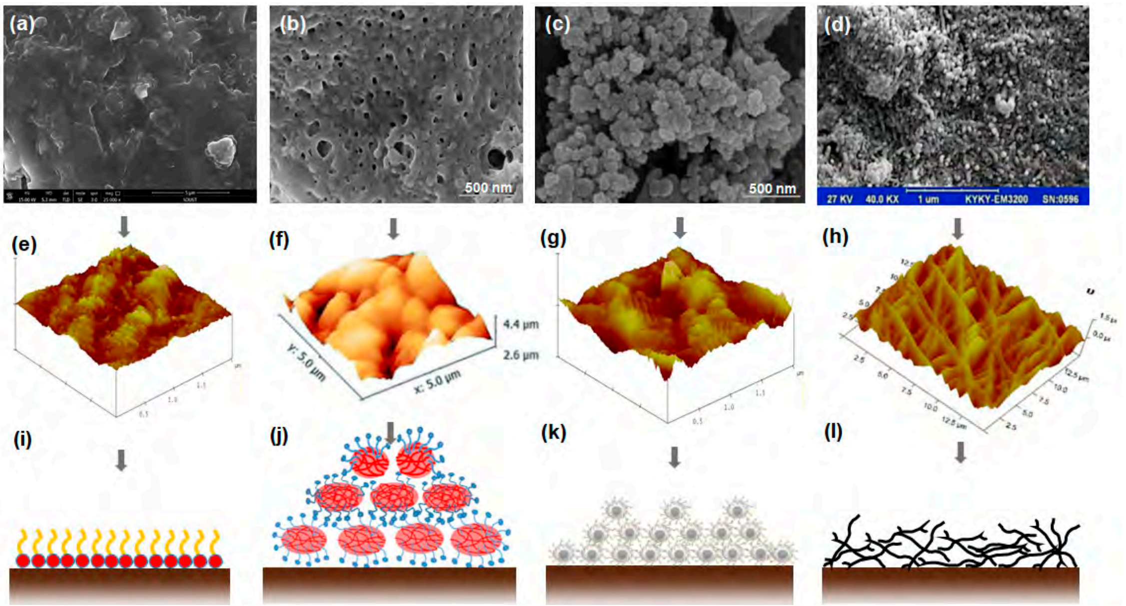

Figure 6. Morphology and adsorption of fluorochemicals with varying structures: (**a**) fluorosurfactant [32]; (**b**) fluoropolymer [87]; (**c**) fluorosurfactant-modified nanoparticle [94]; (**d**) fluoropolymer-modified CNT [89]; (**e**) AFM of fluorosurfactant [86]; (**f**) AFM of fluoropolymer [97], copyright © The Royal Society of Chemistry 2019; (**g**) AFM of fluorosurfactant-modified nanoparticle [86], Copyright © 2019, American Chemical Society; (**h**) AFM of fluoropolymer-modified CNT [98], Copyright © 2016, Springer Nature; (**i**–**l**) schematic of fluorochemicals and modified nanomaterials adsorption layer.

In summary, the greater the number of nano-sized cavities on the rock surface, the stronger the gas-wetting [99]. Despite the excellent gas-wetting of fluorochemicals, the fragile nature of the adsorption layer under external force hinders its large-scale application. Recently, a novel approach to strengthening the mechanical stability of superhydrophobic surfaces has been proposed by designing an inverted-pyramidal structure, which can resist high friction without reducing superhydrophobicity [100]. More work on fabricating super gas-wetting surfaces with different morphologies is encouraged to facilitate the application of new technology in petroleum engineering.

4. Effects of Factors on Fluorochemicals

The stability of fluorochemicals under harsh reservoir conditions is another major concern that can impact the stability of gas-wetting adsorption under complex conditions, such as high temperature, high pressure, high salinity, and long-term waterflooding [101].

4.1. Temperature

Complex and harsh environmental conditions in gas-condensate reservoirs, such as ultra-high temperature and high pressure, often degrade the fluid flow in porous media. Hence, it is pivotal for fluorochemicals to remain stable under high temperatures. In the 1960s, Johnson and Dettre [102] found that increasing the temperature could increase the hydrophobicity and oleophobicity of fluoropolymers (referred to as "temperature effects"), because the adsorption process of fluoropolymers on the solid surface can accelerate as the temperature changes. Esmaeilzadeh et al. [89] prepared a series of gas-wetting nanofluids to decrease the liquid accumulation and improve the gas deliverability, which are of permanent stability at a temperature of 160 °C; the contact angles of water and decane on sandstone samples treated with gas-wetting nanofluids slightly increase over time, as shown in Figure 7, and the velocity and amount of imbibition significantly decrease due to the change of capillary force. One potential reason for this could be that the molecule structures of fluorochemicals unfold as the temperature exceeds the evaporating temperature of crystal water [103], leading to the exposure of more C-F bonds on the rock surface. Currently, contact angle measurements are often conducted at room temperature without considering the impact of temperature and pressure, whereas the measurement under complex conditions could be able to reflect the actual wettability regime of reservoir rock. Recent research has confirmed that the contact angles of liquid on solid surfaces treated by fluorochemicals increase with the increase of both temperature and pressure; this phenomenon can be attributed to the enhancement of intermolecular interactions between gas and substrate under the conditions of high temperature and high pressure, leading to a weak liquid-wetting of the substrate [104].

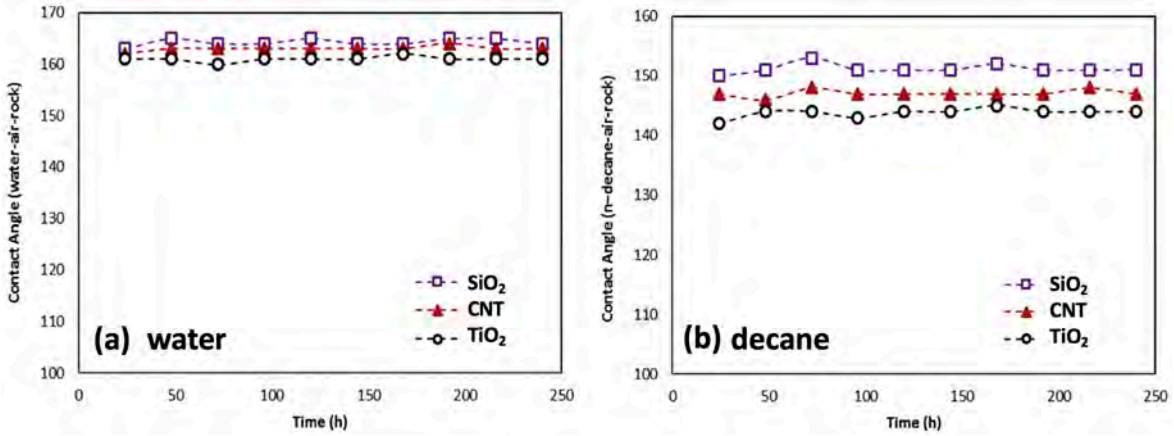

Figure 7. Impact of temperature on gas-wetting performance. Reprinted with permission from [89].

4.2. pH

CO_2 injection into the depleted gas-condensate reservoir can improve the gas deliverability of the condensate reservoir [105]; however, an overdose of CO_2 could cause the formation water to become weakly acidic. The pH of the formation water has a direct impact on rock wettability by changing the charge of rock surface, and H^+ or OH^- could weaken the adsorption of fluorochemicals due to electrostatic repulsion, especially for these charged fluorosurfactants. Cationic fluorosurfactants tend to adsorb onto negatively charged surfaces, while positively charged surfaces attract fluorosurfactants with negative charge. Wu et al. [106] investigated the influence of pH value on a gas-wetting surface prepared by fluorosurfactant, finding that calcite with positive charge tends to bond with cationic fluorosurfactant if the pH value of the formation water is greater than 9. Karandish et al. [107] reported that the anionic fluorosurfactant Zonyl UR exhibited a better affinity to the solid surface when the pH value of the solution was approximately 2; rock wettability could be changed from strongly liquid-wetting to intermediate gas-wetting under acidic conditions. Jin et al. [87] explored the effect of pH value on the performance of fluoropolymers, and found that the rock surface could remain intermediate gas-wetting if the pH value of the solution was in the range of 5 to 7, as shown in Figure 8. Therefore, the adsorption of fluorochemicals on the rock surface would be tunable by adjusting the pH value of the solution, and the C-F bonds on fluorochemical would remain stable under the peracid or peralkaline condition.

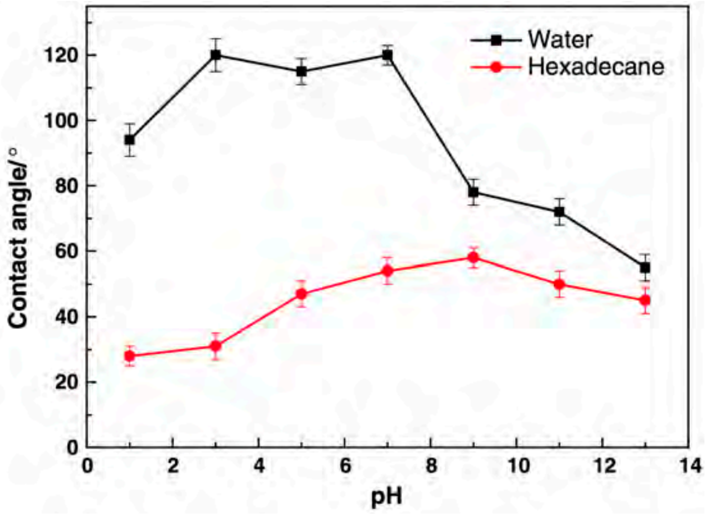

Figure 8. Impact of pH in the performance of fluoropolymer. Reproduced with permission from [87].

4.3. Salinity

Inorganic ions in aqueous condensate may derive from formation water and fracturing water, and high salinity of the gas-condensate reservoir often increases the difficulty of their development, such as through blockage induced by salt deposition, and destruction of fluorochemical stability by salt, resulting in colloidal coagulation. Tweheyo et al. [108] investigated the influence of salinity on the wettability of reservoir rock, and found that divalent inorganic ions, such as Ca^{2+}, Mg^{2+}, and SO_4^{2-}, had the potential to change rock wettability to water-wet at high temperature. However, the multivalent inorganic ions could impose compression of the electrical double layer (EDL) of fluorochemical molecules when exposed to formation water with high salinity. In a high-salinity solution, fluorochemical molecules tend to develop a coiled structure due to the electrostatic repulsion between the charged chain and inorganic cations, leading to a colloidal agglomeration [109]. Safaei et al. [110] investigated the effect of salinity on gas-wetting of the core surface, and found that the contact angles of water and oil decreased with increasing concentration of salts, and the mixture of salts had a more pronounced effect on the gas-wetting of the rock surface than did salt alone, as shown in Figure 9. Generally, multivalent inorganic cations (Al^{3+}, Fe^{3+}) impose a more notable influence in the performance of fluorochemicals than low-valent inorganic cations [87], meaning that the gas-wetting of rock becomes weaker in a solution with a high concentration of multivalent inorganic cations. A possible reason for this phenomenon is that the ionic strengths of multivalent inorganic cations are distinctly higher than those of low-valent inorganic cations under equal concentration. Furthermore, there might exist competitive adsorption between inorganic ions and fluorochemical molecules on the rock surface [111]. The cations could adsorb on the negatively charged rock, and then form an electric double layer that is unfavorable for the adsorption of positively charged fluorochemicals.

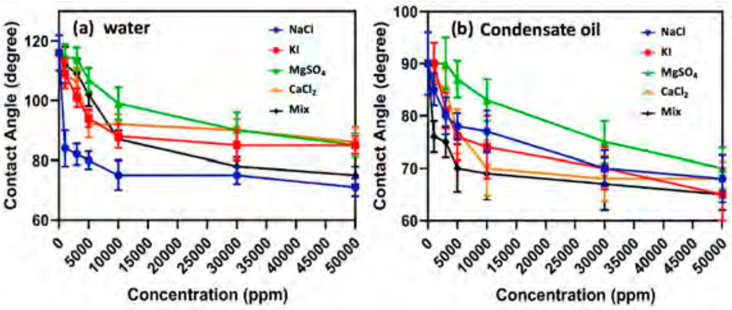

Figure 9. Impact of salinity on the performance of fluoropolymer. Reprinted with permission from [110], copyright © 2019 Elsevier B.V.

4.4. Zeta Potential

Most gas-condensate reservoirs are composed of carbonate, and the zeta potential of carbonate is also a vital parameter that determines gas deliverability. The potential determining ions, such as calcite and sulfate ions, can directly influence the water film thickness between condensate and rock by changing the surface charge of the carbonate rock, further affecting the rock wettability [111]. Xie et al. [112] investigated the effect of the expansion of the electric double layer on oil recovery, finding that wettability alteration could be induced by elevating the repulsive forces between water and rock interface. A recent study suggested that combinations of potential determining ions could be more pronounced in wettability alteration compared to ions alone, and sulfate ions are necessary for wettability alteration by calcite ions [113]. Saboori et al. [114] studied the effects of nanofluid potential on gas-wetting, and found that the liquid saturation decreased after treatment with nanofluids with high zeta potential. Ahmadi et al. [115] prepared gas-wetting $CaCO_3$ nanoparticles, which were able to remediate the condensate blockage by gas-wetting alteration under positively charged conditions. Therefore, the zeta potentials of ions are closely associated with gas-wetting alteration, and the combination of potential determining ions and fluorochemicals could be a promising approach for mitigating the liquid-blockage.

5. Effects of Fluorochemicals on Fluids in Porous Media

Reservoir wettability is one of the vital factors that control the distribution and flow behavior of fluids in porous media [116]. The adsorption of fluorochemicals affects the fluid saturation in porous media, and then redistributes the fluid in the pore and throat. When considering a strongly gas-wetting system, gas functions as the wetting phase, and tends to occupy small pores with higher capillary forces, while the non-wetting phase (water or oil) would be distributed in the larger pores with lower capillary forces. This fluid distribution in porous media is most energetically favorable because it lowers the total energy of the system [116–118]. Consequently, the liquid-blocking effect can be relieved due to the improvement of the flow efficiency of water and oil.

5.1. Effect on Liquid Saturation

Fluid in the liquid-blocking region mainly consists of water and condensate, which could instantaneously be imbibed into the capillary and block the flow channels for gas. Fluorochemicals can reduce water saturation by promoting the flow efficiency of trapped water. However, it is a great challenge to accurately characterize the influence of wettability alteration on liquid saturation in pore throat. Freedman et al. [119] proposed an improved nuclear magnetic resonance method for measuring liquid saturation, by which the diffusion-free brine and oil distributions in saturated rocks can be accurately measured without causing damage to the core sample. A featured way of measuring the liquid saturation in a gas-wetting micro-model was suggested in [32], and the principle of this method is to calculate the pixel number of water and oil before and after gas-wetting alteration, respectively. This method has the advantages of high accuracy and continuous measurement compared with the previous methods, and could be a promising candidate for quantitively evaluating the effect of gas-wetting on liquid saturation.

5.2. Effect on Flow Behavior in Porous Media

5.2.1. Detachment

Detachment is a phenomenon in which the air–solid interface of liquid is replaced by a liquid–solid interface. The movement of a liquid droplet on a gas-wetting surface is different from that on a liquid-wetting surface, and the detachment of liquid droplets from surfaces with varying wettability is a critical point in improving flow efficiency. Zhu et al. [120] simulated the dynamic detachment of water droplets in a two-dimensional tube, and found that the pore structure and droplet volume were vital factors affecting the detachment efficiency of the water droplets. Jin and Wang [32] studied the detachment of water droplets on a super gas-wetting pore wall, and discovered that decreasing the resistance force of liquid on the rock surface was key to mitigating the liquid-blocking effect; the lower the resistance force, the greater the detachment efficiency of the liquid. Figure 10a shows the detachment of liquid droplets in a liquid–liquid–rock system; gas-wetting nanoparticles can impose a structural separation pressure over the junction of liquid–liquid–rock system, forcing the liquid phase to detach from the solid surface, leading to an increase in oil recovery. Figure 10b shows the distribution of fluid in liquid-wetting porous media. Figure 10c shows that the contact angle of a water droplet on a gas-wetting pore wall is about 125°; this droplet detaches easily under the interaction of displacing force compared with that on a liquid-wetting surface. It is worth noting that the detachment efficiency of the liquid droplet is proportional to the migration efficiency of gas in the liquid-blockage area. Figure 10d shows a sketch of a capillary rise test; the tube can be recognized as gas-wetting when the imbibition level of liquid in the tube is negative ($h < 0$). Then, the capillary force can be considered to be a displacing force for liquid, as can be observed in the lower part of Figure 10e. However, for liquid in a liquid-wetting tube, the capillary force acts as the resistance force when the liquid intends to move, as shown in the upper part of Figure 10e. Hence, the flow behavior of fluid in channels can be tuned through gas-wetting alteration by fluorochemicals [121]. Figure 10f represents the liquid levels in a gas-wetting capillary tube, a sharp reduction in liquid level can be observed after gas-wetting alteration, the calculated contact angles of water and oil are more than 90°.

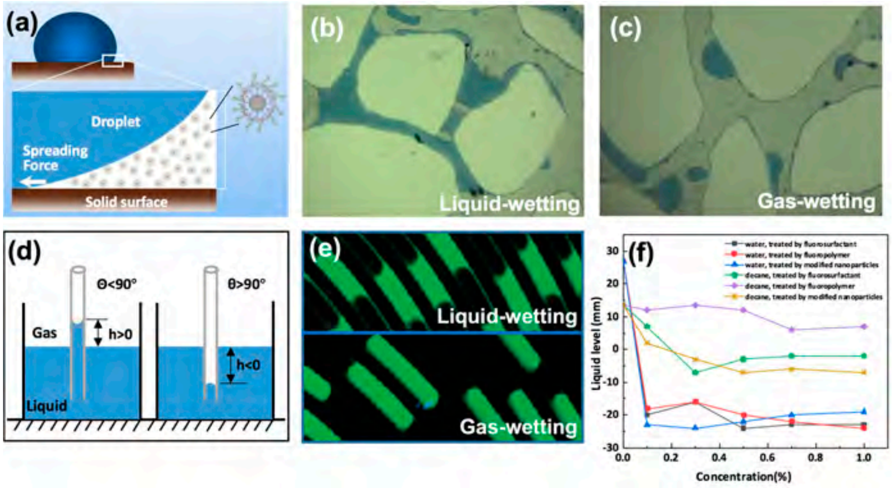

Figure 10. The movement of fluids in porous media and capillary: (**a**) detachment of liquid droplet in a liquid–liquid–solid system; (**b**) water in a pore throat with liquid-wetting; (**c**) water in a pore throat with gas-wetting (Reprinted with permission from [32]); (**d**) sketch of capillary rise test; (**e**) liquid in capillary before and after being treated with fluoropolymer, adapted with permission from [121], Copyright © 2011, American Chemical Society; (**f**) the liquid levels in a gas-wetting tube. Reproduced with permission from [94], Copyright © 2016 Elsevier.

5.2.2. The Transition of the Liquid Bridge

The liquid bridge refers to the liquid trapped in a multiphase flow system where the neighboring pore throats can be connected by small volumes of encountered liquid, which can tremendously confine the gas flow in the wellbore region, leading to a sharp decline in gas production. Generally, the larger the contact surface between the droplet and the solid, the greater the viscous resistance required for its movement. Figure 11 demonstrates the transition of a liquid bridge in the pore throat; the liquid bridge can transform from a concave shape (large contact area) to a convex shape (small contact area) after gas-wetting alteration, and an obvious decline in liquid saturation can be observed as the liquid bridge transition occurs. Therefore, the capillary force in the pore throat switches from resistance force to displacing force after gas-wetting alteration, which can substantially accelerate the migration efficiency of the liquid bridge [122]. The efficient transition of the liquid bridge can effectively reduce the saturation of the discontinuous phase in the liquid-blocking region. Additionally, the pressure difference between the two sides of the liquid bridge also has an impact on the transition of the liquid bridge, which has a close relationship with the geometry, contact angle, and volume of the liquid bridge.

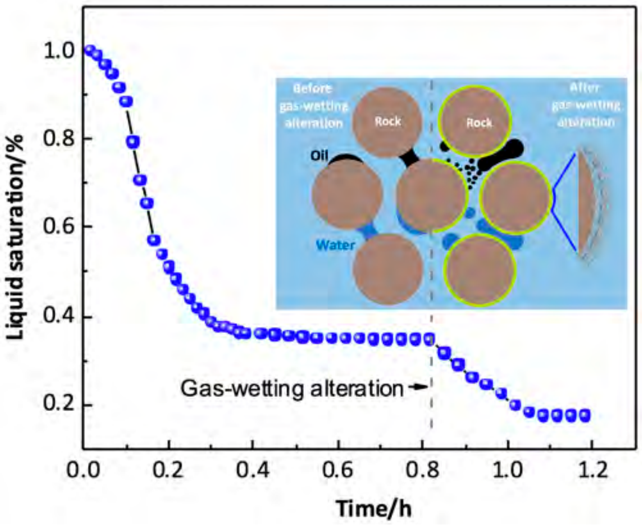

Figure 11. Liquid bridge transition in the pore throats with varying wettability. Adapted with permission from [86], Copyright © 2019, American Chemical Society.

5.3. Gas-Wetting Model

Both the Wenzel model and the Cassie-Baxter model are classical theories used to describe the wetting regime of a solid surface. However, the above models are subject to limitations when it comes to gas-wetting. The liquid phase can only wet the upside pillars on a solid surface, and cannot enter the bottom regions of the pillars, which are occupied by air due to the high capillary force. Therefore, the bottom regions remain non-wettable because of the existence of numerous cavities on the rock surface; hence, the wettability model for gas-wetting can be regarded as a complex of the Wenzel model and the Cassie-Baxter model, as shown in Figure 12a,b. It is worth noting that the movement of liquid on a gas-wetting surface is also different from that on a water-wet or oil-wet surface. Hao et al. [123] investigated the movement of liquid droplets on a superhydrophobic surface under airflow, and found that the advancing contact angle of the droplet continuously increased, and the wetting front of the liquid contacted the neighboring pillar during detachment. Given this reality, it is reasonable to conclude that the wetting regime of liquid droplets could continuously switch between the Wenzel regime and the Cassie-Baxter regime when they move on the gas-wetting surface under external force, as shown in Figure 12c.

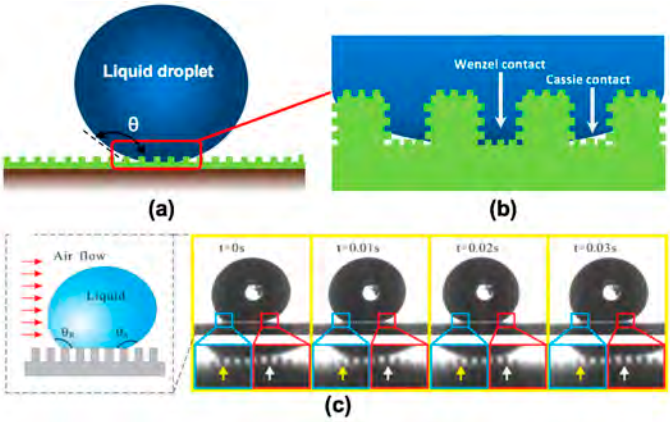

Figure 12. The movement of water on a solid gas-wetting surface: (**a**) the wetting regime of gas-wetting; (**b**) the gas-wetting model consists of the Wenzel model and the Cassie-Baxter model (reproduced with permission from [86], Copyright © 2019, American Chemical Society); (**c**) dynamic liquid on a solid surface with hydrophobicity. (Reproduced with permission from [123], Copyright © 2013, American Chemical Society).

6. Outlook/Future

Natural gas constitutes more than 25% of global energy demand, and a further increase can be predictable. Gas-condensate reservoirs exhibit complex couplings between multi-phase flow, interfacial behavior, and fluid distribution, and more proactive approaches are needed to bear the responsibility of improving gas deliverability. Fluorochemicals are well known for their excellent hydrophobicity and oleophobicity under harsh conditions, which can improve flow efficiency by gas-wetting alteration; surface modification of nanomaterials by fluorochemicals also is a versatile approach for enhancing the degree of gas-wetting. The morphologies of fluorochemicals and modified nanoparticles can be tuned to improve flow efficiency. There have been numerous studies focused on the synthesis and application of cost-effective fluorochemicals, and environmental protection with respect to fluorochemicals has also been one of the biggest concerns for the industry, since fluorine emissions during the petroleum refining process would devastate the ecosystem. Additionally, more accurate methods for evaluating the gas-wetting of rock under reservoir conditions are needed. Further research with respect to the flow mechanism in the pore throat after gas-wetting alteration by fluorochemicals can be anticipated.

7. Summary

This review provides an overview of gas-wetting alteration and the mechanism by which it improves flow efficiency. The conclusions can be drawn as follows:

(1) The liquid-blocking effect occurring during the development of the gas-condensate reservoir has aroused wide attention because of its severe damage; gas-wetting alteration by fluorochemicals could be regarded as a promising remediation approach;
(2) The methods for evaluating the gas-wetting of reservoir rock were summarized; the factors that affect gas-wetting were investigated;
(3) Varying sizes and kinds of nanomaterials can be modified by fluorochemicals, the mechanisms of fluorochemicals adsorption layer with varying surface morphologies were illustrated; the surfaces with more air cavities tend to exhibit stronger gas-wetting;
(4) The flow behavior of the fluids in a gas-wetting pore throat is distinctly different from that in a liquid-wetting pore throat. The wetting regime of the solid surface with gas-wetting might be a complex of the Wenzel regime and the Cassie-Baxter regime.

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Fluorosurfactants in Enhanced Oil Recovery

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Abstract: Fluorosurfactants are effective in a variety of Enhanced Oil Recovery (EOR) techniques including (i) improving subterranean wetting, (ii) increasing foam stability, and (iii) modifying the surface properties of the reservoir formation. While fluorosurfactants have been used in gas and oil exploration for four decades, the increased demand for petroleum and the greater understanding of the benefits of fluorosurfactants have led to growing acceptance for fluorosurfactants throughout the petroleum industry. This mini-review summarizes the published research for fluorosurfactants in EOR from 1977 to 2007. The references in this mini-review are mostly patents (*vs* peer reviewed articles) and laboratory models of the benefits of fluorosurfactants in EOR (*vs* actual oil and gas recovery experiments). This summary of the published reports on fluorosurfactants in EOR provides petroleum scientists and engineers an overview of this emerging technology.

Keywords: Fluorosurfactant, enhanced oil recovery, foam, wetting, petroleum.

INTRODUCTION

Petroleum is the most critical energy source in the world, especially for transportation. In 2008, the U.S. Department of Energy projected worldwide consumption of "liquids and other petroleum grows from 83.6 million barrels oil equivalent per day in 2005 to 95.7 million barrels per day in 2015 (+14%) and 112.5 million barrels per day in 2030 (+35%)" [1]. While estimates vary, the peaking of worldwide conventional oil production is a serious concern that has perhaps already taken place or will occur within the next few decades [2]. The pressures of increasing oil demand, limited proven oil reserves, and forecasts for tightening oil supply are driving the need to maximize the extraction of the Original Oil-In-Place (OOIP) for every reservoir, which is accelerating the development of Enhanced Oil Recovery (EOR) technologies. The presence of many interfaces and the complexity of the physico-chemical and geological characteristics of the reservoirs make EOR an immense scientific and technical challenge [3].

The production of crude oil and gas occurs in three distinct phases [4]. Primary Oil Recovery combines the natural pressure of the reservoir with pumping equipment to bring the oil to the surface, which typically produces only up to about 10% of the OOIP. In Secondary Oil Recovery, water or gas (such as natural gas, carbon dioxide, and air) is injected into the reservoir using pressure to drive the oil to a wellbore, recovering an additional 20% to 40% of the OOIP. Tertiary Oil Recovery (also known as EOR or Improved Oil Recovery) uses one or more sophisticated techniques including chemical flooding, thermal recovery, and gas injection to recover up to an additional 60% of the OOIP. Thermal techniques normally employ steam to reduce the viscosity of the oil, thus improving its flow. Chemicals used in EOR include polymers, surfactants, foaming agents, acids, alkalines, and solvents [5]. The gases successfully used in EOR include nitrogen, carbon dioxide, natural gas, and flue gas. Many fluid/rock interactions affect EOR including adsorption, cation exchange, precipitation-dissolution, capillary phenomena, wetting, and dispersion [6].

Surfactants are widely used in oil recovery for particle dispersion, emulsion stabilization, foam generation, reservoir wetting, and many other applications [7]. The use of fluorosurfactants is a recent but growing trend due to (i) the exceptional hydrophobic and oleophobic nature of the perfluoroalkyl and perfluoroalkyl ether groups, (ii) the effectiveness of fluorosurfactants at extremely low concentrations, and (iii) the availability of anionic, cationic, nonionic, and amphoteric fluorosurfactants which can modify surfaces and interfaces better than conventional hydrocarbon surfactants [8]. The variety of choices of fluorosurfactants allows for compatibility with nearly any formulation including water-in-oil emulsions, oil-in-water emulsion, detergents, foams, etc. The bond strength of the carbon-fluorine bond in perfluoroalkyl and perfluoroalkyl ether groups has been demonstrated as the key to remarkable overall stability for fluorochemicals and fluoropolymers. Commercially available fluorosurfactants provide exceptional wetting, levelling, emulsifying, foaming, or repellency characteristics in a wide range of industrial and consumer products [9].

IMPROVED SUBTERRANEAN WETTING

Fluorosurfactants possess a combination of excellent chemical and thermal stability, and wetting ability. Table **1** shows these characteristics of fluorosurfactants with their exceptionally low aqueous surface tension (even lower than alcohol-water mixtures) being unaffected by 20 hours at 100°C in either KCl or HCl [10]. Complete drainage of aqueous KCl containing fluorosurfactants through sandpacks or sandstone was attributed to these low surface tension values overcoming the capillary forces commonly seen in underground oil and gas reservoirs. The choice of the hydrophilic portion of a fluorosurfactant was critical to minimize

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its adsorption to the formation and loss of wetting effectiveness. Anionic and nonionic fluorosurfactants demonstrated significantly less adsorption to Oklahoma No. 1 sand than cationic or amphoteric fluorosurfactants. The adsorption of any particular fluorosurfactant to a solid matrix varied considerably depending on temperature, liquid phase composition, and the chemistry of the simulated formation. Concerns about capillary blockage due to adsorption of the fluorosurfactant to the formation were examined using coreflow studies with low-permeability sandstone cores. At 75ºC and 6850 kPa of nitrogen, essentially no difference was observed in initial flow rate with or without a cationic fluorosurfactant in 2 wt% KCl.

Nonionic fluorosurfactants enhanced the oil recovery of waterflooding due to their benefits of enhanced wetting, low surface tension, and low interfacial tension. Using a mixture of 10% ASTM oil No. 3 and 90% Ottawa standard 20-30 mesh sand to simulate waterflooding in the laboratory, hydrocarbon surfactants gave between 8% and 52% oil recovery, while nonionic fluorosurfactants gave between 10% and 87% oil recovery. Blends of hydrocarbon surfactants and nonionic fluorosurfactants gave between 12% and 78% oil recovery [11].

Cationic fluorosurfactants, when combined with cationic and nonionic hydrocarbon surfactants in water, brine, or various concentrations of aqueous HCl provided improved foaming, better silt suspension, and enhanced wetting for treating subterranean formations, important predictors of the effectiveness of acidizing treatments [12]. A blend of hydrocarbon surfactants containing only about 10 ppm of cationic fluorosurfactant lowered the surface tension of aqueous HCl (ranging from 3 to 28 weight percent HCl in both fresh acid and simulated spent acid containing calcium carbonate) to between 18 to 24 mN/m.

Acid fracturing is a well stimulation technique that injects aqueous HCl or HF (typically 3 weight percent to 28 weight percent acid) into the well at high pressures causing the porous media to fracture and release gas and oil for recovery. Surfactants are mixed with these acids to increase their wetting of the hydrophobic carbonate surfaces in the reservoir. When less than 30 ppm of cationic fluorosurfactants were added to mixtures of aqueous acid and hydrocarbon surfactant, the surface tension of these aqueous acids dropped to between about 19 and 24 mN/m [13]. Similar reductions in surface tension and improved wetting were observed when fluorosurfactants were added to brine solutions used for non-acid fracturing. A formulation containing hydrocarbon surfactants and a cationic fluorosurfactant reduced the surface tension of a solution of 8 weight percent sodium chloride and 2.5 weight percent calcium chloride to 22.8 mN/m compared to 74.3 mN/m without the addition of the fluorosurfactant and hydrocarbon surfactants.

For Thermal EOR, the choice of surfactant and pH control were found to be critical to achieve the desired low surface tension in the steam condensate necessary for effective recovery of the OOIP [14]. Unless sufficient fluorosurfactant condensed in the steam/gas phase, the reduction of surface tension would be insufficient. Hydrocarbon surfactants or inappropriate pH control for fluorosurfactants gave steam condensate with relatively high surface tension values of between 47 and 51 mN/m. But with pH less than about 11 in the liquid phase, nonionic or anionic fluorosurfactants were able to accumulate in the steam/gas phase and to lower the surface tension values in the steam condensate to between 22 and 25 mN/m.

In non-aqueous systems, fluorosurfactants have improved the wetting and emulsion stability of hydrocarbons in liquefied CO_2 formulations for fracturing fluids [15]. Both labstock diesel and Frac Oil 200^{TM} were successfully emulsified in liquid CO_2 with hydrofluoroether surfactants to produce a fracturing fluid with increasing stability when subject to shear. Fluorosurfactants also improved emulsion stability in multiphase systems of perfluoroethers used for drilling, completion, or workover fluids [16]. High fluid density and thermal stability are the essential properties of liquid fluorinated compounds which make them suitable as the continuous phase of well fluids. Fluorosurfactants stabilized the brine-in-perfluoroether emulsion which can contain other organic materials, minerals, clays, and inorganic salts. Examples of stable formulations ranging from 88% to 13% fluorinated liquid by volume, with the remainder barite, calcium carbonate, or saturated calcium chloride brine were demonstrated.

INCREASED FOAM STABILITY

For foam injection EOR, fluorosurfactants have the unique benefit to generate foam that is stable in contact with the crude oil, while imbibing and transporting the oil through the subterranean formation. Three types of oil-foam interactions are contrasted [17]. In Type A foams, oil will neither spread over nor enter the surface of foam. In Type B foams, oil will enter but not spread over the surface of foam. In Type C foams, oil will enter the surface of foam lamellae, then spread over the lamellae surfaces and destabilize the foam. Type B foams resulted in increased oil recovery by reducing and controlling the mobility of the foam in the underground formation. While brine alone (waterflooding) recovered 56% of the OOIP from a Berea sandstone saturated with crude oil, the Type B foam containing hydrocarbon and fluorinated surfactants recovered 68% of the OOIP. The higher oil recovery for Type B foams was attributed to the "oil-imbibing and transporting properties of Type B foams".

Table 1. Surface Tension and Stability of Fluorosurfactants in Aqueous KCl or HCl

Surface Tension (mN/m)	No Fluorosurfactant	Cationic Fluorosurfactant	Nonionic Fluorosurfactant	Anionic Fluorosurfactant	Amphoteric Fluorosurfactant
2 wt% aqueous KCl	73	18	21	17	18
2 wt% aqueous KCl after 20 hours at 100ºC	-	19	24	18	19
15 wt% aqueous HCl	71	18	21	16	19
15 wt% aqueous HCl after 20 hours at 100ºC	-	17	23	16	21

Betaine fluorosurfactant generated very stable foam in the presence of different alkanes or crude oils. Detailed analyses of the foam characteristics of either (i) an amphoteric fluorosurfactant or (ii) a C14-C16 sulfonate (AOS) formulation showed that only the fluorosurfactant had negative spreading coefficients for all crude oils tested, which explained the consistent stability of these foams in the presence of the oils [18]. For the betaine fluorosurfactant the Lamella number was less than one for a series of hydrocarbons from C_5 through C_{16}, indicating a Type A foam. The corresponding Lamella number and spreading coefficient for the AOS surfactant was between one and seven, and greater than zero, respectively. The betaine fluorosurfactant also gave consistently more dense foam in the presence of crude oil than the AOS foam. While both surfactants gave stable foam with the addition of methanol, only the betaine fluorosurfactant gave stable foam with low to moderate concentrations of butanol.

The addition of betaine fluorosurfactants to anionic or amphoteric hydrocarbon foaming agents improved aqueous foam stability in the presence of crude oil by up to nearly 300% at low crude oil concentrations [19]. At higher crude oil concentrations, the hydrocarbon foaming agents failed to sustain any stable foam, while the addition of fluorosurfactants continued to provide a robust foam. Coreflood foam modelling using Berea sandstone flooded with crude oil and brine showed the benefits for the blends of fluorosurfactant and hydrocarbon foaming agent in EOR. When tested at the residual oil saturation point (28% of pore volume), hydrocarbon foaming agents gave Mobility Reduction Factor (MRF is the ratio of pressure drops with *vs* without surfactant) of about 2 to 3, while blends of fluorosurfactant and hydrocarbon foaming agent increased the MRF to between 10 and 40.

Cationic, amphoteric, and betaine fluorosurfactants dramatically improved the recovery of OOIP from silica (500 micron diameter glass balls) compared to either nitrogen gas purging alone or sodium benzene sulfonate (SBS) foaming [20] (Table **2**). Photographic evidence showed that the oil bank was pushed through the silica packed cell by a stable fluorosurfactant foam front, perpendicular to the axis of the porous medium. Bi-strata porous media formed from two layers of glass balls with different diameters also showed a fluorosurfactant foam front moving simultaneously through both zones, first sweeping the oil from the more permeable zone, then clearing the oil from the less permeable layer.

Table 2. Simulated Oil Recovery from Silica

Purge	Gas Volume (Multiples of Pore Volume)	OOIP Recovery
Nitrogen only	100	50%
Sodium benzene sulfonate foam	100	100%
Cationic fluorosurfactant foam	1	100%

MODIFYING THE SURFACE PROPERTIES OF THE RESERVOIR

Water blocking occurs in gas or oil wells when water, mud, brine, or crude oil accumulates near the wellbore, resulting in reduced permeability to oil and gas, and thus reduced recovery. Water blocking was reduced when sandstone was treated with a variety of fluorosurfactants to simulate modifying the wetting characteristics of an underground gas and oil reservoir formation. Core testing on sandstone treated with fluorosurfactants showed greater brine removal and lower pressure drop across the structure due to reduced capillary pressure in the small pores, which was attributed to altered wettability of the fluorosurfactant-treated sandstone [21]. With polymeric fluorosurfactants, the sandstone was rendered durably repellent to water, which offered the best remedy to alleviate water blocking by transforming the formation from water-wet or oil-wet to intermediate-wet or gas-wet. Water contact angles on the untreated sandstone were essentially zero. After treatment with fluorosurfactants, the contact angles on the treated sandstone were greater than 90°. Water imbibition test on dry untreated sandstone compared to dry fluorosurfactant treated sandstone showed both (i) a reduction in the rate of water uptake (saturation at 1 hour for untreated sandstone *vs* more than 12 hours for fluorosurfactant treated sandstone) and (ii) a decrease in percent water imbibed at equilibrium (about 45% to 55% for untreated sandstone *vs* 15% to 30% for fluorosurfactant treated sandstone).

Cationic polymeric fluorosurfactants in methanol were used to treat sand and "…resist or substantially reduce the wetting of the surfaces by water and hydrocarbons and provided high interfacial tensions between the surfaces and water and hydrocarbons … and significantly increases the flow of hydrocarbons through capillaries or flow channels in the formations [22]." Laboratory tests showed that oil flowed through the fluorosurfactant-treated sand at a rate between 60 and 150 times faster than untreated sand. This EOR technique using fluorosurfactants was employed at a well in Moffat County, Colorado from the Fort Union Sand Formation using methanol, 0.2 weight percent C_{10-12} alcohol ethoxylates, and 0.01 weight percent of a cationic polymeric fluorosurfactant. After treatment, the gas productivity increased from 100 million cubic feet (MCF) per day to 300 MCF per day.

When used in combination with methanol hydraulic fracturing, various nonionic polymeric fluorosurfactants improved the gas permeability of methane, butane, and higher alkane blends for Berea sandstone by between 13% and 282% [23]. The benefits of the nonionic polymeric fluorosurfactants in this EOR technique could include better capillary wetting, inhibiting water blocking, delaying condensate bank formation, or modifying the wetting characteristics of the sandstone. Polymeric fluorosilane surfactants were used to durably alter the surface properties of three wettability states of Berea sandstone (water-wet, weakly water-wet, weakly oil-wet) to intermediate gas-wetting [24]. Gas recovery by oil injection for the untreated Berea sandstone was 60% at oil breakthrough compared to 80% for the polymeric fluorosilane treated sample. Total gas recovery for the untreated Berea sandstone was 80% compared to 90% for the polymeric fluorosilane treated sample. Total oil recovery with simulated water injection for the untreated Berea sandstone was 54% compared to 76% for the polymeric fluorosilane treated sample.

Laboratory studies showed that fluorosilane surfactants also provided durable changes in the wetting characteristics of calcite, marble, mica, and silica. As the chain length of the perfluoroalkyl portion of the fluorosilane surfactant increased, the rocks became less water-wet and more repellent. Brine contact angles on calcite and mica increased from about 33° and about 17°, respectively, for the untreated surfaces to between 64° and 118° for either mineral surface treated with fluorosilane surfactants [25]. Significantly altered wetting can only occur if the contact angle is greater than 90°. For carbonate cores treated with fluorosurfactants, the residual brine saturation was reduced by 25% and the gas relative permeability increased almost 160 times. These high contact angles and increased gas permeabilities are attributed to the success of fluorosurfactants in lowering the surface energy of the mineral surfaces. By reducing the water wettability of the formation, the capillaries are less blocked, pressure drops are reduced, and gas recovery is more effective.

CONCLUSION

The published patents and papers describing the use of fluorosurfactants in Enhanced Oil Recovery (EOR) show the exceptional benefits for this technology in (i) improving subterranean wetting, (ii) increasing foam stability, and (iii) modifying the surface properties of the reservoir. Technical advances and economic trends point toward the increasing use of fluorosurfactants in EOR. Future research in this field should include (a) the benefits of fluorosurfactants in EOR from more actual oil/gas formation recovery, (b) the details of fluorosurfactant recycling and recovery in EOR, (c) the impact of fluorosurfactants in EOR on the entire oil/gas recovery and refinery processes, and (d) the economics and environmental benefits of fluorosurfactants in EOR.

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US007772162B2

(12) **United States Patent**
Pope et al.

(10) **Patent No.: US 7,772,162 B2**
(45) **Date of Patent: Aug. 10, 2010**

(54) **USE OF FLUOROCARBON SURFACTANTS TO IMPROVE THE PRODUCTIVITY OF GAS AND GAS CONDENSATE WELLS**

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(73) Assignees: **Board of Regents, The University of Texas System**, Austin, TX (US); **3M Innovative Properties Company**, St. Paul, MN (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 183 days.

(21) Appl. No.: **12/185,571**

(22) Filed: **Aug. 4, 2008**

(65) **Prior Publication Data**

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Related U.S. Application Data

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C09K 8/60 (2006.01)
E21B 43/16 (2006.01)

(52) **U.S. Cl.** **507/205**; 166/305.1; 166/308.1; 166/308.4; 507/224; 507/910; 507/922

(58) **Field of Classification Search** 507/205, 507/204, 910, 922; 166/305.1, 308.1, 308.4
See application file for complete search history.

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(57) **ABSTRACT**

The present invention includes composition having a non-ionic, fluorinated polymeric surfactant, water and solvent. Embodiments of compositions according to the present invention are useful, for example, for recovering hydrocarbons from subterranean elastic formations.

21 Claims, 10 Drawing Sheets

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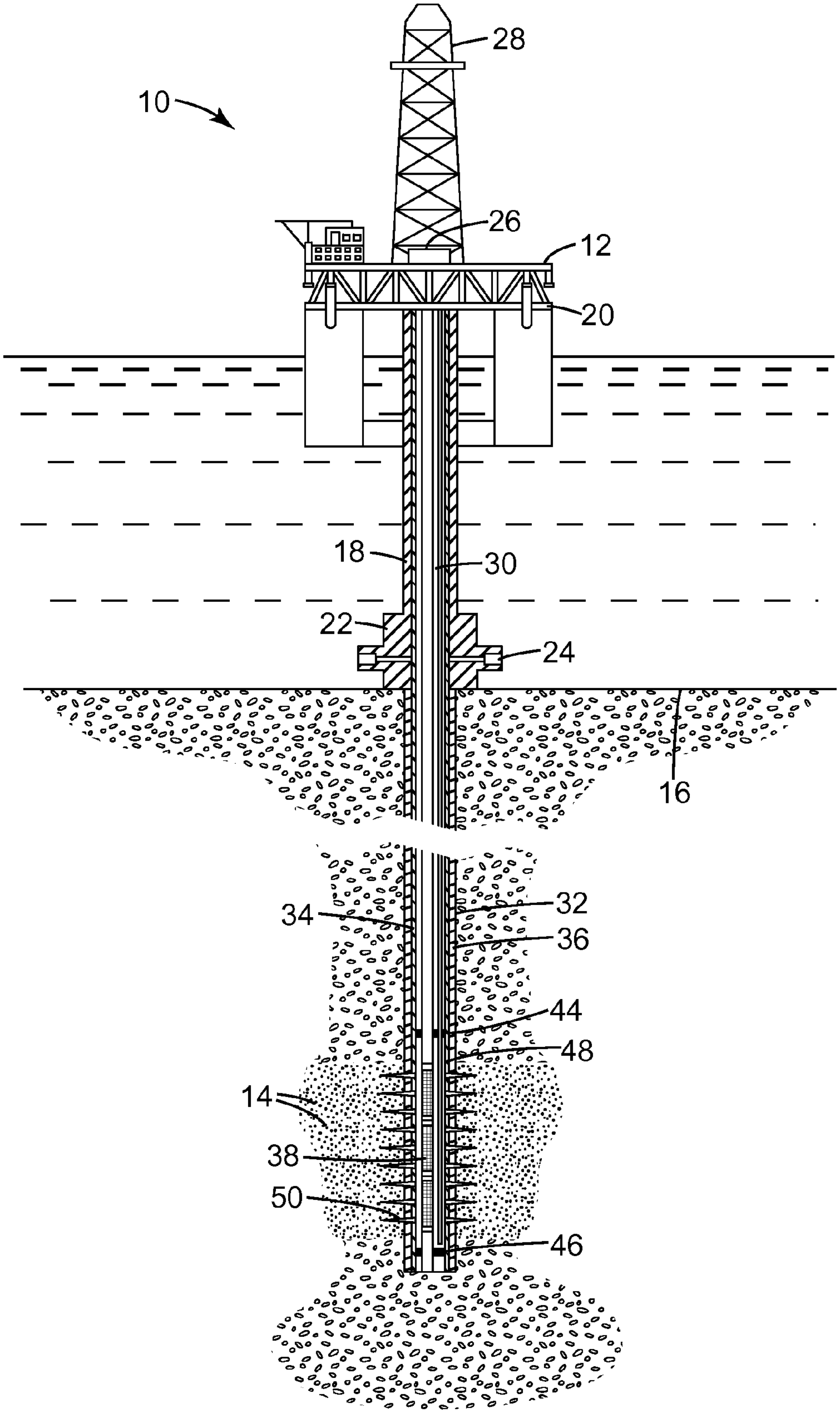


Fig. 1

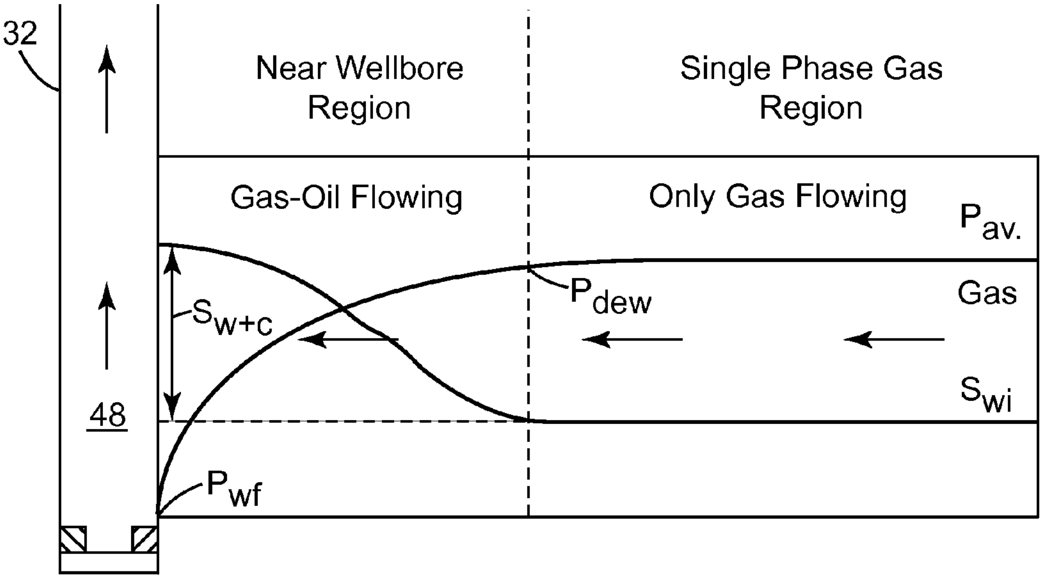

32
Near Wellbore Region
Single Phase Gas Region
Gas-Oil Flowing
Only Gas Flowing
$P_{av.}$
S_{w+c}
P_{dew}
Gas
S_{wi}
48
P_{wf}

Fig. 2

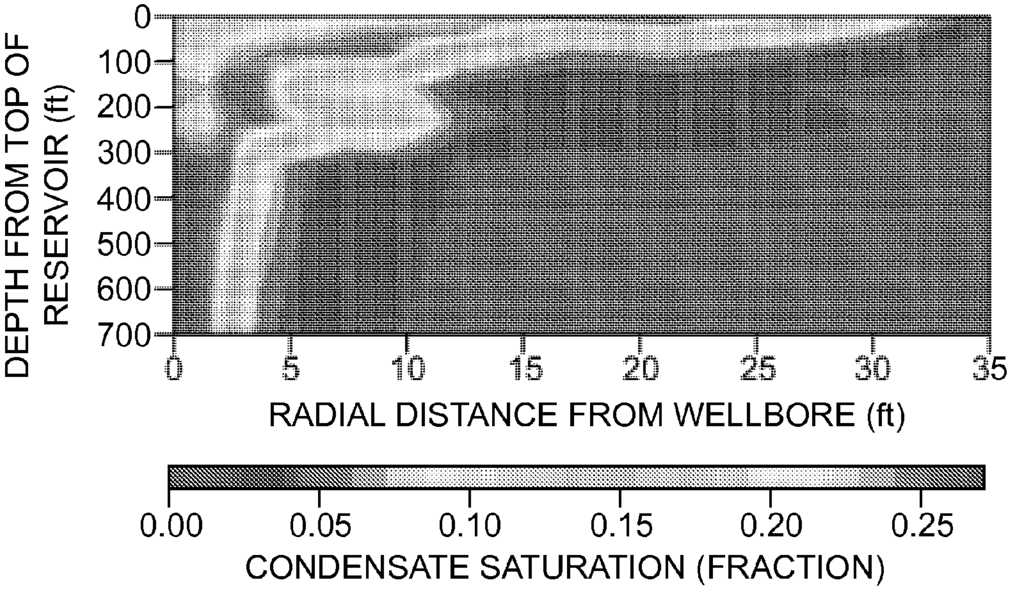

DEPTH FROM TOP OF RESERVOIR (ft)
0
100
200
300
400
500
600
700
0
5
10
15
20
25
30
35
RADIAL DISTANCE FROM WELLBORE (ft)
0.00
0.05
0.10
0.15
0.20
0.25
CONDENSATE SATURATION (FRACTION)

Fig. 3

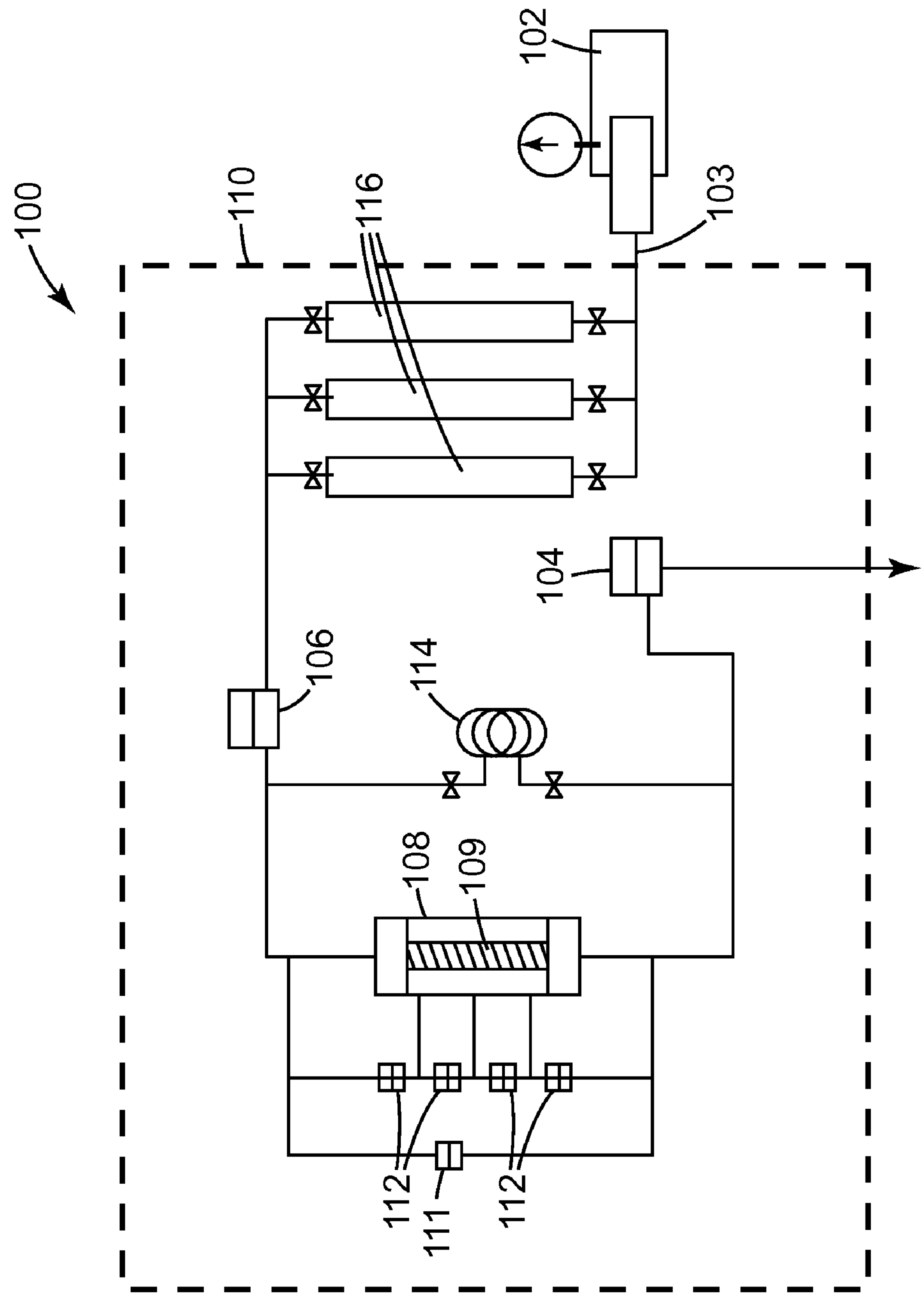


Fig. 4

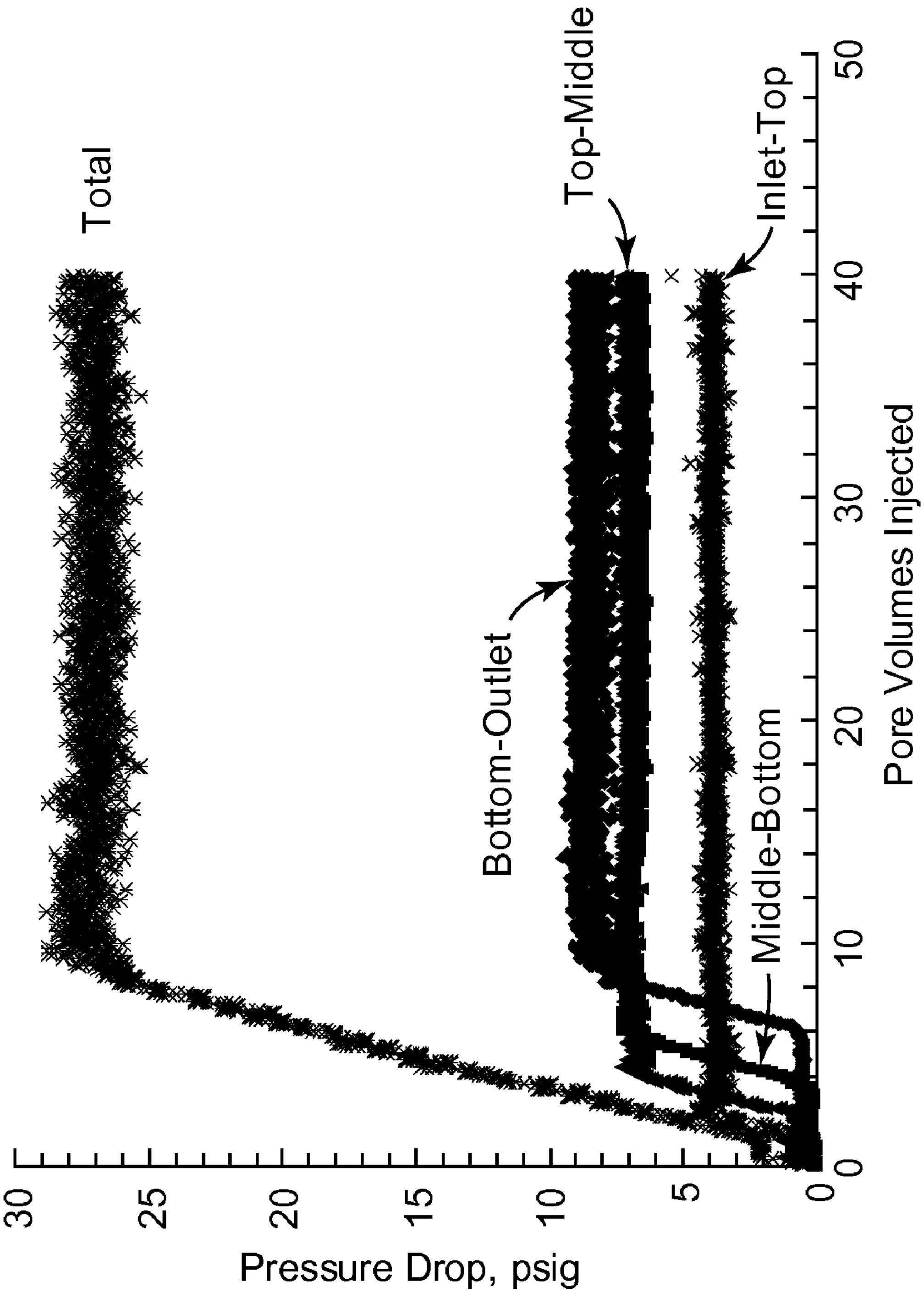
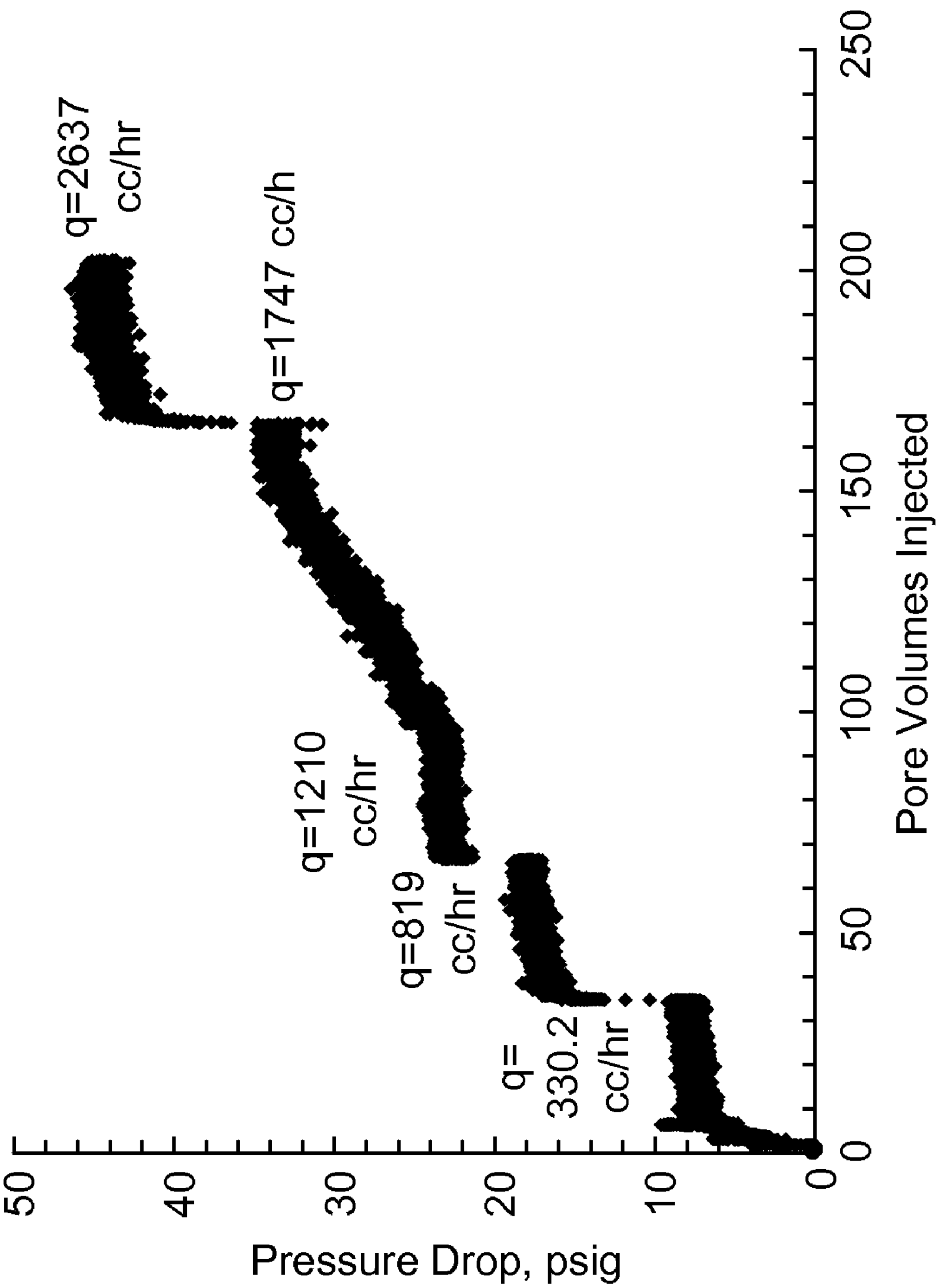

Pressure Drop, psig
30
25
20
15
10
5
0
0
10
20
30
40
50
Pore Volumes Injected
Total
Top-Middle
Bottom-Outlet
Inlet-Top
Middle-Bottom

Fig. 5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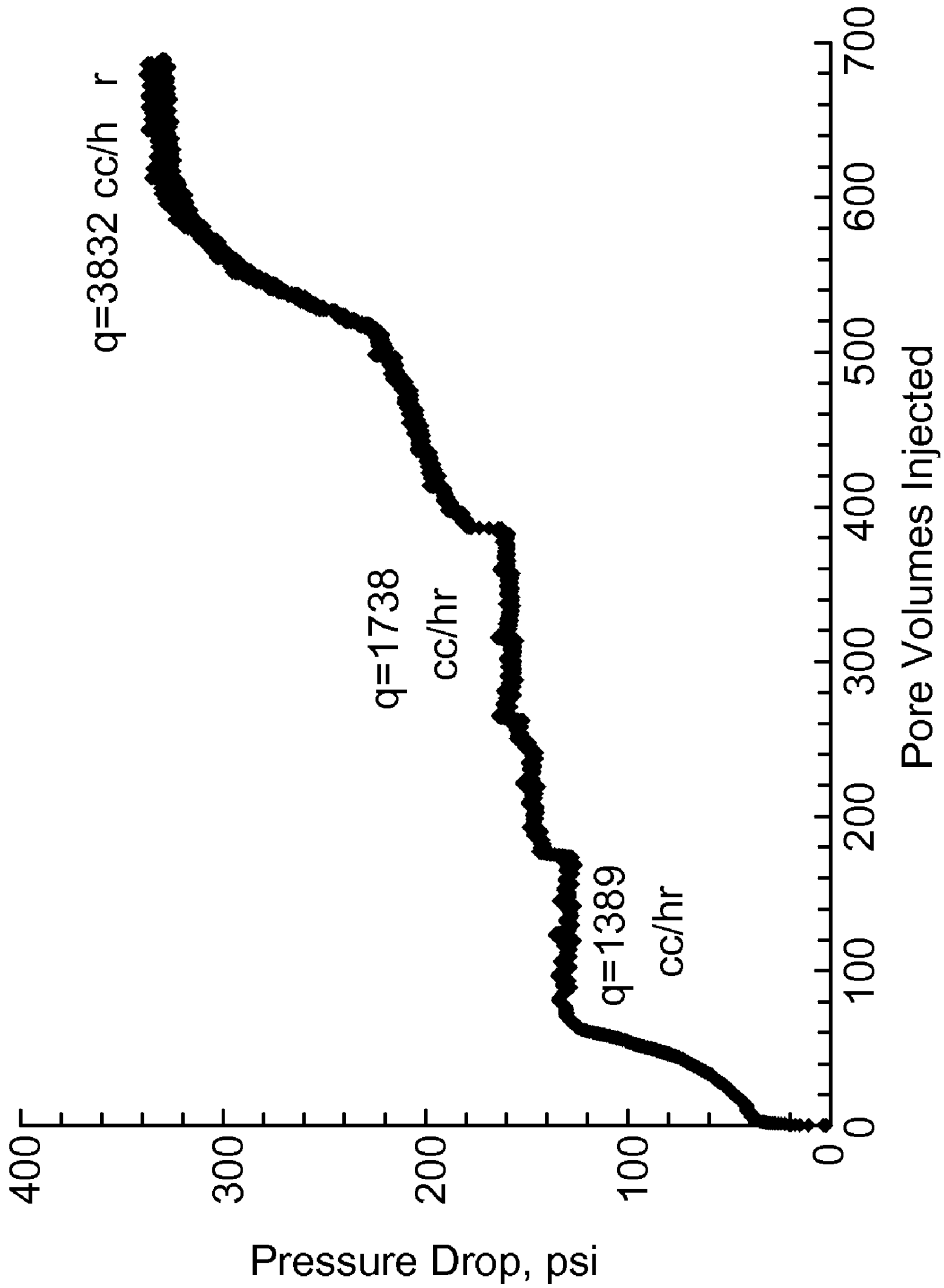
q=1210 cc/hr
q=819 cc/hr
q= 330.2 cc/hr
Pressure Drop, psig
0
10
20
30
40
50
Pore Volumes Injected
0
50
100
150
200
250

Fig. 6


Pressure Drop, psi
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300
200
100
0
0
100
200
300
400
500
600
700
Pore Volumes Injected
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q=1738 cc/hr
q=3832 cc/h r

Fig. 7

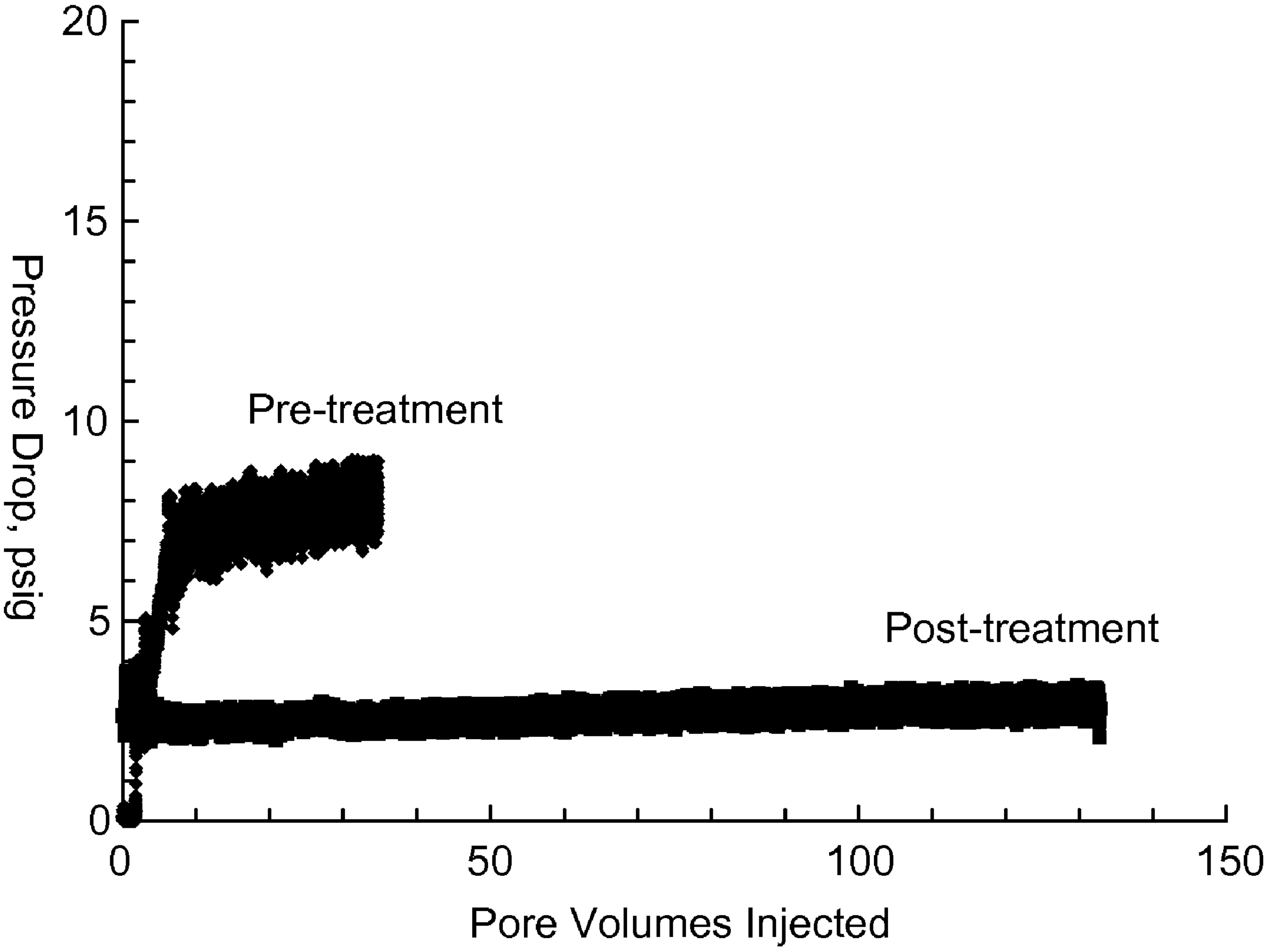
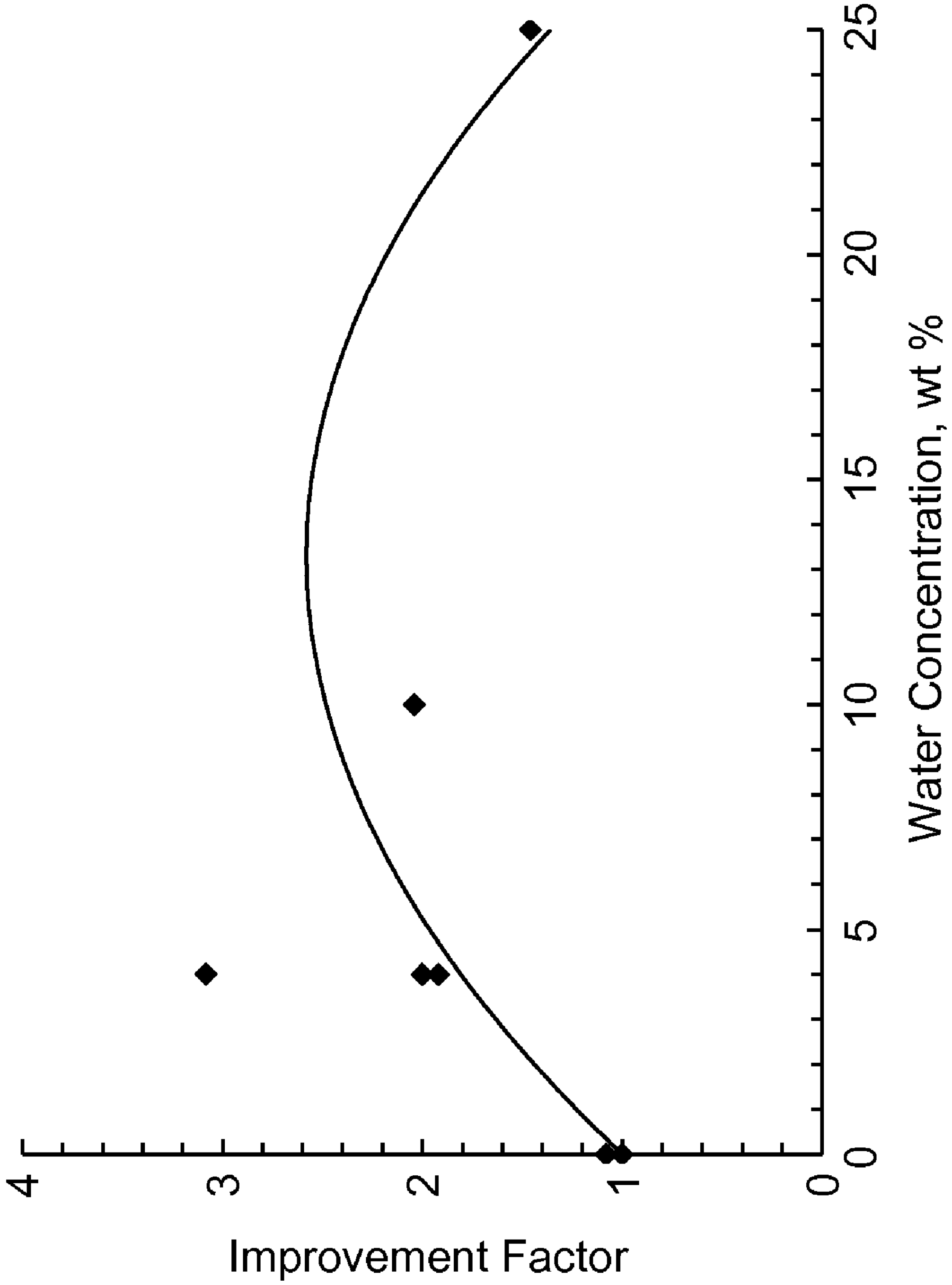

Pressure Drop, psig
20
15
10
5
0
Pre-treatment
Post-treatment
0
50
100
150
Pore Volumes Injected

Fig. 8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1
2
3
4
Water Concentration, wt %
0
5
10
15
20
25

Fig. 9

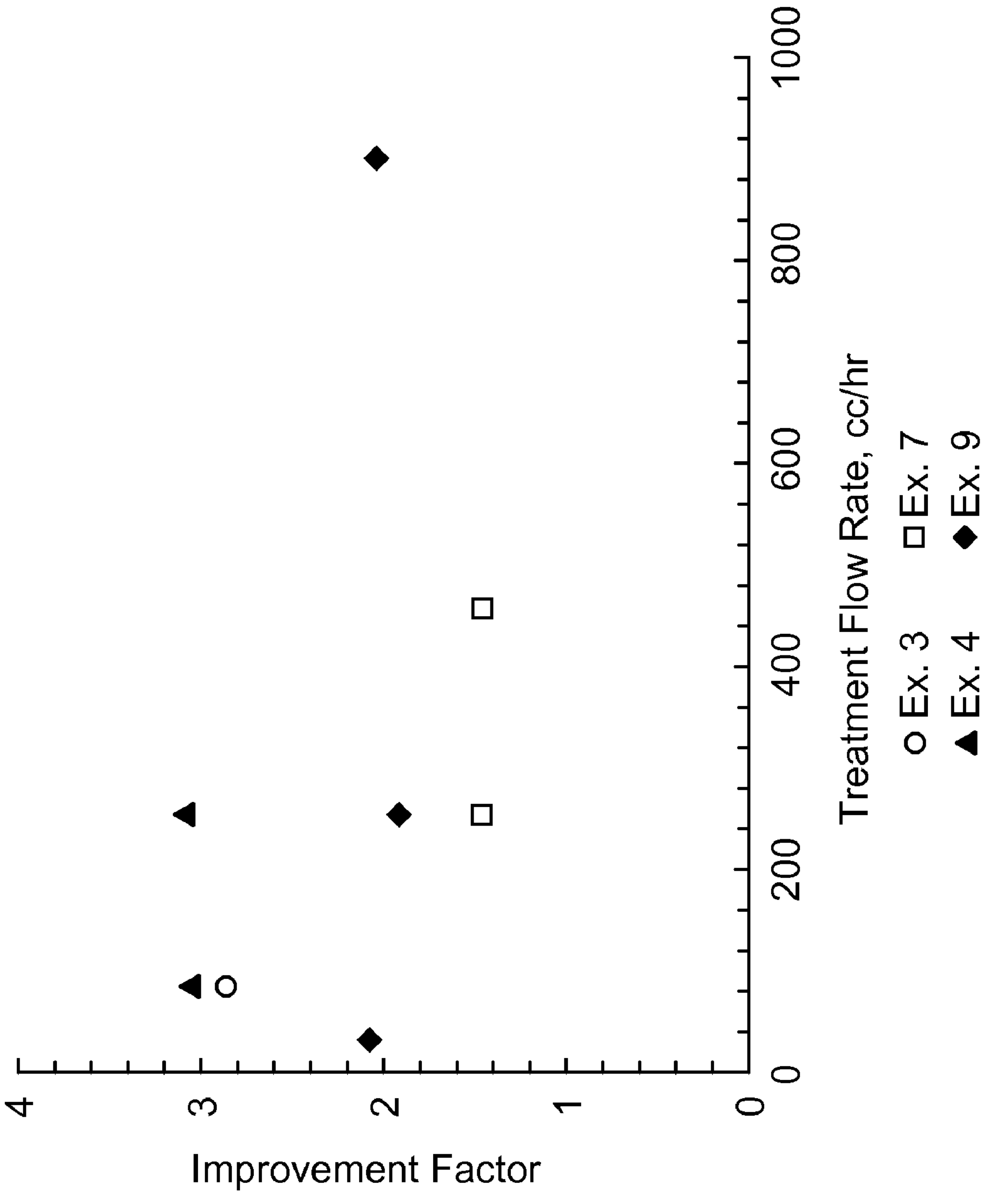

Improvement Factor
0
1
2
3
4
Treatment Flow Rate, cc/hr
0
200
400
600
800
1000
○ Ex. 3
□ Ex. 7
▲ Ex. 4
◆ Ex. 9

Fig. 10

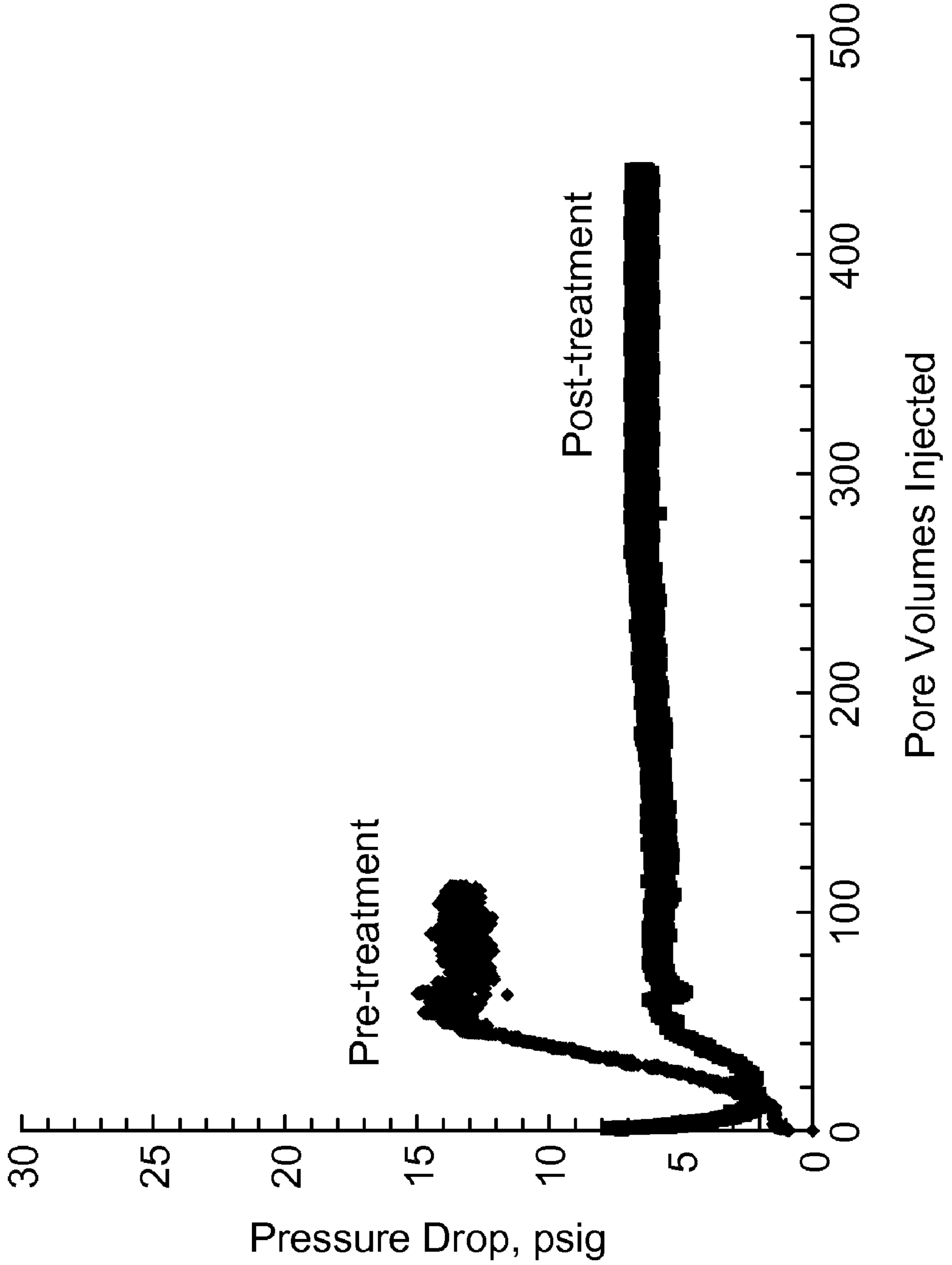

Pressure Drop, psig
0
5
10
15
20
25
30
Pore Volumes Injected
0
100
200
300
400
500
Pre-treatment
Post-treatment

Fig. 11

USE OF FLUOROCARBON SURFACTANTS TO IMPROVE THE PRODUCTIVITY OF GAS AND GAS CONDENSATE WELLS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application Ser. No. 11/390,960, filed Mar. 27, 2006, now abandoned, the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND

It is known in the subterranean well drilling art that in some gas wells, liquid hydrocarbons (condensate) can form and accumulate in the vicinity of the well. In such reservoirs (sometimes referred to as retrograde condensate reservoirs), the presence of condensate can cause a large decrease in both the gas and condensate relative permeabilities, and thus the productivity of the well decreases. In some instances, the liquid blocking the flow of gas may be both condensate and water. The water may be from the subterranean formation or from operations conducted on the well.

One solution known in the art to address the formation of the condensate is to perform a formation fracturing and propping operation (e.g., prior to, or simultaneously with, a gravel packing operation) to increase the permeability of the production zone adjacent to the wellbore. For example, a fracture fluid such as water, oil, oil/water emulsion, gelled water or gelled oil is pumped down the work string with sufficient volume and pressure to open one or more fractures in the production zone of the formation. Optionally, the fracture fluid may carry a proppant, into the fractures to hold the fractures open following the fracturing operation. Proppants provide an efficient conduit for production of fluid from the reservoir to the wellbore, and may be naturally occurring sand grains, man-made or specially engineered (e.g., resin-coated sand), or high-strength ceramic materials (e.g., sintered bauxite).

The fracture fluid is forced into the formation at a flow rate great enough to fracture the formation allowing the entrained proppant to enter the fractures and prop the formation structures apart, producing channels that create highly conductive paths reaching out into the production zone, and thereby increasing the reservoir permeability in the fracture region. Although not wanting to be bound by theory, it is believed that the effectiveness of the fracture operation is dependent upon the ability to inject large volumes of hydraulic fracture fluid along the entire length of the formation at a high pressure and at a high flow rate.

Injection of methanol into condensate-blocked wells has been used to remove both water and condensate, and restore gas productivity for a period of time that may last up to several months. Again, not wanting to be bound by theory, it is believed that methanol provides an enhanced flow period by delaying the condensate bank formation and in some instances by removing the water from the near well region.

Despite advances in addressing the formation of the condensate, there is a continuing desire for alternative and/or improved techniques for addressing the condensate and/or water blocking issue.

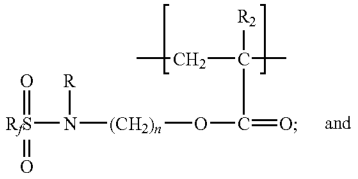
SUMMARY

Compositions and methods according to the present invention are useful, for example, for increasing production of

methane and/or gas-condensate (typically containing at least one of methane, ethane, propane, butane, hexane, heptane, or octane) from hydrocarbon-bearing clastic formations (in some embodiments, predominantly sandstone).

In one aspect, the present invention provides a composition including nonionic fluorinated polymeric surfactant, water, and at least 50 percent by weight solvent, based on the total weight of the composition, wherein the nonionic fluorinated polymeric surfactant includes:

(a) at least one divalent unit represented by the formula:



$$-\!\left[CH_2-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle R_f\!-\!S(=O)_2\!-\!N(R)\!-\!(CH_2)_n\!-\!O\!-\!C\!=\!O}{|}}{C}}\right]\!-$$

and

(b) a poly(alkyleneoxy) segment;

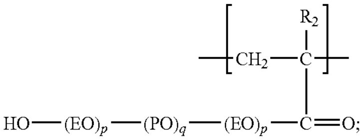
wherein

R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

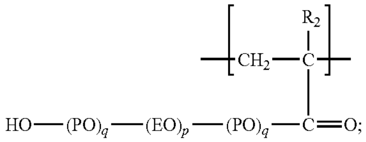
R and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms; and

n is an integer from 2 to 10.

In some embodiments, the nonionic fluorinated polymeric surfactant comprises at least one divalent unit represented by a formula selected from the group consisting of:

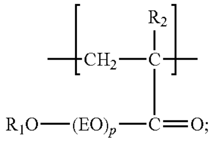


$$-\!\left[CH_2-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle HO\!-\!(EO)_p\!-\!(PO)_q\!-\!(EO)_p\!-\!C\!=\!O}{|}}{C}}\right]\!-;$$



$$-\!\left[CH_2-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle HO\!-\!(PO)_q\!-\!(EO)_p\!-\!(PO)_q\!-\!C\!=\!O}{|}}{C}}\right]\!-;$$

and



$$-\!\left[CH_2-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle R_1O\!-\!(EO)_p\!-\!C\!=\!O}{|}}{C}}\right]\!-;$$

wherein

R_1 and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

EO represents $-CH_2CH_2O-$;

PO represents $-CH(CH_3)CH_2O-$;

each p is independently an integer of 1 to about 128; and

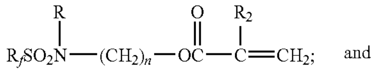
each q is independently an integer of 0 to about 55.

In some embodiments, R_f has from 4 to 6 carbon atoms. In some embodiments, R_f is perfluorobutyl. In some embodiments, the nonionic fluorinated polymeric surfactant is free of (i.e., has no) hydrolyzable silane groups.

The present invention also provides a composition including the nonionic fluorinated polymeric surfactant, a liquid vehicle including at least 50 weight percent water-miscible solvent, based on the total weight of the composition, and water, wherein the nonionic fluorinated polymeric surfactant has a solubility in the liquid vehicle that decreases with an increase in temperature.

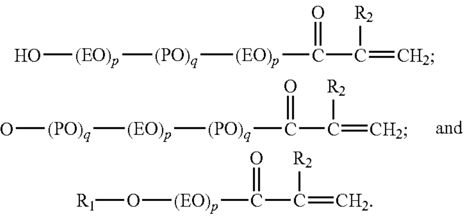
In some embodiments, the nonionic fluorinated polymeric surfactant is preparable, for example, by copolymerization of:

(a) at least one compound represented by the formula



$$\mathrm{R_fSO_2}\overset{\mathrm{R}}{\mathrm{N}}\text{—}(\mathrm{CH_2})_n\text{—}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}\overset{\mathrm{R_2}}{\mathrm{C}}=\mathrm{CH_2};\quad\text{and}$$

(b) at least one of a poly(alkyleneoxy) monoacrylate or diacrylate. In some of these embodiments, the poly (alkyleneoxy) monoacrylate comprises at least one compound represented by a formula selected from the group consisting of:



$$\mathrm{HO}\text{—}(\mathrm{EO})_p\text{—}(\mathrm{PO})_q\text{—}(\mathrm{EO})_p\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}\overset{\mathrm{R_2}}{\mathrm{C}}=\mathrm{CH_2};$$

$$\mathrm{HO}\text{—}(\mathrm{PO})_q\text{—}(\mathrm{EO})_p\text{—}(\mathrm{PO})_q\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}\overset{\mathrm{R_2}}{\mathrm{C}}=\mathrm{CH_2};\quad\text{and}$$

$$\mathrm{R_1}\text{—}\mathrm{O}\text{—}(\mathrm{EO})_p\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}\overset{\mathrm{R_2}}{\mathrm{C}}=\mathrm{CH_2}.$$

Generally, the amount of the nonionic fluorinated polymeric surfactant, water, and solvent (and type of solvent) is dependent on the particular application. In some embodiments, compositions described herein include at least 0.01 (in some embodiments, at least 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, 0.055, 0.06, 0.065, 0.07, 0.075, 0.08, 0.085, 0.09, 0.095, 0.1, 0.15, 0.2, 0.25, 0.5, 1, 1.5, 2, 3, 4, 5, or even at least 10; in some embodiments in a range from 0.01 to 10, 0.1 to 10, 0.1 to 5, 1 to 10, or even in a range from 1 to 5) percent by weight of the nonionic fluorinated polymeric surfactant, based on the total weight of the composition. In some embodiments, compositions described herein include at least 0.1 (in some embodiments, at least 0.2, 0.25, 0.3, 0.4, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, or even at least 49.99; in some embodiments in a range from 0.1 to 49.99, 1 to 40, 1 to 25, 1 to 10, 1 to 4, or even in a range from 4 to 25) percent by weight water, based on the total weight of the composition. In some embodiments, compositions described herein include at least 51, 52, 53, 54, 55, 60, 65, 70, 75, 80, 85, 90, 95, or even at least 99.89 (in some embodiments, in a range from 50 to 99, 60 to 99, 70 to 99, 80 to 99, or even in a range from 90 to 99) percent by weight solvent, based on the total weight of the composition. In some embodiments, compositions described herein include about 2 percent by weight the nonionic fluorinated polymeric surfactant, about 4 percent by weight water, and about 94 percent by weight solvent (e.g., methanol), based on the total weight of the composition.

Embodiments of compositions described herein are useful, for example, for recovering hydrocarbons (e.g., at least one of methane, ethane, propane, butane, hexane, heptane, or octane) from hydrocarbon-bearing subterranean clastic formations (in some embodiments, predominantly sandstone). In some embodiments, compositions described herein are interactive with a subterranean clastic formation under downhole conditions (e.g., conditions including a pressure in a range from about 1 bar to 1000 bars (in some embodiments, in a range from about 10 bars to about 1000 bars, or even about 100 to about 1000 bars) and a temperature in a range from about 100° F. to 400° F. (in some embodiments, in a range from about 200° F. to about 300° F.; or even about 200° F. to 250° F.)). In some embodiments, compositions described herein are interactive with a hydrocarbon-bearing geological clastic formations (in some embodiments, predominantly sandstone (i.e., at least 50 percent by weight sandstone)).

In one embodiment, the present invention provides a method of treating a hydrocarbon-bearing subterranean clastic formation (in some embodiments, predominantly sandstone), wherein the method includes injecting a composition described herein into the hydrocarbon-bearing subterranean clastic formation. In some embodiments, the subterranean clastic formation is downhole.

In one embodiment, the present invention provides a method of stimulating hydrocarbon well productivity flow from a hydrocarbon-bearing subterranean clastic formation (in some embodiments, predominantly sandstone), wherein the method includes injecting a composition described herein into the subterranean clastic formation. In some embodiments, the subterranean clastic formation is downhole.

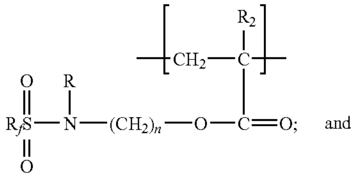
In one embodiment, the present invention provides a method of stimulating hydrocarbon flow from a hydrocarbon-bearing subterranean clastic formation (in some embodiments, predominantly sandstone), wherein the method includes injecting a composition described herein into the subterranean clastic formation and obtaining hydrocarbons therefrom. In some embodiments, the subterranean clastic formation is downhole.

In one embodiment, the present invention provides a method for recovering hydrocarbons from a hydrocarbon-bearing subterranean clastic formation (in some embodiments, predominantly sandstone), wherein the method includes injecting a composition described herein into the subterranean clastic formation and obtaining hydrocarbons therefrom. In some embodiments, the subterranean clastic formation is downhole.

Typically, the methods described herein include contacting the surface of the clastic formation with a composition described herein.

In one aspect, the present invention provides a gas-bearing clastic formation penetrated by a well bore comprising a region near the well bore treated with a nonionic polymeric surfactant, wherein the nonionic polymeric surfactant comprises:

(a) at least one divalent unit represented by the formula:



$$\mathrm{R_f}\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}}\text{—}\overset{\mathrm{R}}{\mathrm{N}}\text{—}(\mathrm{CH_2})_n\text{—}\mathrm{O}\text{—}\underset{\left[\mathrm{CH_2}\text{—}\overset{\mathrm{R_2}}{\mathrm{C}}\right]}{\mathrm{C}}=\mathrm{O};\quad\text{and}$$

(b) a poly(alkyleneoxy) segment;

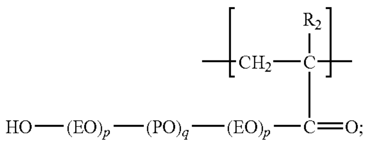
wherein

R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

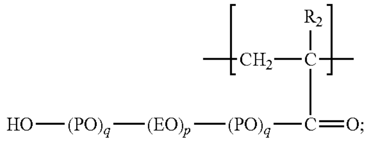
R and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms; and

n is an integer from 2 to 10.

In some embodiments, the nonionic fluorinated polymeric surfactant comprises at least one divalent unit represented by a formula selected from the group consisting of:

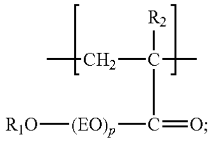


$$-\!\left[\mathrm{CH_2}-\overset{\displaystyle \mathrm{R_2}}{\underset{\displaystyle \mathrm{HO}-(\mathrm{EO})_p-(\mathrm{PO})_q-(\mathrm{EO})_p-\mathrm{C}{=}\mathrm{O}}{\mathrm{C}}}\right]\!- ;$$



$$-\!\left[\mathrm{CH_2}-\overset{\displaystyle \mathrm{R_2}}{\underset{\displaystyle \mathrm{HO}-(\mathrm{PO})_q-(\mathrm{EO})_p-(\mathrm{PO})_q-\mathrm{C}{=}\mathrm{O}}{\mathrm{C}}}\right]\!- ;$$

and



$$-\!\left[\mathrm{CH_2}-\overset{\displaystyle \mathrm{R_2}}{\underset{\displaystyle \mathrm{R_1O}-(\mathrm{EO})_p-\mathrm{C}{=}\mathrm{O}}{\mathrm{C}}}\right]\!- ;$$

wherein

R_1 and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

EO represents $—CH_2CH_2O—$;

PO represents $—CH(CH_3)CH_2O—$;

each p is independently an integer of 1 to about 128; and

each q is independently an integer of 0 to about 55.

One advantage of embodiments of the present invention is that formulations of composition described herein can be customized for a particular application. For example, the present invention provides a method of making a composition described herein, wherein the method includes:

selecting a hydrocarbon-bearing subterranean clastic formation (in some embodiments, predominantly sandstone), the clastic formation having a temperature, water content, and ionic strength;

determining the temperature, water content, and ionic strength of the hydrocarbon-bearing subterranean clastic formation;

generating a formulation including a nonionic fluorinated polymeric surfactant (such as described above) and at least one of solvent or water, the formulation based at least in part on the determined temperature, water content, and ionic strength of the hydrocarbon-bearing subterranean clastic formation, wherein the nonionic fluorinated polymeric surfactant has a cloud point when placed in the hydrocarbon-bearing subterranean clastic formation that is above the temperature of the hydrocarbon-bearing subterranean clastic formation; and

making a composition having the formulation.

Methods of using compositions described herein are useful, for example, on both existing and new wells. Typically, it is believed to be desirable to allow for a shut-in time after compositions described herein are contacted with the subterranean clastic formations. Exemplary set in times include a few hours (e.g., 1 to 12 hours), about 24 hours, or even a few (e.g., 2 to 10) days.

In one embodiment, the present invention provides a gaseous composition including methane and a thermal decomposition product of a nonionic fluorinated polymeric surfactant, wherein the thermal decomposition product includes a fluorinated organic compound. The present invention also provides a gaseous composition including methane and a product resulting from hydrolysis of a nonionic fluorinated polymeric surfactant, wherein the decomposition product includes a fluorinated organic compound. The present invention also provides a gaseous composition including methane and a poly(alkylene oxide) or derivative thereof. The gaseous compositions may include water and/or solvent (e.g., methanol).

The skilled artisan, after reviewing the instant disclosure, will recognize that various factors may be taken into account for use of the present invention including, for example, the ionic strength of the composition, pH (e.g., a range from a pH of about 4 to about 10), and the radial stress at the wellbore (e.g., about 1 bar to about 1000 bars). In some circumstances, the solvent may include, for example, one or more lower alkyl alcohols. In some embodiments of methods according to the present invention, the measured gas relative permeability of the clastic formation increases at least 2, 3, 4, 5, 10, 25, 50, 75, 100, 150, 200, 250, or even at least 300 percent and/or condensate relative permeability increases at least 2, 3, 4, 5, 10, 25, 50, 75, 100, 150, 200, 250, or even at least 300 percent as compared to the hydrocarbon flow prior to the injection of the composition (i.e., the hydrocarbon production flow just prior to when the composition was used). In some cases, the increase in hydrocarbon recovery from the clastic formation may be at least 10, 25, 50, 75, 100, 200, 300, 500, 1000 or even 2000 percent. The increased recovery may be in the form of a gas, a liquid (e.g., a condensate), or a combination thereof. The compositions and methods of the present invention will typically find particular use at or about the critical point in phase space to release, reduce, or modify a condensate blockage. One method to measure the effect of the composition on a clastic formation is to measure the increase in hydrocarbon production as a result of decreased liquid saturation or change in wettability. The present invention may even be used in clastic formations during the process of fracturing or in formations that have already been fractured and that may be at least partially oil wet, water wet, or mixed wet.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the features and advantages of the present invention, reference is now made to the detailed description of the invention along with the accompanying figures and in which:

FIG. **1** is a schematic illustration of an exemplary embodiment of an offshore oil and gas platform operating an apparatus for progressively treating a zone of a wellbore according to the present invention;

FIG. **2** is a cross-section view of an exemplary embodiment of a production zone at the wellbore next to a graph that describes the problem associated with the productivity of gas-condensate wells;

FIG. **3** is a graph that depicts a calculated near-wellbore condensate saturation;

FIG. **4** is a schematic of core flood set-up used for the Examples;

FIG. **5** is a graph that illustrates pressure drop data observed across different sections and the total length of the core as the process of condensate accumulation occurred in Example 4;

FIG. **6** is a graph that depicts the pressure drop in the core for Example 4 during dynamic condensate accumulation at 1,500 psig and 250° F. at different flow rates ranging from 330 cc/hr to 2637 cc/hr;

FIG. **7** is a graph that depicts the pressure drop across the reservoir core A, for dynamic condensate accumulation at 1,500 psig and 275° F. at flow rates ranging from 1389 cc/hr to 3832 cc/hr for Example 10;

FIG. **8** is graph that depicts the pressure drop in a sandstone core (obtained from Cleveland Quarries, Vermillion, Ohio, under the trade designation "BEREA SANDSTONE") during dynamic condensate accumulation at 1,500 psig and 250° F. before and after Example 4 treatment;

FIG. **9** is a graph that depicts the effect of water concentration in various compositions (i.e., Example 4, Example 7, Example 8, Example 9, Comparative Example D, and Comparative Example E) on the improvement in gas relative permeability after treatment;

FIG. **10** is a graph that depicts the effect of treatment flow rate on the relative permeability after treatment with the compositions at different temperatures; and

FIG. **11** is a graph that depicts the durability of the Example 9 composition.

DETAILED DESCRIPTION

To facilitate the understanding of this invention, a number of terms are defined below. Terms defined herein have meanings as commonly understood by a person of ordinary skill in the areas relevant to the present invention. Terms such as "a", "an" and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terminology herein is used to describe specific embodiments of the invention, but their usage does not delimit the invention, except as outlined in the claims.

As used herein, the term "downhole conditions" refers to the temperature, pressure, humidity, and other conditions that are commonly found in subterranean clastic formation.

As used herein, the term "hydrolyzable silane group" refers to a group having at least one Si—O—Z moiety that undergoes hydrolysis with water at a pH between about 2 and about 12, wherein Z is H or substituted or unsubstituted alkyl or aryl.

As used herein, the term "interactive" refers to the interaction between the nonionic fluorinated polymeric surfactant, solvent and other components with a clastic formation under downhole conditions as measured by a change in the permeability of gas and condensate at a productive zone. Interactive is a functional definition that refers to changes to the wettability of a rock surface and/or clastic formation, and may include some other interaction (e.g., adsorption). Other methods of determining the interaction of the compositions according to the present invention include an increase in the relative permeabilities for gas and condensate recovery. Another method of determining the interaction of the compositions includes the amount or percentage of residual oil saturation in the pore space. For example, the present invention may be used to reduce the residual oil (i.e., condensate or other liquid hydrocarbon) saturation of a clastic formation from, for example, 30 percent to 15 percent.

As used herein, the term "nonionic" refers to being free of ionic groups (e.g., salts) or groups (e.g., $—CO_2H$, $—SO_3H$, $—OSO_3H$, $—P(=O)(OH)_2$) that are readily substantially ionized in water.

As used herein, the term "polymer" refers to a molecule of molecular weight of at least 1000 grams/mole, the structure of which essentially includes the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

As used herein, the term "polymeric" refers to including a polymer.

As used herein, the term "solvent" refers to a liquid material (exclusive of any water with which it may be combined) that is capable of at least partially dissolving the nonionic fluorinated polymeric surfactant with which it is combined at room temperature (25° C.).

As used herein, the term "surfactant" refers to a surface-active material.

As used herein, the term "water-miscible" refers to molecules soluble in water in all proportions.

As used herein, the term "well productivity" refers to the capacity of a well to produce hydrocarbons. That is, it is the ratio of the hydrocarbon flow rate to the pressure drop, where the pressure drop is the difference between the average reservoir pressure and the flowing bottom hole well pressure (i.e., flow per unit of driving force).

Suitable solvents include, for example, water-miscible solvents. Examples of solvents for use with the present invention include polar solvents such as, for example, alcohols (e.g., methanol, ethanol, isopropanol, propanol, or butanol), glycols (e.g., ethylene glycol or propylene glycol), or glycol ethers (e.g., ethylene glycol monobutyl ether or those glycol ethers available under the trade designation "DOWANOL" from Dow Chemical Co., Midland, Mich.); easily gasified fluids such as, for example, ammonia, low molecular weight hydrocarbons or substituted hydrocarbons including condensate, or supercritical or liquid carbon dioxide; and mixtures thereof. In some embodiments, the solvent is methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol, acetone, a glycol ether, supercritical carbon dioxide, liquid carbon dioxide, or a mixture thereof. The degree of branching, molecular weight and stereo configuration of the solvent may also be considered along with the chemical constituents (e.g., hydrophilic groups and ionic nature) to determine the solubility, attraction, repulsion, suspension, adsorption and other properties that determine the strength of attachment to the clastic formation or suspension in a fluid, as well as the fluid properties including adsorption, hydration, and resistance to or promotion of fluid flow for either aqueous or organic fluids.

Exemplary nonionic fluorinated polymeric surfactants include nonionic polyether and fluorinated polymeric surfactants such as those including a fluoroaliphatic polymeric ester.

The nonionic fluorinated polymeric surfactants include those in which a plurality of nonafluorobutanesulfonylamido groups are linked to poly(alkyleneoxy) moieties through a polymeric chain. Poly(alkyleneoxy) moieties are typically soluble over a wide range of polarity by alteration of the carbon-oxygen ratio.

In some embodiments, the nonionic fluorinated polymeric surfactant includes a fluoroaliphatic polymeric ester with a number average molecular weight in the range from 1,000 to 30,000 (in some embodiments, in a range from 1,000 to 20,000 g/mole, or even from 1,000 to 10,000 g/mole).

It is also within the scope of the present invention to use mixtures of nonionic fluorinated polymeric surfactants.

Nonionic fluorinated polymeric surfactants can be prepared, for example, by techniques known in the art, including, for example, by free radical initiated copolymerization of a nonafluorobutanesulfonamido group-containing acrylate with a poly(alkyleneoxy) acrylate (e.g., monoacrylate or diacrylate) or mixtures thereof. Adjusting the concentration and activity of the initiator, the concentration of monomers, the temperature, and the chain-transfer agents can control the molecular weight of the polyacrylate copolymer. The description of the preparation of such polyacrylates is described, for example, in U.S. Pat. No. 3,787,351 (Olson), the disclosure of which is incorporated herein by reference. Preparation of nonafluorobutanesulfonamido acrylate monomers are described, for example, in U.S. Pat. No. 2,803,615 (Ahlbrecht et al.), the disclosure of which is incorporated herein by reference. Examples of fluoroaliphatic polymeric esters and their preparation are described, for example, in U.S. Pat. No. 6,664,354 (Savu et al.), the disclosure of which is incorporated herein by reference.

Methods described above for making nonafluorobutylsulfonamido-containing structures may be used to make heptafluoropropylsulfonamido group-containing structures by starting with heptafluoropropylsulfonyl fluoride, which can be made, for example, by the methods described in Examples 2 and 3 of U.S. Pat. No. 2,732,398 (Brice et al.), the disclosure of which is incorporated herein by reference.

The nonionic fluorinated polymeric surfactants generally dissolve at room temperature in the solvent-water mixture, but also, remain interactive or functional under downhole conditions (e.g., at typical down-hole temperatures and pressures). Although not wanting to be bound by theory, it is believed the nonionic fluorinated polymeric surfactants generally adsorb to clastic formations under downhole conditions and typically remain at the target site for the duration of an extraction (e.g., 1 week, 2 weeks, 1 month, or longer).

The ingredients for compositions described herein including nonionic fluorinated polymeric surfactants, water, and solvent can be combined using techniques known in the art for combining these types of materials, including using conventional magnetic stir bars or mechanical mixer (e.g., in-line static mixer and recirculating pump).

Referring to FIG. **1**, an exemplary offshore oil and gas platform is schematically illustrated and generally designated **10**. Semi-submersible platform **12** is centered over submerged oil and/or gas (clastic) formation **14** located below sea floor **16**. Subsea conduit **18** extends from deck **20** of platform **12** to wellhead installation **22** including, for example, blowout preventers **24**. Platform **12** is shown with hoisting apparatus **26** and derrick **28** for raising and lowering pipe strings such as work string **30**.

Wellbore **32** extends through the various earth strata including hydrocarbon-bearing subterranean clastic formation **14**. Casing **34** is cemented within wellbore **32** by cement **36**. Work string **30** may include various tools including, for example, sand control screen assembly **38** which is positioned within wellbore **32** adjacent to clastic formation **14**. Also extending from platform **12** through wellbore **32** is fluid delivery tube **40** having fluid or gas discharge section **42** positioned adjacent to clastic formation **14**, shown with production zone **48** between packers **44**, **46**. When it is desired to treat zone **48**, work string **30** and fluid delivery tube **40** are lowered through casing **34** until sand control screen assembly **38** and fluid discharge section **42** are positioned adjacent to clastic formation **14** including perforations **50**. Thereafter, a composition described herein is pumped down delivery tube **40** to progressively treat zone **48**.

While FIG. **1** depicts an offshore operation, the skilled artisan will recognize that the compositions and methods for treating a production zone of a wellbore are equally well-suited for use in onshore operations. Also, while FIG. **1** depicts a vertical well, the skilled artisan will also recognize that compositions and methods for wellbore treatment of the present invention are equally well-suited for use in deviated wells, inclined wells or horizontal wells.

FIG. **2** is a cross-section view of an exemplary production zone at the wellbore **32** next to a graph that describes the problems associated with the productivity of gas condensate wells when the near wellbore pressure drops below the dew point pressure, often referred to as the condensate banking problem. A cross-sectional view of the wellbore **32** is shown next to the basic flow characteristics of oil and gas at a production zone. Briefly, the near wellbore region and the adjacent single-phase gas region are depicted with the flow of gas-oil indicated by arrows. As the average pressure, P_{av}, decreases toward the dew pressure, P_{dew}, an increase in oil-gas is observed over gas alone. As the formation pressure reaches P_{dew}, oil blocks the flow of gas thereby reducing the efficiency of gas flow and recovery of gas. The productivity of gas condensate wells is reduced substantially (by a factor of 2 to 3) when the near wellbore pressure drops below the dew point pressure. This problem is commonly encountered in gas wells producing from gas condensate fields.

FIG. **3** depicts a calculated near wellbore gas-condensate saturation. The present invention includes compositions and methods for the injection of nonionic fluorinated polymeric surfactants that modify the wetting properties of the rock in the near wellbore region to allow the water and the gas-condensate to flow more easily into the wellbore. The compositions and methods taught herein cause an increase in the relative gas and condensate permeabilities at the site of treatment, namely, the near wellbore region.

Hydraulic fracturing is commonly used to increase the productivity of gas-condensate blocked wells, that is, wells that having a gas-condensate bank near the wellbore. However, the hydraulic fracturing method is relatively expensive, and may not be applicable in cases where a water bearing clastic formation exists near the gas bearing clastic formation (for concern of fracturing into the water bearing sand).

However, in some instances it may be desirable to utilize fracturing techniques and/or proppants as known in the art in conjunction with the instant invention to increase the production of hydrocarbon extraction from subterranean clastic formations. It may also be desirable to treat proppant with a composition described herein prior to injecting the well. Sand proppants are available, for example, from Badger Mining Corp., Berlin, Wis.; Borden Chemical, Columbus, Ohio; Fairmont Minerals, Chardon, Ohio. Thermoplastic proppants are available, for example, from the Dow Chemical Company, Midland, Mich.; and BJ Services, Houston, Tex. Clay-based proppants are available, for example, from CarboCeramics, Irving, Tex.; and Saint-Gobain, Courbevoie, France. Sintered bauxite ceramic proppants are available, for example, from Borovichi Refractories, Borovichi, Russia; 3M Company, St. Paul, Minn.; CarboCeramics; and Saint Gobain. Glass bubble and bead proppants are available, for example, from Diversified Industries, Sidney, British Columbia, Canada; and 3M Company.

Advantages and embodiments of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

Core Flood Setup

A schematic diagram of core flood apparatus **100** used to determine relative permeability of the substrate sample is shown in FIG. **4**. Core flood apparatus **100** included positive displacement pumps (Model No. 1458; obtained from General Electric Sensing, Billerica, Mass.) **102** to inject fluid **103** at constant rate in to fluid accumulators **116**. Multiple pressure ports **112** on core holder **108** were used to measure pressure drop across four sections (2 inches in length each) of core **109**. Two back-pressure regulators (Model No. BPR-50; obtained from Temco, Tulsa, Okla.) **104**, **106** were used to control the flowing pressure upstream **106** and downstream

104 of core **109**. Pressure Volume Temperature (PVT) cell (Model No. 310; obtained from Temco, Tulsa, Okla.) was used to visually measure liquid drop out. The flow of fluid was through a vertical core to avoid gravity segregation of the gas. High-pressure core holder (Hassler-type Model UTPT-1x8-3K-13 obtained from Phoenix, Houston Tex.) 108, back-pressure regulators **106**, fluid accumulators **116**, and tubing were placed inside a pressure- and temperature-controlled oven (Model DC 1406F; maximum temperature rating of 650° F. obtained from SPX Corporation, Williamsport, Pa.) at the temperatures tested. The maximum flow rate of fluid was 7,000 cc/hr.

Three synthetic gas-condensate fluids were prepared having the compositions listed in Table 1, below.

TABLE 1

	Component	Mole %
Fluid I	Methane	78.5
	n-Butane	15
	n-Heptane	5
	n-Decane	1.5
Fluid II	Methane	83
	n-Butane	4
	n-Heptane	7.2
	n-Decane	4
	n-Dodecane	1.8
Fluid III	Methane	93
	n-Butane	4
	n-Decane	2
	n-Pentadecane	1

Various properties of Fluids I, II, and III were determined as described below, and are listed in Table 2, below.

TABLE 2

	Fluid I (145° F.)	Fluid II (250° F.)	Fluid III (275° F.)
Dewpoint (psig)	2,875	3,850	4,153
Core pressure (psig)	1,200	1,500	1,500
Liquid dropout (V/Vt) %	7.1	10.2	3.2
Gas viscosity (cP)	0.0173	0.0170	0.0165
Oil viscosity (cP)	0.128	0.167	0.216
Interfacial tension (dynes/cm)	4.2	4.3	5.0

Dew point and Liquid drop out was measured using the pressure volume temperature cell described above. Gas viscosity and oil viscosity values were determined using the capillary viscometer **114**. The capillary viscometer consists of a stainless steel (SS-316) capillary tube with 1/16th inch outer diameter purchased from Swagelok. Interfacial tension was measured using a spinning drop tensiometer (available from The University of Texas at Austin, Austin, Tex.).

Substrates

The substrates for core flooding evaluation were sandstone core plugs obtained from Cleveland Quarries, Vermillion, Ohio, under the trade designation "BEREA SANDSTONE" (there were 14 similar "BEREA SANDSTONE" cores used for the Examples 1-9 and Comparative Examples A-E (i.e., one core for each example)). Example 10 used a reservoir sandstone core from a gas-condensate well in the North Sea. Various properties of these core plugs are listed in Table 3, below. The pore volume and porosity values were determined as describe below. The porosity was measured using either a gas expansion method or by the weight difference between a dry and a fully saturated core sample. The pore volume is the product of the bulk volume and the porosity.

TABLE 3

	Sandstone Core
Diameter (inch)	1.0
Length (inch)	8.0
Pore volume (cc)	20.6
Porosity (%)	20.0

The cores were dried for 72 hours in a standard laboratory oven at 95° C., and then were wrapped in aluminum foil and heat shrink tubing (obtained under the trade designation "TEFLON HEAT SHRINK TUBING" from Zeus, Inc., Orangeburg, S.C.). The wrapped core was placed in core holder **108** inside oven **100** at 145° F. After four hours, an axial pressure was applied by screwing the end pieces of the core holder. An overburden pressure of 3,400 psig was applied. Holes were drilled through the pressure taps (⅛ inch). The initial gas permeability was measure using methane at a flowing pressure of 3,000 psig.

Water Saturation Procedure

Water was introduced into the core **109** using a vacuum push-pull technique. Core holder **108** was taken outside the oven to cool at room temperature. The outlet end of the core holder was connected to a vacuum pump and a full vacuum was applied for 5 hours. The inlet end was closed. The core holder **108** was placed inside the oven **100** at 145° F. and opened to atmospheric pressure. The core holder **108** was allowed to reach an equilibrium temperature. Then, a series of push-pull cycles were applied using a hand pump (Catalog No. 1458/59 WI, obtained from Ruska Instrument Corporation, Houston, Tex.) through the outlet of the core holder **108**. Between each push and pull cycle, a break of 15 minutes was taken to allow water vapor to distribute through core **109**. The water saturation procedure was completed after 32 push-pull cycles.

Composition

The Example 1 composition was 2 percent by weight nonionic fluorinated polymeric surfactant (obtained from 3M Company, St. Paul, Minn., under the trade designations "NOVEC FLUOROSURFACTANT FC-4430"), 0 percent by weight water, and 98 percent by weight methanol, prepared by mixing the ingredients together using a magnetic stirrer and magnetic stir bar. An initial water saturation of 0.4 was present in the core.

Core Flooding Procedure

The following procedure was used to determine the single-phase gas permeabilities of the substrates listed in Table 3, above. Referring again to FIG. **4**, the single-phase gas permeability of each core was measured before treatment by flowing methane through core **109** at a flow rate of 85 cc/hour using positive displacement pump **102** until a steady state was reached. The composition described above was then injected in core **109** at a flow rate of 85 cc/hour to study the effect of capillary number on gas and condensate relative permeabilities. Upstream back-pressure regulator **106** was set at 3,000 psig the dew point pressure of the fluid and downstream back-pressure regulator **104** was set at a 1,200 psig the dew point pressure corresponding to the bottom hole flowing well pressure. Results are listed in Table 4, below.

TABLE 4

	Ex-1	Ex-2	Comparative Ex A	Ex 3	Ex-4	Ex-5	Comparative Ex B
Gas permeability, md	230.0	230.0	220.0	95	115.0	216.0	236.0
Initial water saturation	0.4	0.4	0.0	0.0	0.0	0.0	0.0
Temperature (° F., ° C.)	145, 63	145, 63	145, 63	145, 63	250, 121	250, 121	250, 121
Water concentration (wt %)	0.0	0.0	4.0	4.0	4.0	4.0	4.0
Surfactant concentration (wt %)	FC4430 (2.0)	FC4432 (2.0)	FS10 (2.0)	FC4430 (2.0)	FC4430 (2.0)	FC4430 (0.25)	FS10 (2.0)
Capillary number	1.38×10^{-5}	1.38×10^{-5}	1.01×10^{-5}	4.54×10^{-6}	7.76×10^{-6}	6.34×10^{-5}	7.77×10^{-5}
Gas relative permeability before treatment	0.011	0.011	0.014	0.036	0.08	0.067	0.062
Gas relative permeability after treatment	0.011	0.011	0.028	0.103	0.246	0.181	0.072
Improvement factor	1.0	1.0	2.00	2.86	3.08	2.70	1.16

	Ex 6	Ex-7	Ex-8	Ex 9	Comparative Ex C	Comparative Ex D	Comparative Ex E
Gas permeability, md	225.0	512.0	348.0	487.0	220.0	260	260
Initial water saturation	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Temperature (° F., ° C.)	250, 121	250, 121	250, 121	250, 121	145, 63	250, 121	250, 121
Water concentration (wt %)	4.0	25.0	10.0	4.0	4.0	0.0	0.0
Surfactant concentration (wt %)	FC4432 (2.0)	FC4430 (2.0)	FC4430 (2.0)	FC4430 (2.0)	Fluorosyl (2.0)	FC4430 (2.0)	FC4430 (2.0)
Capillary number	8.35×10^{-5}	5.07×10^{-5}	5.28×10^{-5}	8.05×10^{-5}	*plugged	2.77×10^{-5}	2.77×10^{-5}
Gas relative permeability before treatment	0.064	0.074	0.062	0.127	0.01	0.079	0.064
Gas relative permeability after treatment	0.072	0.108	0.126	0.263	*plugged	0.079	0.069
Improvement factor	1.13	1.46	2.03	2.07	**N/A	1.0	1.08

Plugged means that after the treatment the core was impermeable

**N/A There was no improvement since the core was plugged

EXAMPLE 2

The procedure described above for Example 1 was followed for Example 2, except the "NOVEC FLUOROSURFACTANT FC-4430" surfactant was replaced with a surfactant obtained from 3M Company under the trade designation "NOVEC FLUOROSURFACTANT FC-4432". Results are listed in Table 4, above.

EXAMPLE 3

The procedure described above for Example 1 was followed for Example 3 except no water saturation procedure was performed, and the water concentration in the composition was 4%. Results are listed in Table 4, above.

EXAMPLE 4

The procedure described above for Example 1 was followed for Example 4, except no water saturation procedure was performed, the testing was conducted at 250° F. (121° C.), water concentration in the composition was 4%. Results are listed in Table 4, above.

FIG. **5** illustrates pressure drop data observed across different sections and the total length of the core as the process of condensate accumulation occurred for Example 4. The relative permeability of the gas and condensate was then calculated from the steady state pressure drop.

FIG. **6** shows the pressure drop in a "BEREA SANDSTONE" core for Example 4 during dynamic condensate accumulation at 1,500 psig and 250° F. at different flow rates ranging from 330 cc/hr to 2637 cc/hr. The gas relative permeability decreases by 90% of the initial value during condensate accumulation corresponding to a condensate bank. FIG. **5** shows the overall pressure drop and sectional pressure drops across the Example 4 "BEREA SANDSTONE" core during dynamic condensate accumulation at 1,500 psig and 250° F. at a flow rate of 302 cc/hr.

FIG. **8** shows the pressure drop in a "BEREA SANDSTONE" core during dynamic condensate accumulation at 1,500 psig and 250° F. before and after Example 4 treatment at 330 cc/hr.

EXAMPLE 5

The procedure described above for Example 4 was followed for Example 5, except the concentration of the nonionic fluorinated polymeric surfactant ("NOVEC FLUOROSURFACTANT FC-4430") was 0.25%. Results are listed in Table 4, above.

EXAMPLE 6

The procedure described above for Example 4 was followed, except the "NOVEC FLUOROSURFACTANT FC-4430" surfactant was replaced with the "NOVEC FLUOROSURFACTANT FC-4432" surfactant. Results are listed in Table 4, above.

EXAMPLE 7

The procedure described above for Example 4 was followed for Example 7, except the water concentration in the composition was 25%. Results are listed in Table 4, above.

EXAMPLE 8

The procedure described above for Example 4 was followed for Example 8 except the water concentration in the composition was 10%. Results are listed in Table 4, above.

EXAMPLE 9

The procedure described above for Example 4 was followed. Results are listed in Table 4, above.

The durability of the Example 9 composition was evaluated by injecting almost 4,000 pore volumes of gas mixture at 300 cc/hr following the treatment of a "BEREA SANDSTONE" core at 250° F. (See FIG. **11**). The improvement factor was not observed to change during the entire time the gas mixture was injected.

EXAMPLE 10

The procedure described for Example 1 above was followed, except the coreflooding was conducted on a Reservoir Core A sandstone treated at the temperature and pressure listed in Table 5, below. The Various properties of this substrate are listed in Table 6, below. The pore volume and porosity values were determined as describe above in Example 1 for the "BEREA SANDSTONE" core plugs. Results are listed in Table 5, below.

TABLE 5

	Reservoir Core A
Gas permeability, md	72.0
Initial water saturation	0.0
Temperature (° F.)	275
Water in treatment solution (wt %)	4.0
Surfactant concentration (wt %)	FC4430 (2.0)
Capillary number	1.03×10^{-5}
Gas relative permeability before treatment	0.119
Gas relative permeability after treatment	0.248
Improvement factor	2.08

TABLE 6

	Reservoir Core A
Diameter (inch)	1.0
Length (inch)	3.75
Pore volume (cc)	8.01
Porosity (%)	16.6

The gas/oil interfacial tension was determined as described above in Example 1 to be about 4 dynes/cm.

FIG. **7** shows the pressure drop across the reservoir core A, for dynamic condensate accumulation at 1,500 psig and 275° F. at flow rates ranging from 330 cc/hr to 3811 cc/hr.

COMPARATIVE EXAMPLE A

The procedure described above for Example 4 was followed for Comparative Example A, except the "NOVEC FLUOROSURFACTANT FC-4430" surfactant was replaced with surfactant "obtained from Solvay Solexis Thorofare, N.J., under the trade designation "FLUOROLINK S10", and the testing was conducted at 145° F.

COMPARATIVE EXAMPLE B

The procedure described above for Example 4 was followed for Comparative Example B, except the "NOVEC FLUOROSURFACTANT FC-4430" surfactant was replaced with the "FLUOROLINK S10" surfactant.

COMPARATIVE EXAMPLE C

The procedure described above for Example 4 was followed for Comparative Example C except the "NOVEC FLUOROSURFACTANT FC-4430" surfactant was replaced with surfactant obtained from Cytonix, Beltsville, Md., under the trade designation "FLUOROSYL", and the testing was conducted at 145° F.

COMPARATIVE EXAMPLE D

The procedure described above for Example 1 was followed for Comparative Example D except no water saturation procedure was performed, and the testing was conducted at 250° F. (121° C.). Results are listed in Table 4, above.

COMPARATIVE EXAMPLE E

The procedure described above for Example 1 was followed for Comparative Example E except no water saturation procedure was performed, and the testing was conducted at 250° F. (121° C.). Results are listed in Table 4, above.

Table 4 shows the effect of temperature on the gas relative permeability by use of various compositions (i.e., Examples 1-9 and Comparative Examples A-E).

FIG. **9** shows the effect of water concentration in various compositions (i.e., Example 4, Example 7, Example 8, Example 9 (at two different flow rates), Comparative Example D, and Comparative Example E) on the improvement in gas relative permeability after treatment with the compositions at 250° F. (121° C.). The concentration of water in these examples and comparative examples ranged from 0% to 25% by weight. As shown in FIG. **9**, there was no improvement observed in the gas relative permeability when no water was present in the treatment composition.

FIG. **10** shows the effect of treatment flow rate on the relative permeability after treatment with the compositions of Examples 3, 4, 7, and 9 at different temperatures. The treatment flow rate was varied from 32 cc/hr to 1,200 cc/hr.

Following the relative permeability measurements, methane was injected, using a positive displacement pump as described above, to displace the condensate and measure the final (single phase) gas permeability at the end of the study. The final gas permeability was the same as the original (single phase) gas permeability.

It will be understood that particular embodiments described herein are shown by way of illustration and not as limitations of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents are considered to be within the scope of this invention and are covered by the claims.

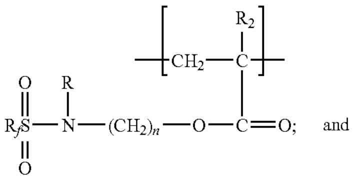
While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention.

What is claimed is:

1. A composition comprising:

a nonionic fluorinated polymeric surfactant, wherein the nonionic fluorinated polymeric surfactant comprises:

(a) at least one divalent unit represented by the formula:



$$R_f\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-\overset{R}{\overset{|}{N}}-(CH_2)_n-O-\overset{-\left[CH_2-\overset{R_2}{\overset{|}{C}}\right]-}{\overset{|}{C}}=O;\quad \text{and}$$

(b) a poly(alkyleneoxy) segment;

wherein

R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

R and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms; and

n is an integer from 2 to 10;

water; and

at least 50 percent by weight solvent, based on the total weight of the composition.

2. The composition of claim **1**, wherein the solvent is water-miscible.

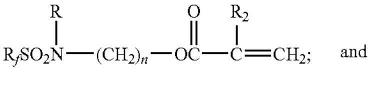
3. The composition of claim **2**, wherein the nonionic fluorinated polymeric surfactant has a solubility in a mixture of the water-miscible solvent and the water that decreases with an increase in temperature.

4. The composition of claim **1**, wherein the composition is interactive with a hydrocarbon-bearing geological clastic formation.

5. The composition of claim **4**, wherein the hydrocarbon-bearing geological clastic formation is downhole.

6. The composition of claim **1**, wherein the nonionic fluorinated polymeric surfactant is preparable by copolymerization of:

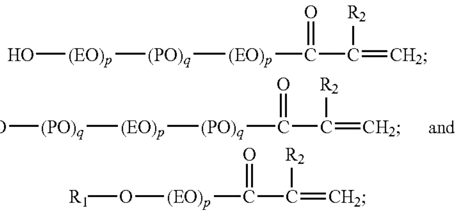
(a) at least one compound represented by the formula



$$R_fSO_2\overset{R}{\overset{|}{N}}-(CH_2)_n-O\overset{O}{\overset{\|}{C}}-\overset{R_2}{\overset{|}{C}}=CH_2;\quad \text{and}$$

(b) at least one of a poly(alkyleneoxy) monoacrylate or diacrylate.

7. The composition of claim **6**, wherein the poly(alkyleneoxy) monoacrylate comprises at least one compound represented by a formula selected from the group consisting of:



$$HO-(EO)_p-(PO)_q-(EO)_p-\overset{O}{\overset{\|}{C}}-\overset{R_2}{\overset{|}{C}}=CH_2;$$

$$HO-(PO)_q-(EO)_p-(PO)_q-\overset{O}{\overset{\|}{C}}-\overset{R_2}{\overset{|}{C}}=CH_2;\quad \text{and}$$

$$R_1-O-(EO)_p-\overset{O}{\overset{\|}{C}}-\overset{R_2}{\overset{|}{C}}=CH_2;$$

wherein

R_1 and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

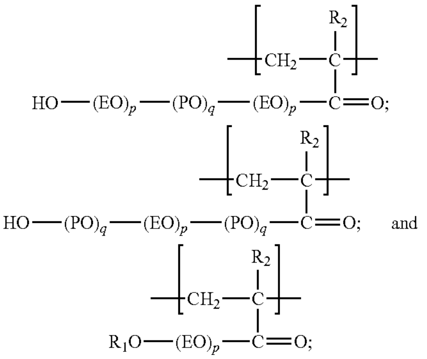
EO represents —CH_2CH_2O—;

PO represents —$CH(CH_3)CH_2O$—;

each p is independently an integer of 1 to about 128; and

each q is independently an integer of 0 to about 55.

8. The composition of claim **1**, wherein the nonionic fluorinated polymeric surfactant comprises at least one divalent unit represented by a formula selected from the group consisting of:



$$HO-(EO)_p-(PO)_q-(EO)_p-\overset{-\left[CH_2-\overset{R_2}{\overset{|}{C}}\right]-}{\overset{|}{C}}=O;$$

$$HO-(PO)_q-(EO)_p-(PO)_q-\overset{-\left[CH_2-\overset{R_2}{\overset{|}{C}}\right]-}{\overset{|}{C}}=O;\quad \text{and}$$

$$R_1O-(EO)_p-\overset{-\left[CH_2-\overset{R_2}{\overset{|}{C}}\right]-}{\overset{|}{C}}=O;$$

wherein

R_1 and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

EO represents $—CH_2CH_2O—$;

PO represents $—CH(CH_3)CH_2O—$;

each p is independently an integer of 1 to about 128; and each q is independently an integer of 0 to about 55.

9. The composition of claim **1**, wherein R_f has from 4 to 6 carbon atoms.

10. The composition of claim **1**, wherein R_f is perfluorobutyl.

11. The composition of claim **1**, wherein the solvent comprises at least one of methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol, acetone, a glycol ether, supercritical carbon dioxide, or liquid carbon dioxide.

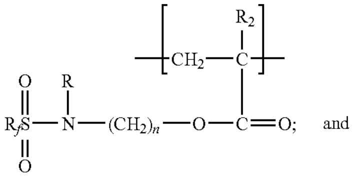
12. The composition of claim **1**, wherein the solvent comprises methanol.

13. The composition of claim **1**, wherein the nonionic fluorinated polymeric surfactant is free of hydrolyzable silane groups.

14. The composition of claim **1**, wherein the nonionic fluorinated polymeric surfactant has a number average molecular weight in the range from 1,000 to 30,000 grams/mole.

15. A gaseous composition comprising methane and a fluorinated product resulting from at least one of hydrolysis or thermal decomposition of a nonionic fluorinated polymeric surfactant, wherein the nonionic fluorinated polymeric surfactant comprises:

(a) at least one divalent unit represented by the formula:



$$R_fS(=O)_2—N(R)—(CH_2)_n—O—C(=O)—\left[CH_2—C(R_2)\right]—;$$

and

(b) a poly(alkyleneoxy) segment;

wherein

R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

R and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms; and

n is an integer from 2 to 10.

16. A method of making a composition, the method comprising:

selecting a hydrocarbon-bearing subterranean clastic formation, the formation having a temperature, water content, and ionic strength;

determining the temperature, water content, and ionic strength of the hydrocarbon-bearing subterranean clastic formation;

generating a formulation comprising nonionic fluorinated polymeric surfactant and at least one of solvent or water, the formulation based at least in part on the determined temperature, water content, and ionic strength of the hydrocarbon-bearing subterranean clastic formation, wherein the nonionic fluorinated polymeric surfactant has a cloud point when placed in the hydrocarbon-bearing subterranean clastic formation that is above the temperature of the hydrocarbon-bearing subterranean clastic formation; and

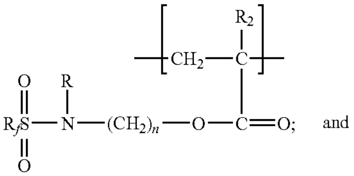
making a composition having the formulation.

17. The method of claim **16**, wherein the composition comprises water.

18. The method of claim **16**, wherein the composition comprises solvent, and wherein the solvent comprises methanol.

19. The method of claim **16**, wherein the nonionic fluorinated polymeric surfactant comprises:

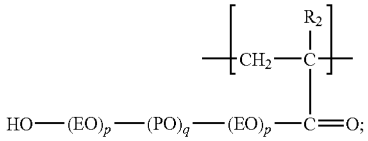
(a) at least one divalent unit represented by the formula:



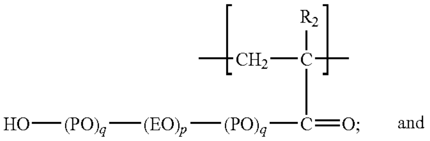
$$R_fS(=O)_2—N(R)—(CH_2)_n—O—C(=O)—\left[CH_2—C(R_2)\right]—;$$

and

(b) at least one divalent unit represented by a formula selected from the group consisting of:

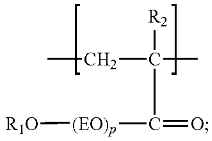


$$HO—(EO)_p—(PO)_q—(EO)_p—C(=O)—\left[CH_2—C(R_2)\right]—;$$



$$HO—(PO)_q—(EO)_p—(PO)_q—C(=O)—\left[CH_2—C(R_2)\right]—;$$

and



$$R_1O—(EO)_p—C(=O)—\left[CH_2—C(R_2)\right]—;$$

wherein

R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

R, R_1, and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

n is an integer from 2 to 10;

EO represents $—CH_2CH_2O—$;

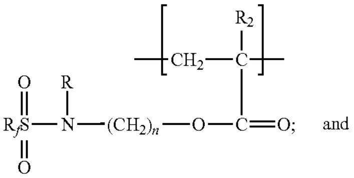
PO represents $—CH(CH_3)CH_2O—$;

each p is independently an integer of 1 to about 128; and

each q is independently an integer of 0 to about 55.

20. A treated gas-bearing clastic formation penetrated by a well bore comprising a region near the well bore treated with a nonionic fluorinated polymeric surfactant, wherein the nonionic fluorinated polymeric surfactant comprises:

(a) at least one divalent unit represented by the formula:



$$R_fS(=O)_2—N(R)—(CH_2)_n—O—C(=O)—\left[CH_2—C(R_2)\right]—;$$

and

(b) a poly(alkyleneoxy) segment,

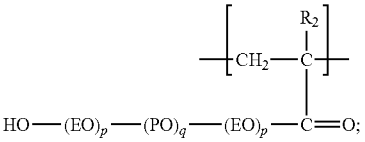
wherein

R_f represents a perfluoroalkyl group having from 1 to 8 carbon atoms;

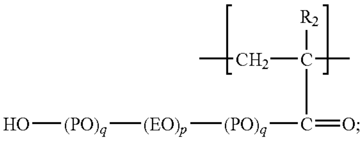
R and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms; and

n is an integer from 2 to 10.

21. The formation according to claim **20**, wherein the nonionic fluorinated polymeric surfactant comprises at least one divalent unit represented by a formula selected from the group consisting of:



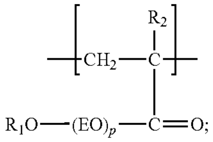
$$-\!\left[CH_2-\underset{\underset{HO-(EO)_p-(PO)_q-(EO)_p-C=O;}{|}}{\overset{R_2}{\overset{|}{C}}}\right]\!-$$



$$-\!\left[CH_2-\underset{\underset{HO-(PO)_q-(EO)_p-(PO)_q-C=O;}{|}}{\overset{R_2}{\overset{|}{C}}}\right]\!-$$

and

-continued



$$-\!\left[CH_2-\underset{\underset{R_1O-(EO)_p-C=O;}{|}}{\overset{R_2}{\overset{|}{C}}}\right]\!-$$

wherein

R_1 and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

EO represents $—CH_2CH_2O—$;

PO represents $—CH(CH_3)CH_2O—$;

each p is independently an integer of 1 to about 128; and

each q is independently an integer of 0 to about 55.

* * * * *

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Chromosome Damage in Liver Cells from Low Dose Rate Alpha, Beta, and Gamma Irradiation: Derivation of RBE

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Chromosome Damage in Liver Cells from Low Dose Rate Alpha, Beta, and Gamma Irradiation: Derivation of RBE

Abstract. *Relative biological effectiveness (RBE) for chromosome damage in liver cells was determined after low dose rate exposures to alpha, beta, or gamma irradiation. Protracted exposures to beta and gamma irradiation were equally effective, whereas low dose rate exposures to alpha emitters were 15 to 20 times more damaging than exposures to beta or gamma irradiation. These data support the use of the quality factor of 10 recommended by the International Commission on Radiological Protection and the National Council on Radiation Protection for estimating the biological hazard from internally deposited alpha emitters. When the dose rates were low, all types of chromosome damage observed were produced by single-hit processes.*

Consideration of the biological effectiveness of different radiation types is important in setting the radiation standards used as guidelines to limit human radiation exposure. The lack of adequate data for high linear energy transfer (LET) radiation delivered at low dose rates creates uncertainties in determining biological effectiveness for such exposure conditions. The LET for ionizing radiation is a measure of the average amount of energy deposited in tissue per unit of distance traveled. Internal deposition of alpha-emitting radioisotopes such as ^{239}Pu results in low dose rate exposure to high LET radiation. The projected inventory of alpha-emitting isotopes related to nuclear power production is very large and creates a potential for incorporation of some of these isotopes into humans and a need to understand the radiobiology of such exposure. The method for determining the relative biological effectiveness (RBE), which is used in estimating hazard, is to divide the dose of a standard irradiation which produces a measured biological effect by the dose of test irradiation required to produce the same biological change. The test irradiation used is usually acute exposure to ^{60}Co gamma rays or 250-kv-peak x-rays (*1*).

We have determined the RBE for exposure to high and low LET radiation delivered at low dose rates, using chromosome damage as the measure of biological change and either brief (*2*) or protracted (*3*) exposure to ^{60}Co as reference irradiation. With protracted ^{60}Co as the test exposure, the RBE values were independent of dose. An RBE of 1 was observed for an internally deposited beta emitter, while values of 15 to 20 were observed for the alpha emitters tested. These RBE's are in general agreement with the quality factors of 1 for beta and 10 for alpha emitters used to estimate hazard by the International Commission on Radiological Protection (ICRP) and the National Council on Radiation Protection (NCRP). When brief exposure to ^{60}Co was used as the reference irradiation, the RBE changed as a function of radiation dose and appeared to be less suitable for estimating hazards from internally deposited alpha-emitting isotopes such as ^{239}Pu. One reason for these different RBE values is that many dose-response curves for brief exposure to x-rays are nonlinear (*4*), while those for high LET radiation are often linear (*5*).

The fact that the frequency of chromosome aberrations produced by high LET radiation increases as a linear function of radiation dose implies a single-hit process (*5*). If protracting the dose of a low LET radiation also results in a linear dose-response relationship, it can be inferred that gamma irradiation can also interact with chromosomes to produce aberrations by a single-hit process. An RBE for protracted exposure to either low or high LET radiation can thus be easily derived by comparing the slopes of the dose-response lines. Since environmental radiation exposure will be protracted, such relationships are important in deriving meaningful quality factors to be used in setting standards for internally deposited alpha-, beta-, or gamma-emitting radionuclides.

For the experiments described in this report metaphase chromosome aberrations in the livers of Chinese hamsters were used as a biological measure of damage, and brief and protracted external ^{60}Co exposures as reference radiation. Radiation doses from intraperitoneally injected ^{144}Ce, ^{239}Pu, ^{241}Am, and ^{252}Cf citrates (*6–8*), all of which localize in the liver, were compared to the reference radiation. Cerium-144 is a beta emitter, whereas ^{241}Am, ^{239}Pu, and ^{252}Cf emit alpha particles. In addition to alpha particles, ^{252}Cf also decays by the emission of neutrons, gamma rays, and fission fragments.

The methods used in these experiments, a detailed breakdown of aberration types, and dose-response data for different aberration types have been previously described (*2, 3, 6–8*). Basic information is included in Table 1 to show the scope of the experiment. Briefly, the livers of Chinese hamsters were exposed for varied lengths of time to the different types of radiation. Most of the cells were probably in the G_0 or nonproliferating stage of the cell cycle at the time of exposure. After accumulation of a predetermined dose, 60 percent of the liver was surgically removed to stimulate cell division. Colchicine was injected 50 hours after partial hepatectomy and the hamsters were killed 4 hours later. Cells were scored in the metaphase stage of the cell cycle. All chromosome slides were coded and scored without the scorer knowing the activity or dose level. Aberrations scored were rings, dicentrics, chromosome deletions, and symmetrical chromosome exchanges. All aberrations were given a value of 1 in calculating the number of aberrations per cell for determining dose-response relationships.

Dose to the liver was determined by external dosimetry after ^{60}Co exposure. For the internal emitters, the dose was calculated by using the estimated time-integrated activity, determined by measuring the activity in microcuries per gram of liver at the time of partial hepatectomy and when the animal was killed. The measured activity was extrapolated over the experimental time interval by using previously determined liver retention curves. The time-integrated activity thus derived for each animal was used to calculate a dose, which was related to the individual chromosome response. Details of dose calculations were previously published (*6*).

At each sampling time, dose-response

Table 1. Experimental design for determining the RBE for chromosome damage following low dose rate exposure to alpha, beta, and gamma irradiation. For example, ^{144}Ce citrate injections at six different dose levels were given to one group of animals, which were killed at 6 days, to another group, which were killed at 15 days, and so forth.

Exposure type	Number of activity or dose levels at each exposure time						Total treatments	Number of animals	Number of cells scored
	20 minutes	6 days	15 days	42 days	122 days	362 days			
Brief ^{60}Co	8						8	78	3,570
Protracted ^{60}Co		4	4	4			12	53	1,734
^{144}Ce citrate injected		6	6	6	6	6	30	252	5,024
^{241}Am citrate injected		6	6	6	6	6	30	156	3,141
^{252}Cf citrate injected		5	5	5			15	53	2,196
^{239}Pu citrate injected		1	1	1	1		4	37	1,360
Totals							99	629	17,025

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curves were generated. Dose-response relationships were also derived for each activity level sampled at a variety of times. Through 362 days, time or dose rate did not change the dose-response curves. The results reported here represent a best fit of all the data through 362 days and are summarized in Fig. 1, where the aberration frequency in liver cells is related to dose in rads. With the exception of brief ^{60}Co exposure, all dose-response data could be adequately described by linear equations of the general form $Y = a + bD$, where Y = aberrations per cell, a is the intercept, b is the slope of the line in aberrations per cell per rad, and D is the dose in rads. These equations were, for protracted (pro) ^{60}Co and injected (inj) ^{144}Ce, ^{239}Pu, ^{241}Am, and ^{252}Cf,

$$^{60}\mathrm{Co}_{\mathrm{pro}} \quad Y = 0.02 + 3.3 \times 10^{-4}D$$
$$^{144}\mathrm{Ce}_{\mathrm{inj}} \quad Y = 0.02 + 3.1 \times 10^{-4}D$$
$$^{239}\mathrm{Pu}_{\mathrm{inj}} \quad Y = 0.04 + 4.8 \times 10^{-3}D$$
$$^{241}\mathrm{Am}_{\mathrm{inj}} \quad Y = 0.06 + 7.2 \times 10^{-3}D$$
$$^{252}\mathrm{Cf}_{\mathrm{inj}} \quad Y = 0.05 + 3.3 \times 10^{-3}D$$

Dose-response data for brief ^{60}Co exposures were best described by a quadratic equation

$$Y = 0.01 + 1.9 \times 10^{-4}D + 1.8 \times 10^{-6}D^2$$

A nonlinear dose-response curve has been observed for a variety of brief exposures (*4*) and is thought to be related to the mechanism of chromosome aberration production. At low total doses, few chromosomes are broken in any given cell and there is little interaction between chromosomes. As the dose increases, more breaks are present and more interaction occurs. This results in the frequency of aberration production increasing as the square of the radiation dose. Thus, high dose rates produce aberrations by two mechanisms: single events, which increase linearly with dose, and double events, which increase as the square of the dose. The combination of these is reflected in the quadratic dose-response relationship for brief ^{60}Co exposure.

When the protracted ^{60}Co is used as a reference, the quality factors for effectiveness can be determined by comparing the slopes of the dose-response curves, since they are all linear. The values derived are 1, 15, 20, and 10 for ^{144}Ce, ^{239}Pu, ^{241}Am, and ^{252}Cf, respectively. Since beta particles and gamma rays are both sparsely ionizing and interact similarly with matter, the value for RBE is 1, as would be expected. The high LET alpha particles seem to be 10 to 20 times more effective than either beta particles or gamma rays in producing chromosome aberrations. Californium-252 emits 11.76 Mev per decay, with 6.02 Mev as alpha particles and most of the rest of the energy as fission fragments. It is about ten times more effective than the sparsely ionizing radiations in producing chromosome damage. It has been postulated (*8*) that this is due to the ineffectiveness of fission fragments in producing chromosome damage which is scorable at metaphase. If only the dose from the ^{252}Cf alpha particles is related to chromosome aberrations, the quality factor is almost 20. These RBE values for alpha emitters are higher than the quality factor of 10 for alpha emitters used in setting radiation standards and illustrate that for this end point with low dose rate exposure, the quality factor may need to be changed by almost a factor of 2.

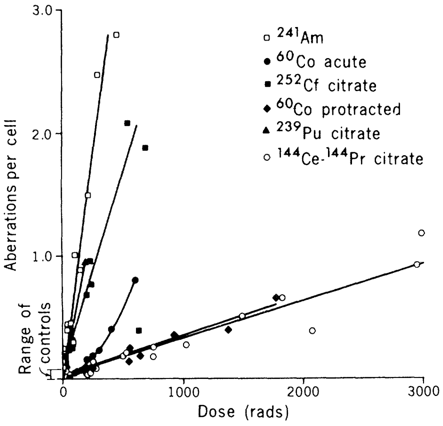

Fig. 1. Dose-response curves for the production of chromosome aberrations in the liver of the Chinese hamster after exposure to alpha, beta, and gamma irradiation.

Since the dose-response curve for brief ^{60}Co exposure is nonlinear, RBE values for which this curve is used as a reference change as a function of dose. Values of RBE at 50-rad intervals of dose were calculated by forcing all the equations through the same intercept (0, 0.01) and obtaining the dose required to produce an equal chromosome aberration frequency at each interval. These are related to dose of ^{60}Co on a log-log plot in Fig. 2. This type of data presentation has been used by Kellerer and Rossi (*9*) and has the advantage that both coordinates refer to physical quantities: the doses to produce equal effects on the RBE scale and the dose of the reference radiation on the dose scale.

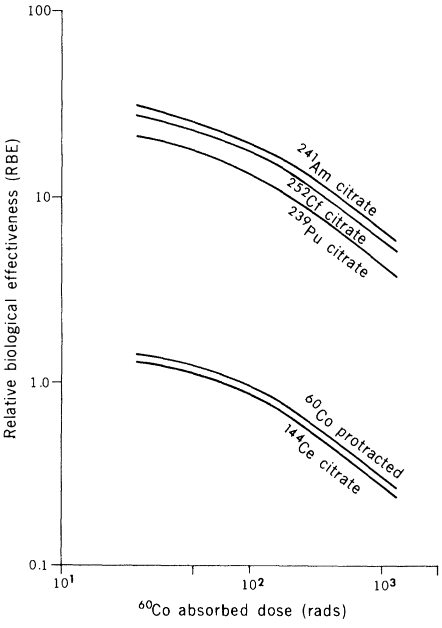

Fig. 2. Relative biological effectiveness of protracted exposure to alpha, beta, and gamma radiation, with brief exposure to ^{60}Co as the reference radiation.

For brief ^{60}Co exposures, since the shape of the ^{60}Co curve is the controlling factor, both high LET radiation and protracted low LET radiation produce RBE-dose curves of the same shape. The protracted ^{60}Co and ^{144}Ce exposures start with an RBE of about 1 and decrease to a value of 0.25 by 600 rads. The high LET radiation from ^{241}Am, ^{239}Pu, and ^{252}Cf alpha exposures have initial values of 20 to 30 and decrease to about 5 when compared with the highest brief ^{60}Co dose measured. The slope of the lines observed for these data on a log-log plot reaches a value of about −1 for each exposure schedule.

Kellerer and Rossi (*9*) postulated that the slope of −1 on a log-log plot of RBE against dose helped to prove that brief x-ray irradiation acts by a two-event process, whereas high LET radiation requires only one event to produce a number of different biological changes. This was the basis for their model of two-step interaction of radiation with biological materials. In the model, cells in state one are normal; state two could perhaps be compared with potentially lethal damage reported by Dewey and co-workers (*10*) for both cell mortality and chromosome aberrations. Cells in state two can return to normal or progress to the final state of the abnormal chromosome configuration or cell death, depending on environmental conditions.

Our results with alpha irradiation agree with this concept. The RBE-dose curve decreases with a slope of about −1, implying that the brief gamma exposure produced most of its damage by a two-step process.

The slope of the dose-response curve for protracted ^{60}Co or ^{144}Ce implies that the damage produced by protracted exposure is due to single-event processes. In fact, the slope of the dose-response curves in Fig. 1 for protracted ^{60}Co and injected ^{144}Ce represents a measure of the probability per unit dose for producing lesions of the single-event type with protracted sparsely ionizing radiation.

In recent work chromosome aberrations have been related to cell death (*11*). They have also been related to the total genetic damage and ultimately to the production of cancer (*12*). Thus, chromosome aber-

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rations are strongly linked to many late pathological changes.

Low dose rate irradiation of human populations will be produced by internally deposited radioactive materials acquired from the environment. When data obtained from experimental animals are used to estimate human risk, it is beneficial to have low LET reference irradiation delivered at both high and low dose rates. Utilizing a slowly dividing cell system, such as the liver, and recording chromosome damage after a variety of exposure types may have a very real relationship to genetic risk from protracted radiation exposures.

Genetic hazards are currently estimated for high LET radiation by using brief low LET exposures as a reference. Under these conditions, RBE increases as dose and dose rate decrease. The ICRP (*13*) has thus speculated that if protracted low LET radiation has been used as a reference standard for genetic damage, it may be necessary to substantially increase the quality factors now used for protection of the human population from genetic effects of high LET irradiation. The results reported here illustrate that this is not the case. The RBE of alpha emitters, when compared with protracted exposures to beta or gamma emitters, ranges from 15 to 20 even when very low dose rates of beta and gamma are used as a reference irradiation. The quality factor of 10 used by the NCRP and ICRP to estimate risk from high LET irradiation may be low by as much as a factor of 2, but no gross reevaluation seems needed.

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23 May 1975; revised 25 August 1975

Albugo-Like Oogonia from the American Carboniferous

Abstract. *Fungal oogonia morphologically similar to those in the extant genus* Albugo *have been discovered in the integumental tissues of the fossil gymnosperm ovule* Nucellangium. *Disease symptoms in the fossil ovule are similar to those produced by* Albugo *in living angiosperm hosts.*

Fungal oogonia found in the integumental tissues of a Paleozoic ovule, *Nucellangium*, bear a striking resemblance to those of the extant Phycomycete (Oomycete) genus *Albugo*. Specimens are preserved in coal ball petrifications collected near Oskaloosa, Iowa, from middle Pennsylvanian strata. Of special significance is the fact that the oogonia are found in the so-called proliferated form of *Nucellangium* ovules (*1*). Proliferated ovules are slightly larger than normal ones and are characterized by irregular masses of parenchyma which extend into the locule of the ovule (Fig. 1a), giving the impression of an uncontrolled cancerous-type growth.

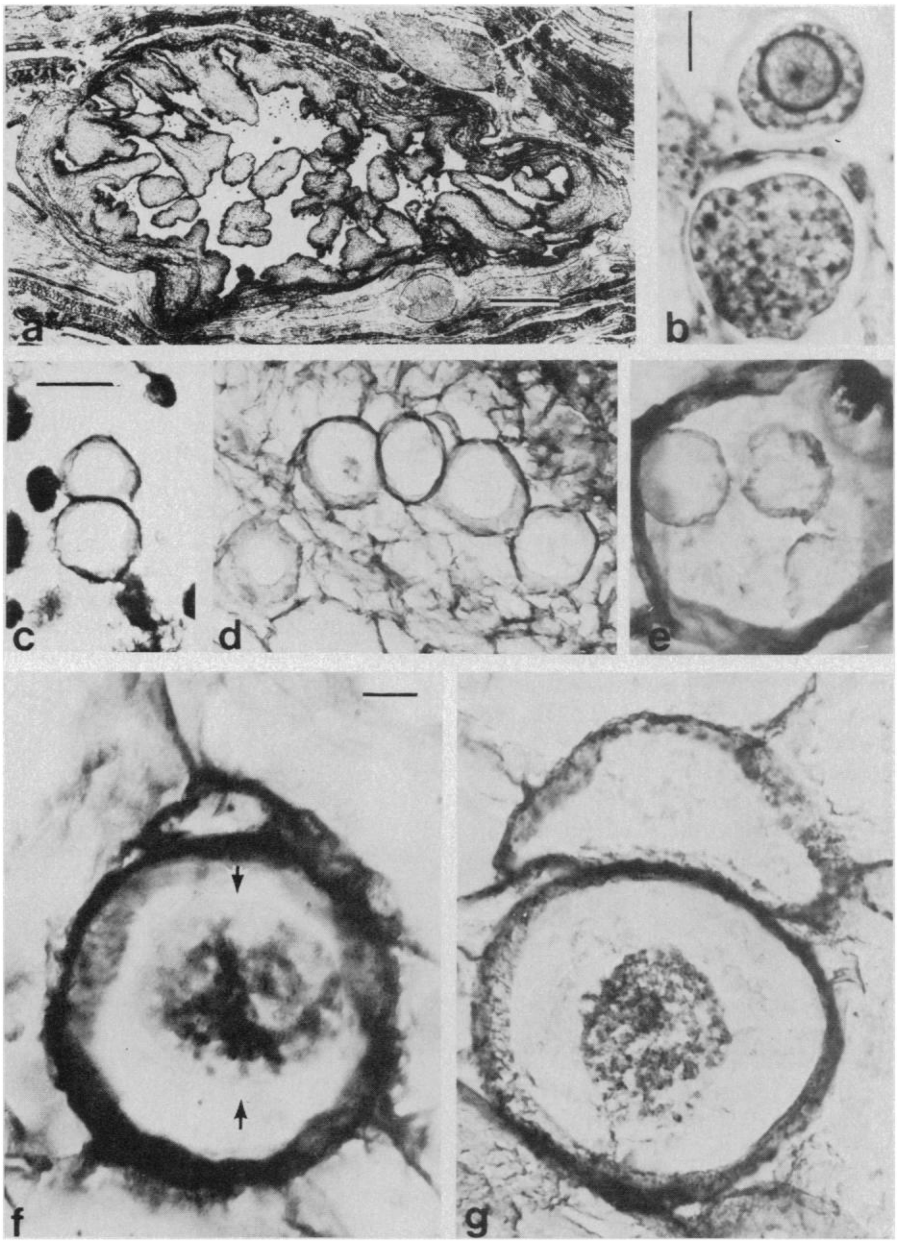

Fig. 1. (a) Section of proliferated ovule showing fingerlike extensions of integument into locule; scale bar, 2 mm. (b) Two *Albugo* oogonia, the top one containing oosphere within surrounding periplasm; scale bar, 20 μm. (c to g) Fossil oogonia. (c) Pair of oogonia free in locule of ovule; scale bar, 100 μm. (d) Oogonia in ovule integument; same scale as (c). (e) Oogonium with two visible spherical inclusions; same scale as (f). (f) Oogonium with membrane-bounded structure (arrows indicate membrane) interpreted as an oosphere; scale bar, 20 μm. (g) Oogonium with antheridium "hat cell" at top; same scale as (f).

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Comparison of organic geochemistry and metal enrichment in two black shales: Cambrian Alum Shale of Sweden and Devonian Chattanooga Shale of United States

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Abstract. In most black shales, such as the Chattanooga Shale and related shales of the eastern interior United States, increased metal and metalloid contents are generally related to increased organic carbon content, decreased sedimentation rate, organic matter type, or position in the basin. In areas where the stratigraphic equivalents of the Chattanooga Shale are deeply buried and and the organic material is thermally mature, metal contents are essentially the same as in unheated areas and correlate with organic C or S contents. This paradigm does not hold for the Cambrian Alum Shale Formation of Sweden where increased metal content does not necessarily correlate with organic matter content nor is metal enrichment necessarily related to land derived humic material because this organic matter is all of marine source. In south-central Sweden the elements U, Mo, V, Ni, Zn, Cd and Pb are all enriched relative to average black shales but only U and Mo correlate to organic matter content. Tectonically disturbed and metamorphosed allochthonous samples of Alum Shale on the Caledonian front in western Sweden have even higher amounts for some metals (V, Ni, Zn and Ba) relative to the autochthonous shales in this area and those in southern Sweden.

Introduction and geological overview

Black shales deposited in the marine environment commonly contain higher amounts of metals than gray shales (Vine and Tourtelot 1970, and references therein; Holland 1978). However, the suites of metals and their degree of enrichment in the black shales vary widely. The main syngenetic controls of metal content are depositional environment, source of metals, sedimentation rate, organic carbon content and organic matter type (Leventhal and Kepferle 1982; Coveney et al. 1987). Epigenetic tectonism and metamorphism can also affect the distribution and content of metals in some cases.

The Alum Shale Formation of Scandinavia is an organic rich marine sequence of Middle Cambrian to Early Ordovician age (Andersson et al. 1985 and references therein). The shales are represented by black laminated, dark brown organically banded and grey mudstones and referred to as "alum shales" because of their K, Al and S content. The Alum Shale Formation (Fig. 1) is generally between 15 to 35 meters thick in southern-central Sweden. Locally it can be separated into upper, middle and lower members based on interlayered carbonate concretions (stinkstones) or other lithologic characteristics and well preserved marine fauna.

The sedimentation rate is estimated to have been between 1 and 5 mm/1000 years (Thickpenny 1984 and references therein) or 1 to 2 meters/m.y. (Andersson et al.

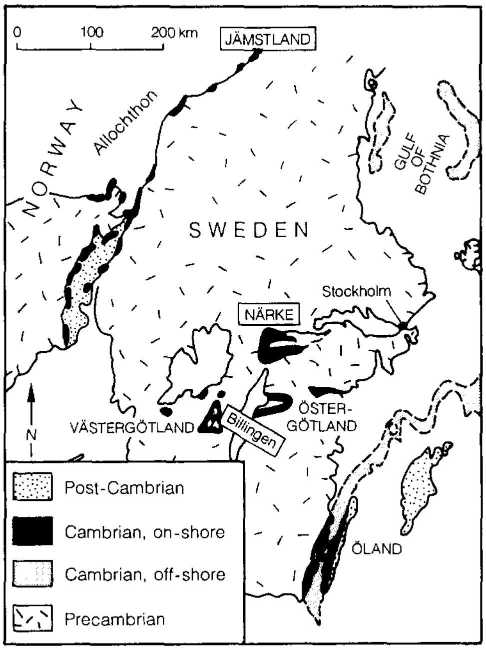

Fig. 1. Map showing extent of Alum Shale Formation in southeastern Baltoscandia (from Andersson et al. 1985). Note localities of samples, outlined: Jämtland in the north on the Caledoninan front; Närke; Sydbillingen/Ranstad samples are from Vastergotland (Billingen)

1985). The geochemistry of the Swedish Alum Shale Formation is presented in the summary papers (Armands 1972; Hessland and Armands 1978; Edling 1974; Andersson et al. 1983, 1985).

The purpose of this study of two organic carbon- and metal-rich shales is to compare their geochemical characteristics and to understand their differences. The work reported here began in 1979 with a suite of core samples from Ranstad, courtesy of David G. Gee (Swedish Geological Survey) and Astrid Andersson (Swedish Alum Shale Co). These samples were supplemented by additional core samples from Närke and Jämtland supplied by David Gee. The initial effort was to extend the earlier inorganic geochemical work and new emphasis on the study of organic matter association and control of uranium and other anomalous elements (Leventhal 1981 a, b, 1986, 1990). Since then, other workers have reported results on various aspects of geology and geochemistry (Andersson et al. 1983, 1985; Thickpenny 1987; Leventhal 1990), sedimentology (Thickpenny 1984; Dworatzek 1987), carbon isotopes (Buchardt et al. 1986), and organic geochemistry and radiation effects (Leventhal et al. 1986; Dahl et al. 1988 a, b; Lewan and Buchardt 1989).

Regional geology and samples

Samples were collected from three general areas in Sweden – the Ranstad-Billingen area in the south, about 100 km north east from Närke, and from Jämtland on the Caledonian in the northwest part of Sweden.

Billingen area

In this area (Fig. 1), the shale is 22–24 meters (m) thick and is near (tens of meters below) the present land surface. The beds are flat lying and undisturbed (Andersson et al. 1983, 1985). Shale samples in this study were from Sydbillingen core 16/74 near Ranstand from 4 depths, 2 in the uranium-rich unit (*P. scaraboeoides* zone) and 2 below this in the middle member (*A. pisiformis* zone). Several other shale samples (E, F and G) and the kolm-facies (cm. thick, organic-rich) samples were hand specimens collected in the Ranstad open pit mine and surrounding area. Near Ranstad there is a diabase sill that lies approximately 100 m above the Cambrian strata, which has caused some local heating (Cobb and Kulp 1961; Dahl et al. 1988 a, b).

Närke area

This area is somewhat different from Ranstad because the middle member is absent; the Alum Shale Formation is approximately 12 to 19 m thick and is buried about 30 m below the present surface (Anderson et al. 1983, 1985). Shale samples were from six intervals from the Kvarntorp 11/53 core. At Närke the organic matter is thermally immature.

Jämtland area

In this region on the Caledonian front the Alum Shale Formation is deformed and has been subjected to low grade metamorphism (Andersson et al. 1985; Snäll 1988). Regional overthrusting has resulted in tectonic repetition of the Alum Shale Formation (total thicknesses often around 150 m) (Andersson et al. 1985, Fig. 19). Analyzed samples were from the southern Storsjön-Myrviken drilling project from cores Mrviken 78001 and 78002 (5 samples) and 1 sample each from cores Häggenas 77001 and Lundkolen 77001. Snäll (1988) gives more information about this area and these boreholes, including lithology, mineralogy and geochemical analyses. The Häggenås and Lundkolen cores contain only autochthonous Alum Shale Formation, whereas samples from Myrviken cores are allochthonous material that has been transported from the west by tectonic overthrusting. The distance of transport may have been considerable because Gee (1980) reports that the Alum Shale is present 200 km west of the Caledonian front in western Norway. Thus the Cambrian shelf-type environment was quite extensive in western Scandinavia where it is now overridden by the allochthon (Bergström and Gee 1985). No kolm-facies has been recognized from this tectonically disturbed area. The maturity of the organic matter and crystallinity of the illite (Snäll 1988) for the entire alum shale (both autochthonous and allochtonous) in this area implies there has also been a Caledonian thermal effect due to loading of thrust sheets and probably also from heated fluids that may have been circulated and expelled during the thrusting.

Chattanooga Shale and its equivalents

The Middle to Upper Devonian (and locally Lower Mississippian) shales of the Appalachian basin have been extensively studied (Leventhal and Hosterman 1982; Leventhal et al. 1981; Leventhal 1987 and references therein) and are known by various names: Chattanooga Shale in Tennessee, New Albany Shale in Kentucky, Ohio Shale in Ohio and various names in New York and Pennsylvania (Marcellus, Genesee, West Falls and Java Formations). Sample SDO is a U.S.G.S. shale standard from Kentucky that is typical of the organic-rich Upper Devonian shales. In most of central to southern Pennsylvania and West Virginia the strata have been deeply buried to more than 1500 meters with the accompanying heating, resulting in thermal maturity of the organic matter into the dry gas zone. In regions further north (northern Pennsylvania), west (Ohio) and south (Kentucky and Tennessee) the shales have experienced much less burial and the organic matter is much less mature.

Analytical methods

Most major, minor and trace elements were determined by inductively coupled plasma-atomic emission spectroscopy (Lichte, Golightly and Lamothe 1987) after mixed-

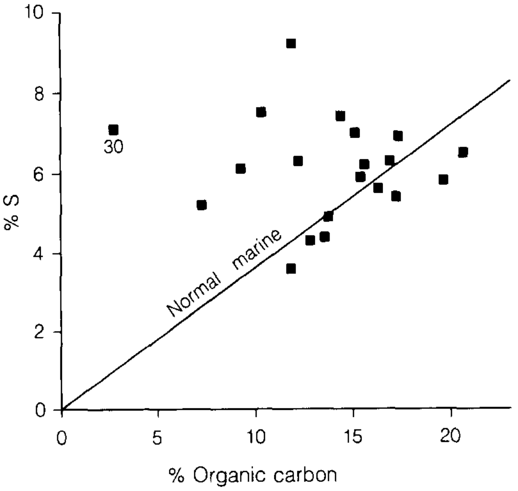

Fig. 2. Sulfur *vs* organic carbon plot; new data for 20 samples of Upper Cambrian alum shale. Line is for normal marine sediments (Leventhal 1983 a). Sample 30 is from Jämtland and has much lower C organic

acid digestion of samples. However, SiO_2 was measured by X-ray fluorescence (Taggart et al. 1987) and uranium by delayed neutron analysis (McKown and Millard 1987).

Organic geochemical methods are described in Leventhal et al. (1986). Rock-Eval pyrolysis was performed on all samples (Tissot and Welte 1978) using a Delsi model II with an organic carbon analyzer. Briefly, Rock-Eval is continuous heating of an aliquot (100 mg) of sample, first isothermally at 250 °C for 2 minutes and then from 255 to 600 °C at 25 °C/min and detecting the evolved materials. Volatile hydrocarbons (hc) released at temperature below 250 °C are designated S_1 (mg hc/g rock). Pyrolysis products released above 250 °C are designated S_2 (mg hc/g). The quantity S_2/% organic C is the hydrogen index (HI) that is correlative to the atomic H/C ratio. Thus a higher HI corresponds to a more organic hydrogen-rich or higher H/C containing material. Carbon dioxide released up to 390 °C is called S_3 (mg CO_2/g); S_3/% org C is the oxygen index (OI) and is analogous to the atomic O/C ratio. A higher OI value corresponds to a more oxygen-rich organic material. The temperature at which the release of S_2 products is a maximum is called T_{max} and this absolute value (not related to geologic temperatures) increases with thermal maturity. Kerogens with T_{max} below 420 °C are thermally immature with respect to petroleum generation, T_{max} values from 430 to about 455 °C represent the petroleum generation zone, values in excess of 455 °C are in the gas generation zone.

Results and discussion

Major, minor and trace elements

New analytical results are shown on Figures 2, 3 and 5 thru 9 for the major, minor and trace constituents, including metals, for 20 samples of alum shale. [This data is presented as Table 4]. Although this is a relatively small sample set it is typical of the larger sets reported by Andersson et al. (1985).

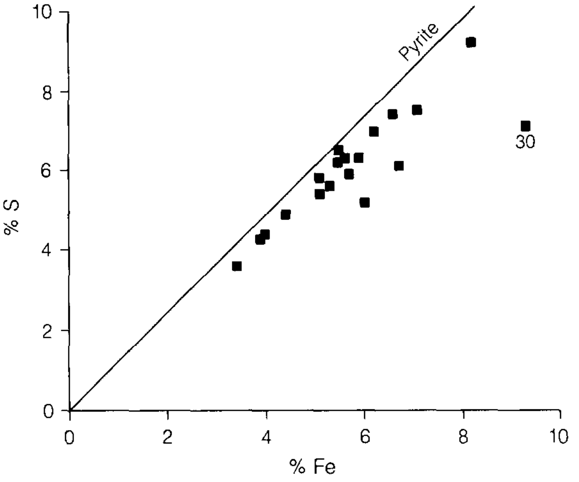

Fig. 3. Plot of sulfur *vs* iron for 20 samples of Upper Cambrian alum shale. Line is for pyrite, FeS_2, stoichiometry. Linear-least squares gives $r = 0.85$ for all data, $r = 0.94$ if sample 30 is omitted

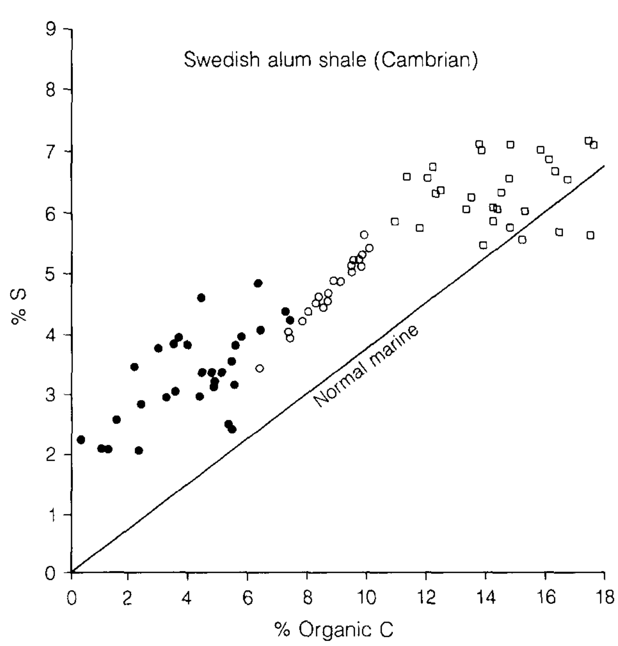

Fig. 4. Plot of sulfur *vs* organic carbon for upper (□) and middle (○ and ●) alum shale (date from Armands 1972). Normal marine line from Leventhal (1983 a)

By examining the relationship of major and minor constituents to each other in the alum shale, it is possible to understand the major geochemical controls. Figure 2 shows new results for organic C versus (vs) total S relationship for the alum shale. It can be seen that the S/C organic ratios for many samples are above the normal marine value (line on Fig. 2) and that there is not a well defined S/C organic trend line either through the origin or giving a clear intercept on the S axis. This can be understood by examining the data on Fig. 3 where the Fe and S data show a trend that is nearly coincident with pyrite stoichiometry (line in Fig. 3). This trend indicates that all reactive iron was sulfidized. This sulfidation re-

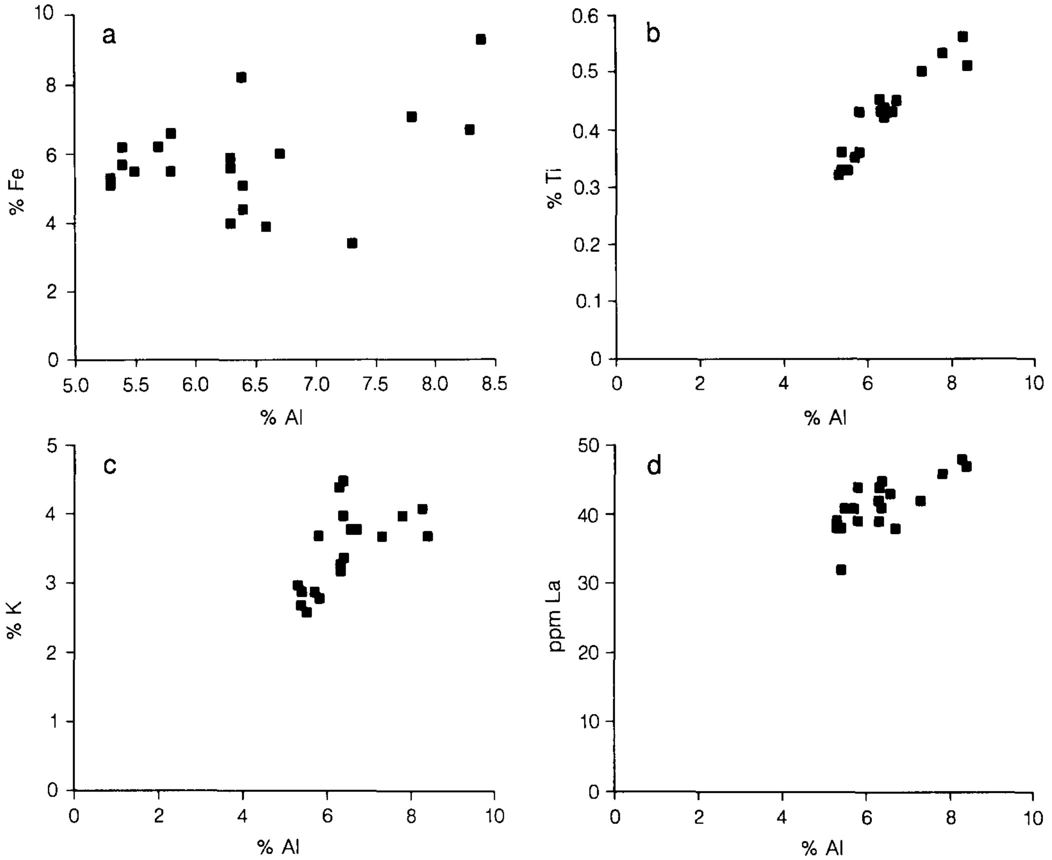

Fig. 5. **a** Plot of iron *vs* aluminum for 20 samples of Upper Cambrian alum shale; **b** plot of titanium *vs* aluminum; **c** plot of potassium *vs* aluminum; **d** plot of lanthanum *vs* aluminum

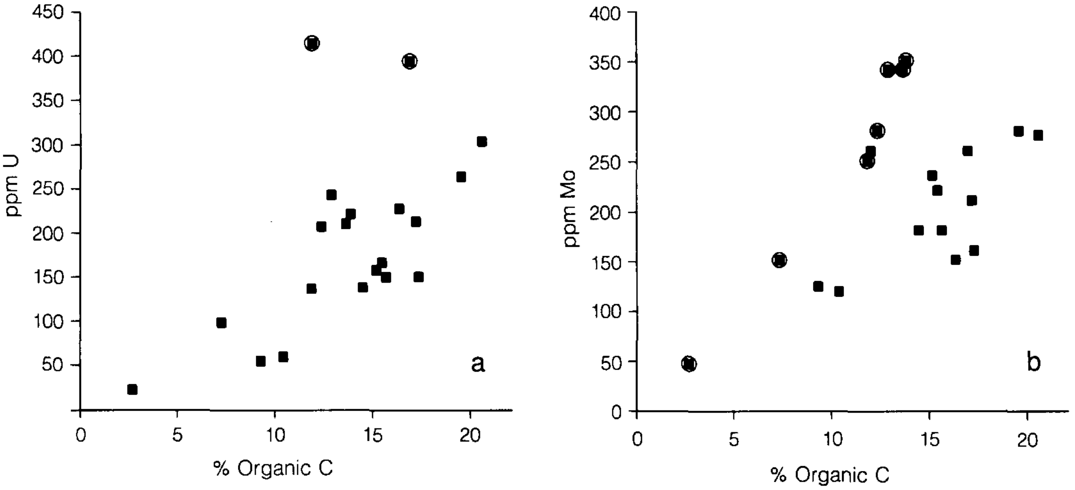

Fig. 6. **a** Plot of uranium *vs* organic carbon [circled squares are two Billingen samples]; **b** plot of molybdenum *vs* organic carbon [circled squares are 7 samples from the Caledonian front]

sults from the high organic C content providing excess substrate metabolizable organic matter with which the sulfate reducing bacteria produce excess hydrogen sulfide (Leventhal 1983a). Excess is required because some of the sulfide does not react with iron or it escapes and is oxidized. As an illustration of this, note that sample 30 with a much lower organic C content that places it far from the other samples in Fig. 2. This resulted in a much lower degree of sulfidation for sample 30, i.e. it plots far from the other samples and the pyrite line (in Fig. 3). Thus, despite the high S-C ratio of samples 30, the iron is not as completely sulfidized as in the other samples that had much higher organic C contents. Therefore, this S vs C plot for these samples from the alum shale will not show a slope or intercept that can be interpreted because of limitation of reactive iron. However, the very high degree of sulfidation of iron and combination of high organic C and very slow deposition rate do indicate a euxinic (H_2S) depositional environment. Figure 4 shows a more complete set of organic C and S data from Ar-

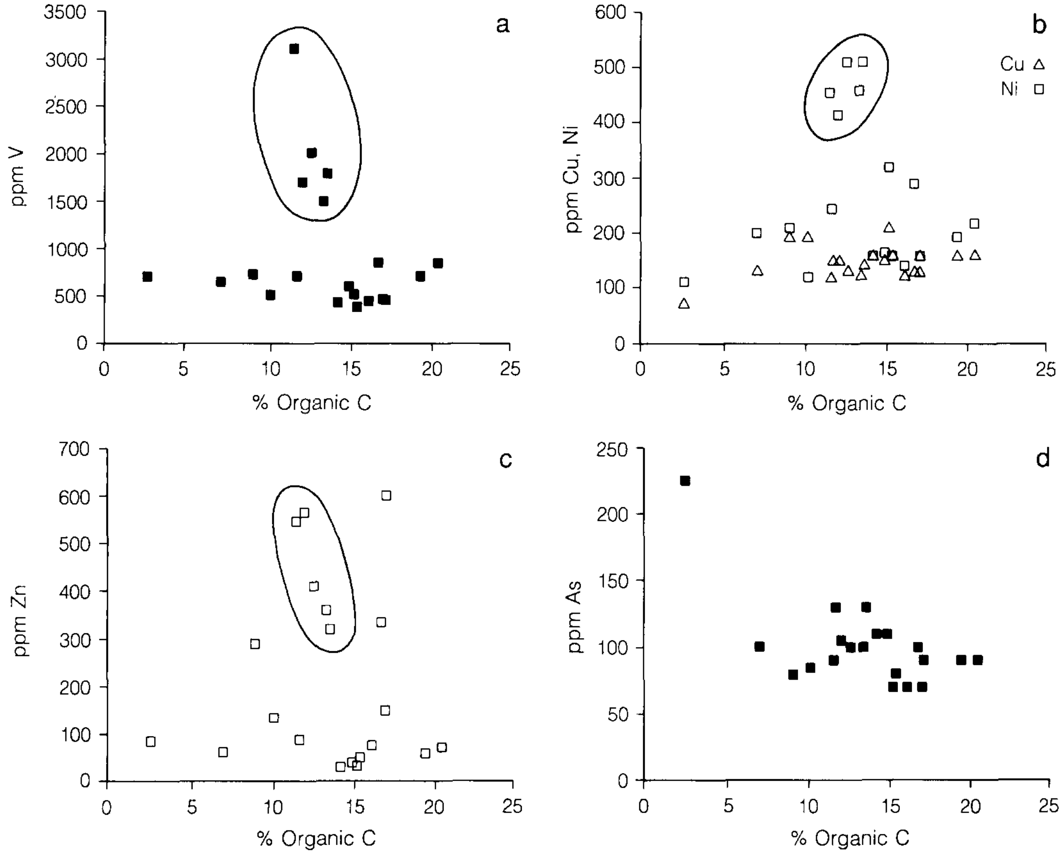

Fig. 7a–d. Plots of organic carbon *vs* vanadium (**a**), copper and nickel (**b**), zinc (**c**), and arsenic (**d**). Circled group is samples from the allochthon on Caledonian front

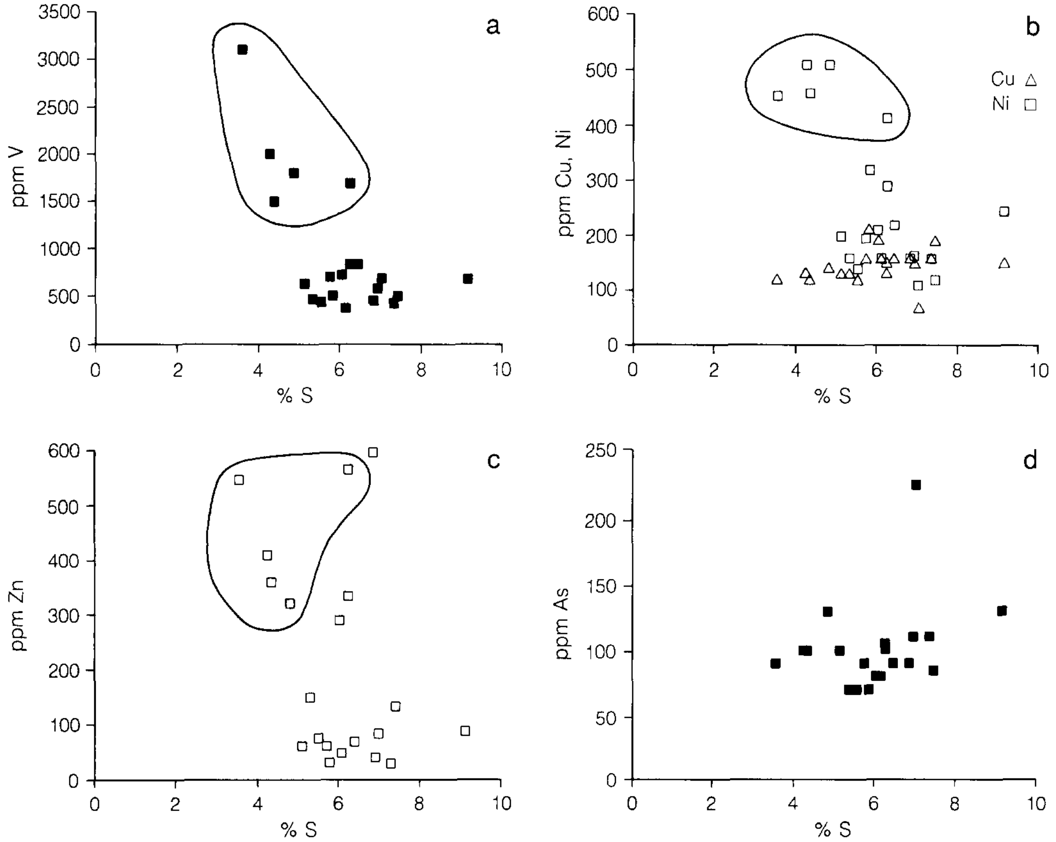

Fig. 8a–d. Plots of sulfur *vs* vanadium (**a**), copper and nickel (**b**), zinc (**c**), and arsenic (**d**). Circled group is allochthonous samples from Caledonian front

mands (1972), which includes both Middle and Upper Cambrian Alum Shale samples, a trend line (not shown) of this S and organic C data would show an intercept on the S axis that is indicative of an euxinic environment (Leventhal, 1979, 1983a, b, 1987).

As expected, a plot of Al vs Fe for the alum shale shows no relationship (Fig. 5a). The plot of Al vs Ti shows a good correlation ($r = 0.94$, significant at >99% level) converging to the origin due to fine grained/clay/refractory minerals, as is typical for shales (Fig. 5b). The plot of Al vs K ($r = 0.63$, significant at the 99% level) shows that some fraction of these elements are together probably feldspar or illite (Fig. 5c). The plot of Al vs La shows a good correlation ($r = 0.76$) as expected for shales (Fig. 5d) as does Ti vs La (not plotted). Neither Fe or Al are correlated with metals U, V, Mo, Ni, Cu, Zn or with As. Only U and Mo are correlated with organic carbon (Fig. 6a, b). The U and organic carbon relationship becomes more striking (correlation coefficient $r = 0.80$, significant at the 99% level) if two samples from Billingen (circled squares) are not considered. In the case of Mo, the 7 samples from the Caledonian front (circled squares) seem to show a greater enrichment of Mo relative to organic carbon ($r = 0.98$), whereas the the samples from southern Sweden have relatively less Mo and a lower correlation ($r = 0.62$, significant at the 97% level). The relationship of increased Mo and U with organic C has been noted before for many shales (Vine and Tourtelot 1970; Leventhal 1981a). Coveney et al. (1987) showed that U and Mo were especially enriched relatively near shore compared to off-shore samples.

Other elements, V, Ni, Cu, Zn and As, are *not* correlated with either organic C or sulfur contents (Figs. 7a–d and 8a–d). This is in contrast to many black shales that are enriched in these elements and do show a positive correlation with organic C or S. However V, Zn, Cd, Ni, Mn and Ba (but not As or Cu, Pb, Cr, Co) are greatly enriched in the 5 allochthonous samples (circled in Figs. 7 and 8). These samples show intermediate S and organic C contents and are all from the northwest part of Sweden on the Caledonian front. This area has been affected tectonicaly (Gee 1980; Sundblad and Gee 1984; Snäll 1988) and probably heated waters have leached these metals from a basement basaltic source (Leventhal 1990).

Table 1. Alum shale Rock-Eval results

Sample	% C_{org}	T_{max}	HI	OI
Närke core				
7.9–8.5[a]	13.5	423	439	44
9.2–9.7[a]	15.0	424	421	48
10.5–11.5[a]	14.1	421	358	50
13.0–13.7[a]	12.3	423	409	49
14.1–14.5[c]	16.1	422	523	36
14.5–15.2[a]	17.4	423	516	46
Sydbillingen core				
4.2–4.3[c]	17.3	437	136	8
6.0–6.1[b]	10.5	430	103	6
″box *[c]	10.9	431	89	18
″vial *[c]	10.6	428	92	17
11.1–11.2[b]	9.5	427	195	10
″box *[c]	9.2	430	185	26
″vial *[c]	9.2	430	191	27
13.0–13.1[c]	6.8	440	183	38
Billingen area (Randtad F, G, Skvode E)				
E[c]	13.1	425	126	12
F[b]	13.2	431	131	16
G[c]	19.6	440	104	12
Jämtland cores Autochthon				
003[b]	7.3	(–)	5	1
030[c]	1.7	(–)	5	29
Jämtland cores Allochthon				
037[b]	12.6	452	19	6
045[c]	7.9	(–)	8	14
045-1 *[c]	6.7	(–)	10	14
045-2 *[c]	6.5	(–)	8	15
068[c]	3.3	(–)	27	28
083[b]	11.6	516	18	3
253[b]	14.1	(–)	10	3
Kolm samples				
Kolm Er[a]	48.2	438	99	17
″*[b]	–	440	87	11
Kolm Ge[c]	53 #	446	105	29
Kolm N[a]	53 #	436	160	27
″*[c]	–	439	166	20

[T_{max} in °C; HI in mg hc/g C; OI in mg CO_2/g C; date of analysis, a = 7/84, b = 11/84, c = 4/87; analyst T. Daws, * replicate of previous sample; # LECO C_{org}. Organic C values for over-mature organic matter by Rock-Eval are lower than LECO due to incomplete combustion; – T_{max} values on over-mature organic matter are often unreliable, in parentheses.]

Organic matter: Rock-Eval results

Rock-Eval results are similar to those given by Buchardt et al. (1986) and by Dahl et al. (1988a, b) for southern Sweden. Replicate analyses (Table 1) of the Sydbillingen core show that storage of ground samples, even in non-air tight containers, has very little, if any, effect on the pyrolysis yields. The HI and T_{max} values (Table 1) show a wide range of values, from Närke where the unit is immature, to the Billingen area where a nearby sill has marginally matured the organic matter, to the Caledonian front (Jämtland) where organic matter is over mature. Despite these widely varying thermal maturity values, the elemental, metal and mineral contents are quite similar except for certain metals in the Jämtland area. Rock-Eval maturity data are important because they show the relative thermal histories, in particular the heating on the Caledonian front where some metal values are enriched.

Rock-Eval HI and T_{max} values for kolm samples show effects of radiation by U and its daughters because the HI is decreased and the T_{max} is increased. Organic C content of kolm samples are rather uniform but Fe and S and other constituents such as metals are quite variable. Complete chemical data, including Rare Earth element contents, of the kolm and a discussion of the kolm geochemistry are presented in Leventhal (1990).

Comparison of element enrichments

Figure 9 shows selected element ratios in samples from the Cambrian Swedish alum shale from Ranstadt and Jämtland and Appalachian Devonian shale (SDO) relative to average shale. Aluminum and other major elements (Si, K, Mg, Ti, Na, Ca, not plotted) are diluted by the organic C. The ratios of trace elements are shown on the right side of Fig. 9. It is clear from this diagram that alum shales from Jämtland on the Caledonian front are more enriched than the samples from southern Sweden. These Alum Shale samples from Jämtland, on the Caledonian front, are enriched in V, Zn, Ni, Ba and P (in that order), relative to the samples from southern Sweden (Billingen and Närke). Similarly, samples from southern Sweden are more enriched than Appalachian Devonian shales (represented by SDO-1). The shale samples from southern Sweden (Ranstad) are enriched in U, Mo, As, V, Ni, Cu and Pb (in that order) relative to average shale.

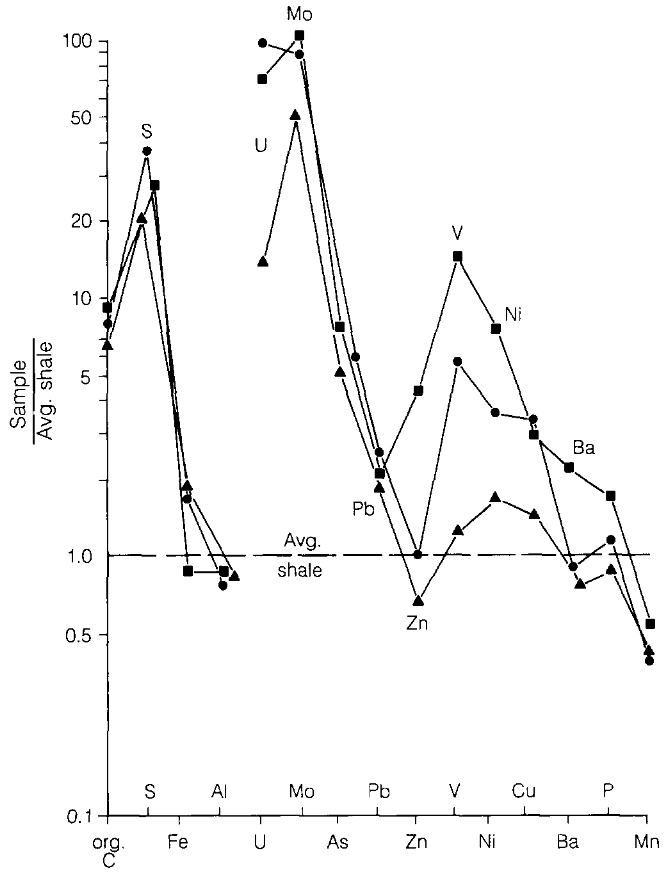

Fig. 9. Plot showing ratios of elements to average shale. SDO is Appalachian Devonian shale; Ran is Ranstad southern Sweden; Jamt is Jämtland (Leventhal 1990). ▲ SDO ● Ran, ■ Jamt

Assuming that the element contents in the Sydbillingen core samples (Ranstad, southern Sweden) represent normal syngenetic unmetamorphosed alum shale, the allochthonous Jämtland samples are especially enriched in V, Zn, Ni, and Ba relative to the Sydbillingen samples. This suite of enriched elements could be derived by the interaction of heated water with rocks (Leventhal 1990) in the Caledonian cover and basement (including subordinate basic rocks) during regional tectonic events (Sundblad and Gee 1984). A basic rock source would be expected to contribute Mn, but Mn is not greatly enriched in the Jämtland samples. This can be explained by the high solubility of Mn under reducing conditions that would be expected in the shale.

The geochemical results for the Appalachian Devonian shales (Table 2) from different localities (Leventhal et al. 1981 give results for 200 samples) can be compared to the alum shale results. Rock-Eval data are summarized

Table 3. Devonian Appalachian Rock-Eval results (see Table 2 for explanation)

Core sample	Depth m	T_{max}	HI	OI
Shallowly buried				
TN-3	120	435	300	20
OH-3	270	430	500	10
KY-4	360	442	400	6
SDO-1	20	421	395	14
Deeply buried				
WV-7	1900	455	30	20
PA-4	2300	>470	<5	40

Table 2. Geochemical results for Appalachian Devonian shales

Core samples	Depth meters	% Fe	% S	%orgC	ppm							
					U	Mo	V	Ni	Zn	Cu	As	Mn
Shallowly buried samples from Penn., N.Y., Ohio, Tenn, Kent												
KY-4	360	4	2	4	20	70	500	150	150	100	20	300
PA-3	270	3.5	3.5	2	11	30	200	80	–	100	–	200
OH-4	270	4	2.5	2.5	8	20	200	70	120	150	30	300
TN-7	120	4	2	2	13	30	200	100	130	100	25	500
NY-x	270	3	2	4	25	70	300	150	–	70	–	150
SDO-1	20	6.6	5.5	10	53	160	160	110	60	62	70	340
Deeply buried samples Pennsylvania and West Virginia												
WV-7	1900	5	1	1	6	5	300	70	–	100	–	–
PA-1	1480	3.5	0.7	1.5	5	5	250	70	80	100	25	700
PA-2	2200	5	3	2	20	70	500	200	70	200	30	200
PA-4	2300	4	1.4	1.2	4	3	200	70	60	70	20	400

Table 4. Chemical analyses of Cambrian Alum shale samples

Sample	Percent						$\delta^{13}C$‰	Parts per million										
	SiO_2	Al	K	Fe	S	OrgC		U	Mo	V	Ni	Zn	Pb	Cu	Cr	Co	Mn	Ba
Närke core (Kvarntorp 11/53)																		
7.9–8.5 m	–	5.4	2.9	5.7	5.9	15.4	–	164	220	510	320	31	60	210	68	30	180	360
9.2–9.9 m	–	5.3	3.0	5.1	5.4	17.2	–	210	210	470	160	150	39	130	66	27	200	340
10.5–11.5 m	–	5.3	3.0	5.3	5.6	16.3	–	224	150	450	140	75	34	120	63	23	190	350
13.0–13.7 m	–	5.8	2.8	6.6	7.4	14.4	−28.2	136	180	430	160	28	30	160	70	35	150	370
14.1–14.5 m	–	5.5	2.6	5.5	6.2	15.6	−28.2	147	180	380	160	49	28	160	62	33	350	340
14.5–15.2 m	–	5.7	2.9	6.2	6.9	17.3	–	147	160	460	160	600	30	160	67	31	140	380
Sydbillingen core 16/74																		
4.2–4.3 *m	45.2	6.4	4.0	5.1	5.8	19.6	−27.9	260	280	710	195	60	43	160	64	22	250	440
6.0–6.1 *m	45.7	6.4	4.5	8.2	9.2	11.9	−28.3	410	260	695	245	90	48	150	80	30	390	490
11.1–11.2 *m	47.2	7.8	4.0	7.1	7.5	10.3	−29.7	58	120	510	120	135	29	190	82	39	220	560
13.0–13.1 *m	48.2	8.3	4.1	6.7	6.1	9.2	−30.1	53	125	730	210	290	32	190	85	39	250	590
Billingen area (F and G, Ranstad; E, Skvode)																		
E*	50.9	5.4	2.7	6.2	7.0	15.1	−28.5	155	235	595	165	40	58	150	55	24	140	540
F*	45.4	6.3	4.4	5.9	6.3	16.9	−28.4	390	260	845	290	335	45	130	64	29	250	630
G*	43.2	5.8	3.7	5.5	6.5	20.6	−29.0	300	275	845	220	70	37	160	60	23	220	490
Jämtland cores Autochthon																		
003*[c]	55.7	6.7	3.8	6.0	5.3	7.2	−29.2	97	150	640	200	60	115	130	72	28	160	490
030*[d]	50.2	8.4	3.7	9.3	7.1	2.7	−30.4	22	47	700	110	85	140	69	89	34	340	310
Jämtland cores Southern Storsjön-Myrviken cores Allochthon																		
037*[e]	52.4	6.6	3.8	3.9	4.3	12.8	−29.4	240	340	2000	510	410	40	130	85	24	430	1200
045*[e]	48.8	6.3	3.3	5.6	6.3	12.3	−28.9[a]	204	280	1700	415	565	85	150	86	22	540	1000
068*[f]	49.1	6.3	3.2	4.0	4.4	13.6	−29.0[b]	207	340	1500	460	360	75	120	90	23	550	2600
083*[f]	52.8	7.3	3.7	3.4	3.6	11.8	−28.8	134	250	3100	455	545	35	120	210	22	400	2100
253[g]	51.0	6.4	3.4	4.4	4.9	13.8	−29.3	218	350	1800	510	320	40	140	85	23	440	1200
Appalachian Devonian reference standard (Leventhal et al. 1978) and average shale (Turekian and Wedepohl 1961)																		
SDO-1*	49.8	6.6	2.8	6.6	5.5	10.2	−29.7	53	160	160	110	60	36	62	67	46	340	410
Avg shale	58.5	8.0	2.7	4.7	0.24	1.6	–	4	3	130	68	95	20	45	90	19	850	580

Replicate analyses [a] −29.5; [b] −29.4; * average of two analyses. [c] Häggenås 77001 7799---; [d] Lundkolen 77001---; [e] Myrviken 78001---; [f] Myrviken 78004---; [g] Myrviken 78002---. (Most analyses in replicate by inductively coupled plasma-atomic absorption spectroscopy, analyst F. Lichte, except U by delayed neutron analysis, analyst D. McKown; C and S by Leco combustion, analyst M. Stanton; SiO_2 by x-ray fluorescence, analyst J. Taggart; complete data available from the author upon request; m depth in meters)

on Table 3 (Ted Daws, USGS, new data) and show the large differences in the T_{max} and HI values for the marginally mature (for example core OH3) to over mature organic matter (in core PA4, for example). However, the organic carbon contents and metal values for the shallowly buried samples are very similar to the data from the deeply buried samples. There is *no* obvious gain or loss of metals that is due to burial and heating.

Conclusions

The Scandinavian Alum Shale Formation is an unusual metal-rich black shale, some of which is on the tectonically disturbed Caledonian front. The Alum Shale Formation is enriched in organic matter of marine origin that was deposited offshore at a depth of at least 100 meters to allow stratification of the water column and formation of a bottom, stable euxinic layer. These euxinic bottom waters caused efficient trapping of metals by reduction and preservation of organic matter and associated metals (Leventhal 1990). A low sedimentation rate also enhanced metal contents because of a lack of clastic dilution. As a result, iron is completely sulphidized and all reducible metals are fixed in the sediment as sulphides or associated with organic matter. Excess organic matter and sulfide reducant accounts for a lack of correlation of most metals because all metals were fixed in the sediments.

The alum shale on the Caledonian front has undergone low-grade metamorphism and during this process the heated waters probably leached metals from the associated metasediments and/or underlying basement rocks. As a result metals (V, Ni, Zn, and Ba) were epigenetically added to the allochthonous materials during the Caledonian orogeny, about 100 m.y. after the shale was deposited (Andersson et al. 1985); these metals were fixed in the shale by the organic matter and pyrite-sulfide acting as reductants. In contrast, the Upper Devonian shales of the Appalachian Basin all show similar metal contents that are generally controlled by organic C or S content, but never by burial-heating history or epigenetic mobility.

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Pyrolysis gas chromatography-mass spectrometry to characterize organic matter and its relationship to uranium content of Appalachian Devonian black shales

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Abstract—Gas chromatographic analysis of volatile products formed by stepwise pyrolysis of black shales can be used to characterize the kerogen by relating it to separated, identified precursors such as land-derived vitrinite and marine-source *Tasmanites*. Analysis of a *Tasmanites* sample shows exclusively *n*-alkane and -alkene pyrolysis products, whereas a vitrinite sample shows a predominance of one- and two-ring substituted aromatics. For core samples from northern Tennessee and for a suite of outcrop samples from eastern Kentucky, the organic matter type and the U content (<10–120 ppm) show variations that are related to precursor organic materials. The samples that show a high vitrinite component in their pyrolysis products are also those samples with high contents of U.

INTRODUCTION

SEVERAL STUDIES have shown that organic matter in sedimentary rocks can be characterized by pyrolysis gas chromatography. (See for example GIRAUD, 1970; LEVENTHAL, 1976, 1978; SIGLEO, 1978; SCRIMA *et al.*, 1974.) However, only a few of these studies have related the pyrolysis products to a precursor biological material or identified marine and terrestrial organic components.

Many syngenetic and low-temperature epigenetic mineral deposits are intimately associated with organic matter. (See for example WEDEPOHL, 1964; GULBRANDSON, 1966; TAYLOR, 1971; MAUGHAN, 1976; DESBOROUGH, 1977; DESBOROUGH *et al.*, 1979; LEVENTHAL, 1979.) In studies of such ore deposits the types of organic matter were sometimes recognized, but the origin of the organic material and its possibly diverse roles in the formation of the ore deposits was not elucidated.

Work done during the 1950's by two groups presented evidence that uranium was concentrated by organic matter in shales (SWANSON, 1960, 1961; BREGER and BROWN, 1962, 1963); however their explanations were somewhat different. SWANSON (1960) discussed the oil yield and uranium content. He distinguished organic matter based on source: sapropelic vs humic, the former being hydrogen rich and derived from algae, spores etc., and latter from cellulose and lignin being H poorer. He attributes the high oil yield to the former and the high uranium content to the latter. His interpretations rely on the uranium content and oil yield of the alga *Foerstia* and wood from *Callixylon* from the Devonian Chattanooga shale which represent the sapropelic and humic prototypes, respectively. He proposes that uranium is preferentially removed from the sea water by the humic type kerogen or its precursor.

BREGER and BROWN (1962, 1963) measured the hydrogen content of the kerogen for many samples as a means to determine the proportions of sapropelic and humic material. They show that sapropelic rich kerogens yield more oil. They propose that since the uranium is highest near the inferred shoreline, the uranium is from the land. They also feel that since the uranium is generally correlated with the organic content the type of organic matter is not important in concentrating uranium.

This study extends the earlier work on the organic matter and uranium contents of Upper Devonian shales of Tennessee by including samples from a larger part of the Appalachian basin and by employing new analytical methods to more clearly define the syngenetic uranium–organic matter association. The overall study was related to the occurrence of gas and oil (CLAYPOOL and THRELKELD, 1978), trace elements (LEVENTHAL, 1979), and uranium (J. S. LEVENTHAL and R. C. KEPFERLE, unpublished data), which all are directly or indirectly related to the amount (LEVENTHAL and SHAW, 1980) and type of organic matter present and to the depositional environment. The uranium and organic matter in these shales is syngenetic, the uranium contents range from <10 to 120 ppm and are sub-economic at this time. However, two points should be made: (1) future economic utilization of the whole shale for minerals and energy; and (2) the role of black shales as a first step enrichment of uranium prior to epigenetic mineralization.

SAMPLES

Core samples were taken from Overton County, Tennessee (Tennessee coordinates 708,550 N. and 2,154,750 E.; API well No. 41-133-01001) (LEVENTHAL, 1979). At this location the Devonian Chattanooga Shale is at a depth of 181–207 ft (55–67 m). The samples used in this study were 10-cm pieces of core (Table 1). The general stratigraphy of this area is given in CONANT and SWANSON (1961).

Table 1. Organic carbon and uranium contents and pyrolysis peak ratios for core samples of Devonian shale from Overton County, Tennessee (see Figure 3 for M/L explanation)

Sample	Depth (ft)	Percent C organic	ppm U	M/L
T-2	182.7	6.5	25	0.83
T-3	184.2	7.7	29	.81
T-4	186.7	12.5	42	.92, .98*
T-5	189.7	11.1	81	1.20
T-6	192.2	13.5	91	1.21
T-7	194.7	10.8	76	1.27
T-8	197.2	4.8	41	<1.05
T-9	199.2	10.2	56	1.01
T-10	199.7	7.1	53	1.06
T-11	200.5	6.8	43	1.0
T-13	205.3	8.8	34	.83
Vitrinite		~60	120	1.47
Tasmanites		>60	<10	0.60

* Replicate.

Outcrop samples were collected from a recent roadcut on Interstate 64 in Rowan County, Kentucky, near the Morehead interchange (PROVO *et al.*, 1978) by the author and R. Kepferle (USGS). The samples represent 15-cm thicknesses of rock taken after removing surface material and were collected at 5-ft (1.5-m) intervals (Table 2).

Vitrinite was collected from a new roadcut north of Nashville, Tennessee, on Interstate 24 by the author and R. Kepferle. At this locality there are several 1–2-cm thick vitrinite layers in which cellular structures can be observed (vitrinite identification confirmed by N. Bostick, USGS).

A sample of shale rich in the marine palynomorph genus *Tasmanites* was supplied by Kepferle, who obtained it from F. Ettensohn (Univ. of Kentucky). It was collected from the Devonian New Albany Shale in Bullitt County, Kentucky.

EXPERIMENTAL

Specimens of *Tasmanites* were hand picked from broken shale pieces or surfaces and then were cleaned ultrasonically and dried. Similarly, pieces of vitrinite were hand picked from outcrop and core material. All samples except the *Tasmanites* specimens were ground with an agate mortar and pestle before pyrolysis. Stepwise pyrolysis–gas chromatography has been described by LEVENTHAL (1976), and so the experimental procedure is only briefly reviewed here. One to ten mg of finely powdered sample is placed in a 2.5-cm by 2-mm quartz tube, which is then put in spiral heating coil of a Pyroprobe* pyrolysis device. The Pyroprobe is inserted in the injection port of a gas chromatograph (GC) in helium carrier gas (~12 cm^3/min) and heated for 10 sec at 250°C. The pyrolysis products then pass into a 15-m by 0.5-mm (i.d.) porous-layer-open-tubular (PLOT) capillary column coated with Apiezon L* on Chromosorb* R-6740 and are trapped within the first 6 cm of the column which has been immersed in liquid nitrogen. In some experiments, packed 3.2-mm (o.d.) by 2-m OV-101 or OV-17* columns were used without the liquid nitrogen trap. After the trap has warmed to room temperature, the pyrolysis products are temperature programmed at 6°C/min from 50 to 280°C. The pyrolysis procedure is repeated 450, 600, 750, and 900°C (and sometimes 1050 and 1200°C), and in some analyses pyrolysis products from several steps are combined. GC output was fed to a Columbia Scientific Industries* Supergrator I electronic integrator and to a strip chart recorder.

Mass spectrometry (MS) was done using the same gas-chromatography columns and pyrolysis system in tandem with an AEI-MS-30* and DS 50* data system. Scan rate was 3 s/decade for the mass range 28-400 AMU. The ionizing voltage was 70 eV with a filament emission of 80 μA (ANDERS *et al.*, 1978). Carbon was analyzed as follows: total was by Leco* combustion, carbonate by acid leach gasometric, and organic by difference (LEVENTHAL *et al.*, 1978). Uranium was analyzed by the delayed neutron technique (MILLARD, 1976).

Table 2. Organic carbon and uranium contents and pyrolysis peak ratios for outcrop samples of Devonian and Mississippian shale from Rowan County, Kentucky

Sample	% C org	ppm U	P/Q
Su + 15	8.7	23	n.a.
Su + 10	12.2	72	1.08
Su + 5	11.1	57	.88
Sun base	14.9	39	.80
Bed	0.4	7	n.a.
Oh + 45	19.1	17	.50
Oh + 40	15.1	22	.49
Oh + 35	15.1	33	.53
Oh + 30	13.8	16	.50
Oh + 25	11.9	22	.54
Oh + 20	10.7	37	.57
Oh + 15	9.4	22	.66
Oh + 10	8.2	39	.64
Vitrinite	~60	120	2.77

Sample name and number refer to stratigraphic unit and distance from base in feet. Su is Sunbury Shale, Bed is Bedford Shale, Oh is Ohio Shale, in ft above Three Lick Bed (PROVO *et al.*, 1978).

See Figure 5 for P/Q explanation; n.a., not analyzed.

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* Mention of a brand name is for identification only and does not imply endorsement by the U.S. Geological Survey.

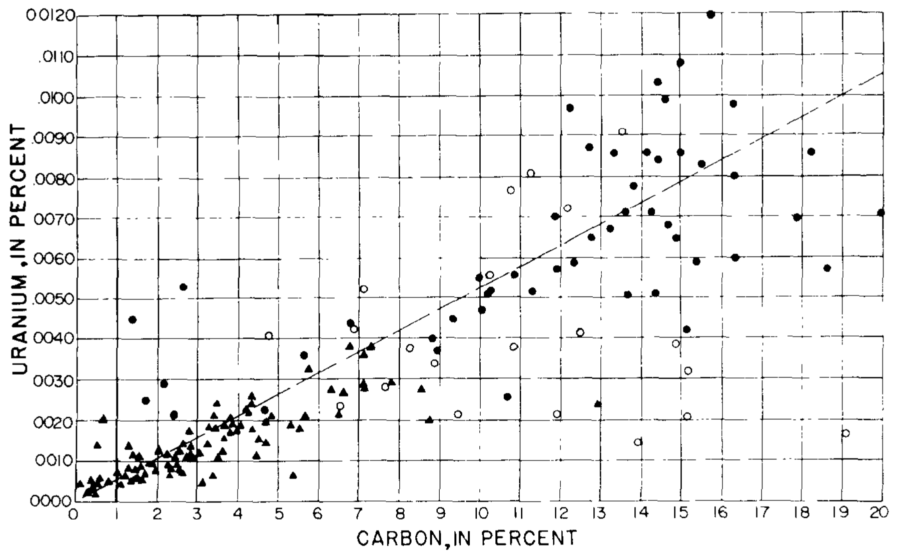

Fig. 1. Organic carbon vs uranium in Appalachian Devonian shale samples. Solid circles and line of correlation represent data from Swanson (1960); triangles show data from Leventhal and Goldhaber (1978), and Leventhal (1979), open circles show data from this study.

RESULTS

General

Organic carbon and uranium contents of the two sample suites are given in Tables 1 and 2. As previously recognized the organic carbon and uranium values show a correlation (Breger and Brown, 1963; Swanson, 1960). Figure 1 adapted from Swanson (1960) has additional new data added, however, the line is the one drawn by Swanson (1960). The data from Swanson (1960) are from central Tennessee, whereas the new data are from core samples from Kentucky, West Virginia, New York, Ohio and Virginia (Leventhal and Goldhaber, 1978; Leventhal, 1979).

Figure 1 also shows the data for the two suites (Tables 1 and 2) reported on here. Several of these samples show high amounts of organic material without the accompanying high uranium contents: this anomalous relation will be discussed later.

Pyrolysis–gas chromatography

Pyrograms of the core and outcrop samples show at least two types of organic matter are present. One type shows a predominance of *n*-alkane and -alkene pyrolysis products, the other shows a predominance

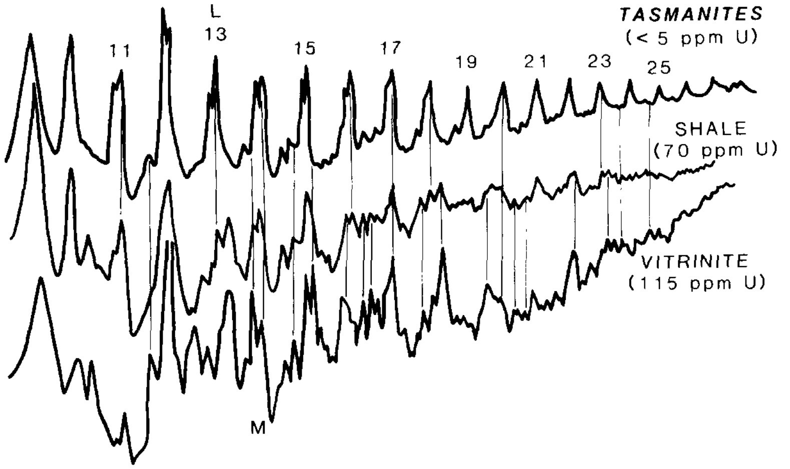

Fig. 2. High-temperature fingerprints showing *n*-alkane–alkene-rich *Tasmanites*, *n*-alkane–alkene-poor vitrinite, and a uranium-rich shale. Column Apiezon L. Numbers refer to *n*-alkane position. (See text for L and M.)

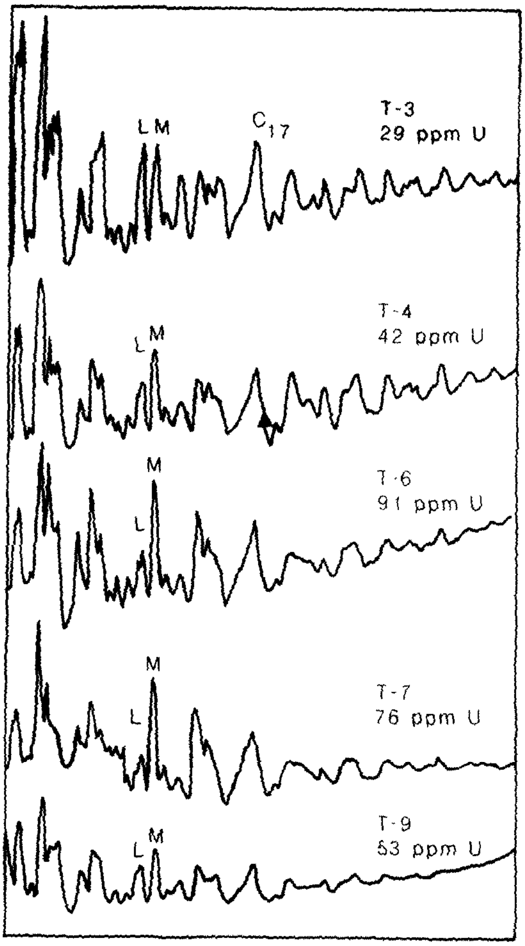

Fig. 3. Pyrogram of selected core samples from Overton County, Tennessee, showing relative heights of *n*-alkane–alkene peak (L) and adjacent non-*n*-alkane peak (M). See Table 1 for peak ratios. Column OV-101.

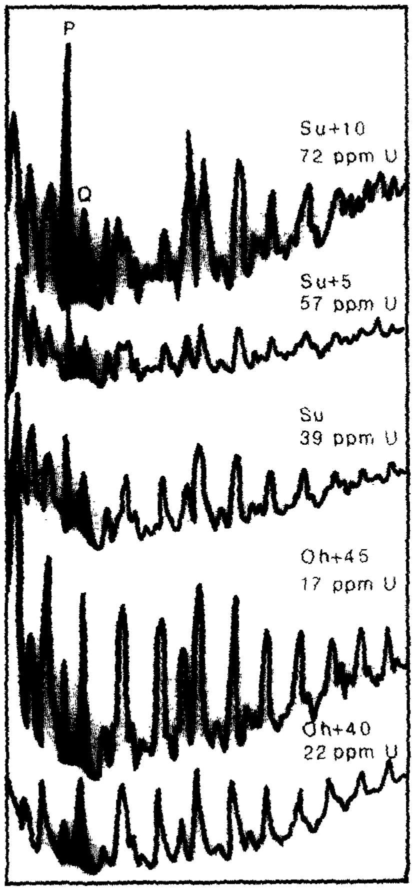

Fig. 5. Pyrograms of selected outcrop samples from Rowan County, Kentucky, showing relative heights of peak P (non-*n*-alkane–alkene) and peak Q (*n*-alkane–alkene). See Table 2 for peak ratios. Column is OV-17.

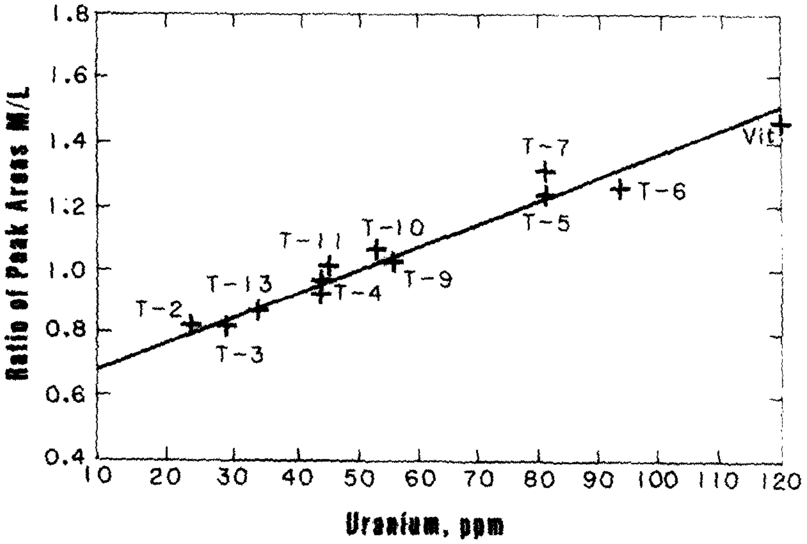

Fig. 4. Uranium content vs M/L peak area ratio for core samples from Overton County, Tennessee. Linear least-squares fit of data, for $U = M/L\ m + b$, $n = 10$, $r = 0.95$. The *Tasmanites*-rich sample and the vitrinite-rich sample were not used in the statistical fit.

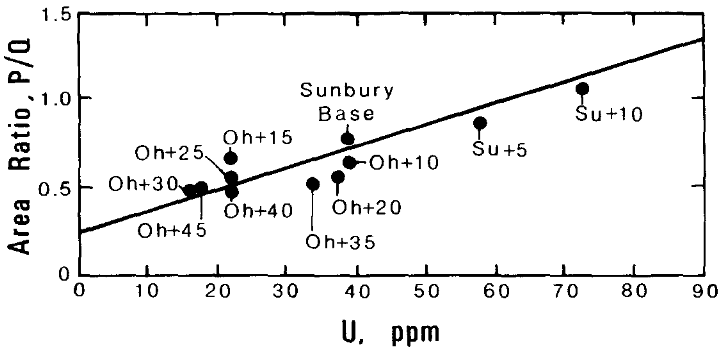

Fig. 6. Uranium content vs P/Q peak area ratio for outcrop samples from Rowan County, Kentucky. Line is linear least squares fit for U = P/Q $m + b$, $n = 11$, $r = 0.91$.

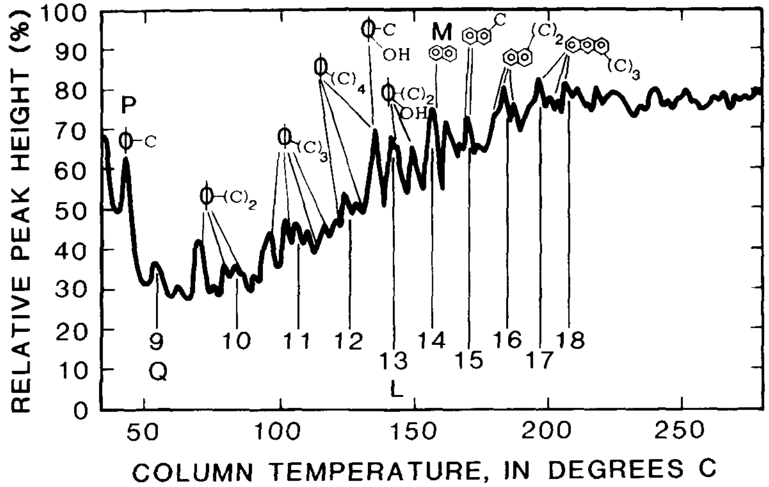

Fig. 7. Total ion plot from mass spectrometer analysis of pyrolysis–gas chromatography (OV-17) of vitrinite collected near Nashville, Tennessee. Numbers are *n*-alkane–alkene peaks, other identification symbols are for dominant substituted aromatic molecules.

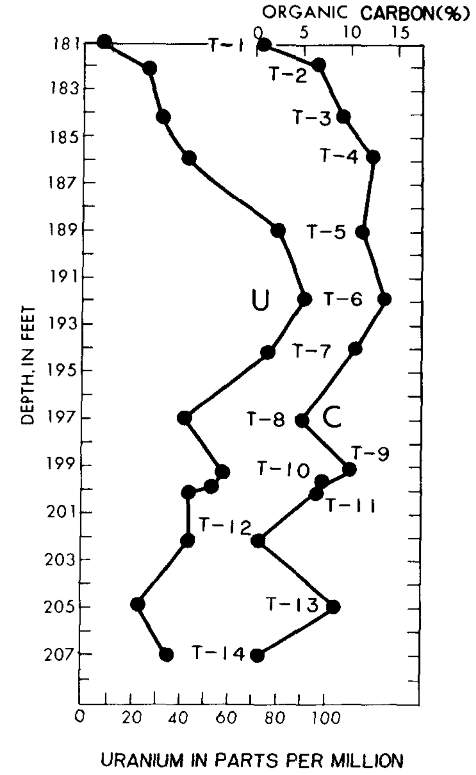

Fig. 8. Down-hole plot for uranium and organic carbon for core samples from Overton County, Tennessee.

of aromatic components. Pyrolysis of *Tasmanites* gives n-alkanes and alkenes; vitrinite pyrolysis produces substituted aromatics. Figure 2 shows the pyrograms for *Tasmanites*, a uranium-rich shale, and a vitrinite; the uranium contents were <5, 70, and 115 ppm, respectively.

Pyrograms of selected core samples from Overton County, Tennessee (Fig. 3), showed a variation in types of organic material which can be related to uranium content. None of these samples shows the n-alkane series as clearly as it was shown in the upper chromatogram of Fig. 2. However, mass spectrometry of these samples identified peak L as the n-C_{13} alkane–alkene peak and the adjacent peak M as naphthalene. Considerable variations in the relative peak height and the area between these two peaks were observed. The integrator areas of L and M were tabulated and their ratio (M/L) plotted vs uranium content (Fig. 4). The linear regression is significant at the 95% level. Thus, the qualitative difference of alkane and aromatic pyrolysis products can be quantified in this way by using two adjacent peaks and then can be related to uranium content.

Figure 5 shows the pyrograms for samples from the roadcut, taken at 5-ft (1.5-m) intervals, in Rowan County, Kentucky. These samples were pyrolyzed, and chromatography was done using an OV-17 column. Peak Q was identified as the n-C_9 alkane–alkene peak. The peak area for Q was compared to adjacent peak P, which was identified as toluene. Figure 6 shows the P/Q ratio vs the ppm U for these samples. The line shows the linear regression, which is statistically significant at the 95% level.

Figure 7 shows the mass spectrometer total-ion plot for a vitrinite sample run on an OV-17 column. This is the same vitrinite plotted in Fig. 4 (run on OV-17) and Fig. 2 (run on Apiezon L). The n-alkene and -alkane peaks are identified, as are the aromatics. The peaks P and M are identified as toluene and naphthalene, respectively, based on parent and fragment ions on GC–MS runs. Figures 8 and 9 (and Tables 1 and 2) show how the uranium and organic carbon contents vary vertically in the Tennessee core and the Kentucky outcrop. In general, a good covariance is seen between organic carbon and uranium content (BREGER and BROWN, 1962, 1963; SWANSON, 1960; LEVENTHAL and GOLDHABER, 1978; J. S. LEVENTHAL, unpublished data), and this covariance is also observed in these two suites of samples. However, there are several exceptions: samples T-4, T-13, Oh + 40, and Oh + 45 show high amounts of organic matter without similarly high amounts of uranium.

Table 3. Rock-Eval results for four samples from Rowan County, Kentucky (see Table 2 for other data)

Sample	H_2 index	O_2 index	Kerogen type
Su + 10	408	21	II-III
Su + 5	380*	30*	II-III
Oh + 45	473	15	I-II
Oh + 30	633	29	I-II

* Average of 3 analyses.

Rock–Eval analysis (TISSOT and WELTE, 1978) was run on several samples for comparison with the pyrolysis. The results for four of the Kentucky samples are shown in Table 3. Samples Oh + 30 and +45 with the lowest U contents show high hydrogen indices from Rock–Eval data which puts them between type I and II kerogen. Conversely, samples Su + 5 and +10 with the highest U contents show lower H indices and plot between type II and III kerogen.

DISCUSSION AND CONCLUSIONS

It was found that the uranium content in these Devonian shales can be correlated with the ratio of aromatic compounds (toluene or naphthalene) to n-alkane compounds derived from pyrolysis of the organic matter in the shales. This association is true even where the total organic carbon does not correlate with total uranium. This distinction between types of organic matter has been suggested by pre-

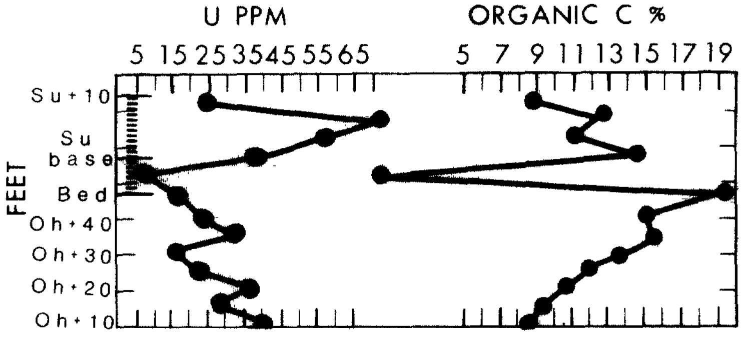

Fig. 9. Vertical plot of uranium and organic carbon contents in outcrop samples from Rowan County, Kentucky. Oh + 10 is 10 ft above the Upper Devonian Three Lick Bed of the Ohio Shale (PROVO *et al.*, 1978); Bed is the Devonian or Mississippian Bedford Shale; Su is the Mississippian Sunbury Shale.

vious workers (SWANSON, 1960) from analysis of pure organic source members but was not recognized (BREGER and BROWN, 1962, 1963) in shale samples themselves. Although the aromatic component is correlated with pyrolysis products from a true vitrinite sample, this component might come from a solubilized amorphous vitrinite-derived material rather than from vitrinite itself; that is, the shale may yield a large amount of vitrinite pyrolysis products but contain only a small amount of visually recognizable vitrinite. If this solubilized material was derived from vitrinite, it probably was a humic material, derived from the land and brought into the Devonian Appalachian sea by rivers (SWANSON, 1960). These same rivers could also have transported the uranium from the inland source areas. However, it is not known whether the land-derived organic material was the transport agent for the uranium. Samples T-13 and Oh + 45, which have high organic contents but relatively low uranium contents, are exceptions to the generally observed uranium and organic-carbon covariance. This circumstance may be explained by the distribution of organic types shown by pyrograms and M/L or P/Q peak ratios. These two samples show a predominance of *n*-alkanes and low P/Q or M/L ratios and corresponding low U in spite of the high amounts of organic matter. This alkane-rich (marine) organic matter is not the type that shows a covariance with uranium.

In summary, pyrolysis–gas chromatography has been used to characterize a marine and terrestrial organic component in Devonian shales. The syngenetic uranium content is related to the terrestrial organic component of the shale. Whether this is due to scavenging of the uranium by the terrestrial organic matter in rivers, the seawater or the sediment–water interface is not known.

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RESEARCH ARTICLE

Occurrence and behavior of uranium and thorium series radionuclides in the Permian shale hydraulic fracturing wastes

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Abstract

Over the last decade, there has been a rapid growth in the use of hydraulic fracturing (fracking) to recover unconventional oil and gas in the Permian Basin of southeastern New Mexico (NM) and western Texas. Fracking generates enormous quantities of wastes that contain technologically enhanced naturally occurring radioactive materials (TENORM), which poses risks to human health and the environment because of the relatively high doses of radioactivity. However, very little is known about the chemical composition and radioactivity levels of Permian Basin fracking wastes. Here, we report chemical as well as radiochemical compositions of hydraulic fracking wastes from the Permian Basin. Radium, the major TENORM of interest in unconventional drilling wastes, varied from 19.1 ± 1.2 to 35.9 ± 3.2 Bq/L for ^{226}Ra, 10.3 ± 0.5 to 21.5 ± 1.2 Bq/L for ^{228}Ra, and 2.0 ± 0.05 to 3.7 ± 0.07 Bq/L for ^{224}Ra. In addition to elevated concentrations of radium, these wastewaters also contain elevated concentrations of dissolved salts and divalent cations such as Na^+ (31,856–43,000 mg/L), Ca^{2+} (668–4123 mg/L), Mg^{2+} (202–2430 mg/L), K^+ (148–780 mg/L), Sr^{2+} (101–260 mg/L), Cl^- (5160–66,700 mg/L), SO_4^{2-} (291–1980 mg/L), Br^- (315–596 mg/L), SiO_2 (20–32 mg/L), and high total dissolved solid (TDS) of 5000–173,000 mg/L compared to background waters. These elevated levels are of radiological significance and represent a major source of Ra in the environment. The recent discovery of large deposits of recoverable oil and gas in the Permian Basin will lead to more fracking, TENORM generation, and radium releases to the environment. This paper evaluates the potential radiation risks associated with TENORM wastes generated by the oil and gas recovery industry in the Permian Basin.

Keywords Fracking · Oil and gas · Radium · Alpha spectrometry · Gamma spectrometry

Introduction

The Permian Basin, which stretches from southeastern New Mexico into west Texas, is now recognized as the largest and most prolific oil and gas producing region in the USA. The area is approximately 482,803-m long by 402,336-m wide and comprises several basins of which the Midland Basin is the largest, followed by the Delaware Basin, with the Marfa Basin being the smallest (Fig. 1). Although the Permian Basin has been drilled continuously for over 100 years, the innovation of hydraulic fracturing technology in 1947 and its combination with horizontal drilling in the 1990s opened access to deep oil-rich shale deposits. This technology has enabled the recovery of oil and natural gas from tight shale formations that were previously considered uneconomical, resulting in a "shale gas boom." In 2019 alone, the Permian Basin accounted for more than 35% of crude oil and more than 16% of total dry natural gas produced in the USA. According to recent estimates by the U.S. Geological

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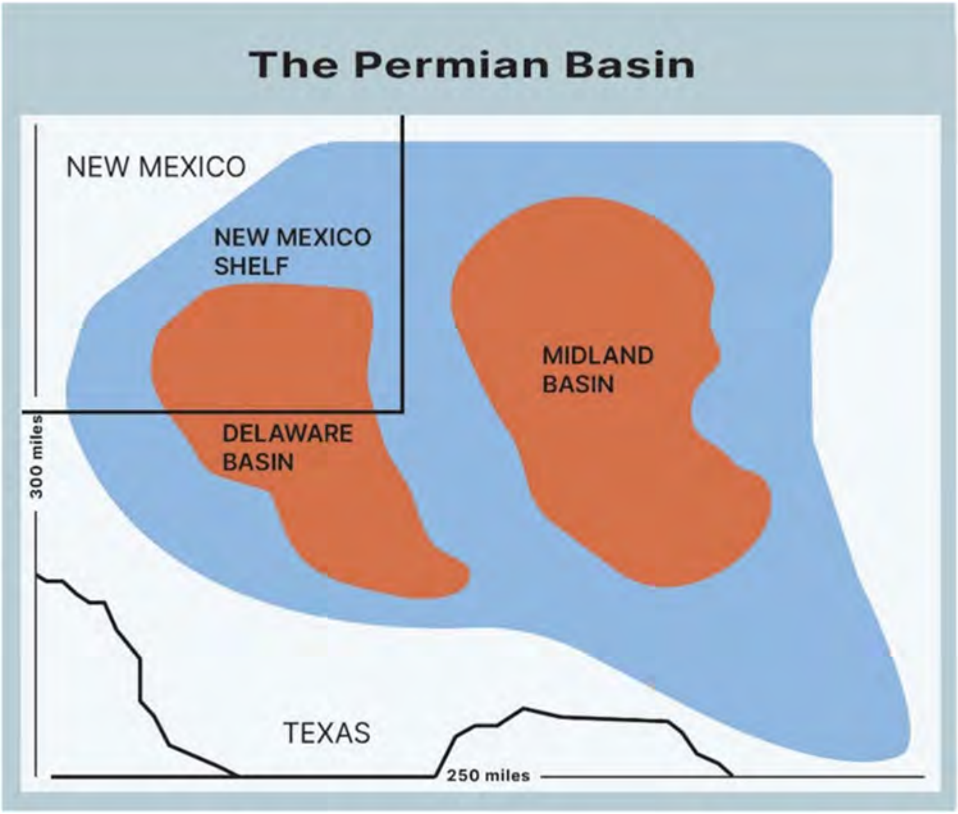


Fig. 1 Map of the Permian Basin

Survey, technically recoverable oil and gas reserves in the Permian Basin are some 7.4×10^{12} L of oil and 80 billion m^3 of natural gas (Gaswirth et al. 2018). Projections suggest that oil and gas production could grow from the current 7.4×10^8 million L per day to nearly 1.9×10^9 L per day by 2030.

Hydraulic fracturing, or fracking, is a well-stimulation technique used to extract oil and natural gas trapped in low-permeability rock-like shale. The process involves drilling down to the sedimentary rocks, sometimes as far as 3000 m, then drilling horizontally for as many as several kilometers. Water is a key ingredient in fracking operations, where each Permian Basin operation requires approximately 4 million L (1.1 million gal) of water (Kondash et al. 2018). This is not much compared to the fracking operations in other basins around the country, which may require as much as 15–22 million L (4–6 million gal). However, the sheer number of wells in the Permian means it produces more wastewater than other basins.

This water is mixed with proppant (crystalline silica sand or engineered ceramics, which holds the cracks in the fractured shale open) and chemical additives before injection into the well under high pressure (7000–12,000 psi) to open existing fractures or initiate new fractures. Fracking generates two major types of wastewater, flowback water, and produced water. Flowback water is the portion of injected water that returns to the surface during the initial period of well completion, whereas produced water is the naturally occurring water that exists in the formation and is generated over the lifetime of the well once the well is in production mode. The typical fracked well generates 1.7 to 14.3 million L (450,000 to 3.8 million gal) of wastewater over the first 5–10 years of production (Kondash 2017). The American Petroleum Institute (API) estimates that oil and gas production generates more than 3×10^{12} L of wastewater each year in the USA (API 2000).

Both flowback and produced waters are usually hypersaline, containing elevated concentrations of anions (Cl^-, Br^-), divalent cations (e.g., Ba^{2+}, Ca^{2+}, Sr^{2+}), metalloids (e.g., Se, As), fracking chemicals, and naturally occurring radioactive material (NORM). These components are transported to the surface with the wastewater and can accumulate in drilling equipment and pipes over time in the form of scale and sludge. With the new wells being drilled at a record pace, increased potential for NORM exposure as well as human health and the environmental impacts must be considered. The generation of NORM by oil and gas production has been documented for decades (Jonkers 1997). The geologic formations that contain oil and gas deposits also contain NORM such as uranium, thorium, and radium (Walter et al. 2012). The anthropogenic enhancement (e.g., mining, milling, processing of uranium ore, and oil and gas exploration) of NORM leads to the generation of TENORM. The level of NORM/TENORM in unconventional oil and gas waste can vary substantially from one facility to another depending on geological formation and the salinity of the produced water. Generally, the concentration of NORM increases with salinity (Rowan et al. 2011). Since salinity often increases with the age of a well, old wells tend to exhibit higher NORM levels than newly drilled ones. For example, black shale, such as the Marcellus, usually contains higher levels of ^{238}U, ^{235}U, ^{40} K, and ^{232}Th than sandstones and limestones that have lower levels of organic matter (Nabhani et al. 2016).

One radionuclide of particular interest in fracking waste is radium, including the isotopes ^{226}Ra (half-life, $t_{1/2} = 1600$ years) and ^{228}Ra ($t_{1/2} = 5.8$ years), both of which are produced by the radioactive decay of uranium (^{238}U decay series) and thorium (^{234}Th decay series) that are present in rocks of the oil-producing formations. Unlike uranium and thorium, radium is a highly water-soluble component of TENORM. Dissolved radium either remains in solution in the flowback and produced waters or coprecipitates with barium, strontium, or calcium to form hard sulfate scales and carbonate sludges (Kraemer and Reid 1984). Radium-bearing scale and sludge can accumulate in oil field equipment, such as pipes and storage tanks, and enter the environment during disposal.

Following the discharge of wastewater, radium tends to associate with suspended sediment particles and accumulate in streambeds. Radium in flowback and produced waters can range from undetectable levels to as high as 1000 Bq/L. Radium concentration in these waters generally shows a positive correlation with total dissolved solids (TDS) and barium content despite variation in reservoir lithology (Rowan et al. 2011). These levels are significantly higher than the maximum contaminant levels for drinking water of 0.56 Bq/L (15 pCi/L) for the gross alpha (excluding uranium and radon) and 0.185 Bq/L (5 pCi/L) for total dissolved radium (USEPA 2000).

Another pathway to dispersal is atmospheric, as both the thorium and uranium decay chains contribute to airborne radionuclides. Radium decays to radon, a radioactive gas, which escapes the ground and subsequently decays as airborne particulate. According to EPA estimates, radon is the number one cause of lung cancer among nonsmokers (USEPA 2000). Radium, together with its daughter product, radon, are the main contributors to environmental radioactivity. Furthermore, radon decay products ^{210}Pb and ^{210}Po can build up in scale on the internal surfaces of oil and gas handling pipes and in sludge in refineries, becoming potential inhalation and ingestion hazards for workers (Thakur and Ward 2020).

In addition to oil and gas exploration, the Permian Basin of southeastern NM is also home to the world's only operational deep geologic transuranic nuclear waste repository, the DOE's Waste Isolation Pilot Plant (WIPP). Plutonium isotopes ($^{239+240}$Pu) and ^{241}Am are expected to account for more than 99% of the total radioactivity scheduled for disposal in the WIPP repository (Thakur and Ward 2019; ATWIR 2020). In this context, accurate measurement of TENORM levels in oil field waste is essential to observe the composition of Permian Basin fracking waste "streamsand" to identify effective strategies to mitigate radiation exposure from these materials. Despite the meteoric rise of fracking in the Permian Basin, radionuclide concentration data for hydraulic fracking waste remains extremely sparse. Here, we determine radioactivity levels in the Permian Basin shale fracking waste samples and evaluate the radiation risks associated with TENORM generated from the recovery of oil and gas by fracking in this region.

Experimental

Reagents

The extraction chromatography materials employed in this work are TEVA Resin, a quaternary ammonium salt, also known as Aliquat® 336, and TRU Resin, which contains octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide [CMPO] dissolved in tri-n-butyl phosphate [TBP]. Both resins were in the 50–100 µm particle size range and obtained from Eichrom Technologies, Inc., (Lisle, IL, USA). Trace metal grade HCl, HNO_3, $HClO_4$, and HF were obtained from Fisher Scientific Inc. (Hampton, NH, USA) Reagent-grade copper chloride ($CuCl_2 \cdot 2H_2O$), sodium sulfide ($Na_2S \cdot 9H_2O$), ascorbic acid, sulfamic acid, and sodium nitrite ($NaNO_2$) were also purchased from Fisher Scientific and were used as received. All other materials were ACS reagent grade and were used as received. The radioactive isotopes ^{209}Po, ^{229}Th, ^{236}Pu (or ^{242}Pu), ^{243}Am, and ^{232}U, obtained from Eckert & Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. A ^{232}U tracer was prepared by removing its ^{228}Th daughter using barium sulfate precipitation (Sill 1974).

Sample collection and pretreatment

Seven samples of flowback and produced waters (1–4 L) were collected from a storage tank in August 2019 and January 2020 from the Delaware Basin, near Carlsbad, in southeastern New Mexico. Three samples of waste proppant sand were also collected from the Carlsbad area. Water samples were collected in 1-L Nalgene bottles, whereas the sand samples were collected in Ziploc® bags. Before sample pretreatment, the pH of the water samples was measured, and samples were filtered through a 0.45-µm Whatman filter. Samples of produced water were difficult to filter and therefore were used without filtration. Water samples were acidified to pH ~ 2 with concentrated HNO_3.

TDS of flowback and produced waters were determined gravemetrically by evaporating waters and measuring the mass of residues left in a high precision balance.

Sample preparation

Samples of 50–150 mL were used for TENORM and actinide measurements. The samples were spiked with 0.5 mL of 50 mg/mL $Fe(NO_3)_3 \cdot 9H_2O$ carrier and approximately 0.050–0.062 Bq of ^{209}Po, $^{236}Pu/^{242}Pu$, ^{243}Am, ^{229}Th, and ^{232}U as tracers for yield monitoring. The samples were digested on a hot plate using 10–20 mL of concentrated HNO_3 and 10 mL of 30% H_2O_2 at 90–100 °C for about an hour. Sand samples were spiked with appropriate tracers and digested with $HF + HNO_3$ up to the complete decomposition of silica. The digested sand samples were then treated with concentrated $HClO_4$ and HNO_3 to remove fluoride ions. The inside walls of the beaker are rinsed carefully with HNO_3 to gather residual HF, and evaporation was repeated to ensure the complete removal of HF. The suspended material retained on the filters was air-dried and then digested with $HNO_3 + HCl$ and HF, if necessary.

Actinides and TENORMs were concentrated by iron hydroxide coprecipitation with ammonium hydroxide (pH ~ 8 to 9). After decantation and centrifugation, precipitates were dissolved in 10 mL of 3 M HNO_3. The oxidation state of Pu was adjusted to Pu(IV) by adding 0.5 mL of 1.5 M sulfamic acid + 1.0 mL of 1.5 M ascorbic acid. After waiting for 3 min, 3.5 M $NaNO_2$ was added dropwise until the solutions became colorless. The sample solutions were covered with a watch glass and heated to ~ 50–60 °C on a hot plate for about 30–40 min to allow oxidation of Pu to Pu (IV). To ensure that Po is present as Po(IV), 2–3 drops of 30% H_2O_2 were added to each column load solution and mixed well prior to loading.

Separation of actinide and TENORM radionuclides

The TEVA + TRU chromatography columns were used to separate individual radionuclides. Plutonium, thorium, and polonium were separated on the TEVA resin, whereas uranium and americium were separated on the TRU resin column. Valence-adjusted samples in 3 M HNO_3 were loaded onto TEVA columns preconditioned with 10 mL of 3 M HNO_3 followed by the washing of columns with 6 mL of 3 M HNO_3. Americium and uranium pass through the column, and these effluents are kept for americium and uranium analysis using TRU chromatography. After washing, polonium was first stripped from the TEVA column with 20 mL of 8 M HNO_3, and thorium was eluted with 15 mL of 9 M HCl. After thorium elution, the Pu was removed from the TEVA column with 20 mL of freshly prepared 0.1 M HCl + 0.05 M HF + 0.03 M $TiCl_3$. The Am/U fractions from the 3 M HNO_3 eluate of the TEVA column were evaporated to dryness and dissolved in 10 mL of 2 M HNO_3. The sample solutions were then loaded onto the TRU columns, preconditioned with 10 mL of 2 M HNO_3. After washing, the column with 12 mL of 2 M HNO_3, americium was first stripped from the column with 20 mL of 4 M HCl followed by elution of uranium with 20 mL of 0.1 M ammonium bioxalate $(NH_4)_2C_2O_4$.

Alpha-source preparation and counting

Alpha-counting sources for plutonium, americium, thorium, and uranium were prepared by the NdF_3-micro coprecipitation method, whereas alpha source for polonium was prepared by the CuS microprecipitation. The alpha sources for uranium, thorium, and polonium were covered with a thin film to prevent daughter recoil contamination of detectors (Inn et al. 2008).

An alpha spectroscopy system (Mirion Technologies, Inc.), equipped with 72 Passivated Implanted Planar Silicon (PIPS) detectors, connected to an Apex-Alpha software system, was used for the acquisition, analysis, and storage of alpha spectra. The PIPS detectors have an active surface area of 450 mm^2. The distance between the sample and the detector surface is ~ 3 mm, and the nominal counting efficiency is ~ 20%. A set of stainless-steel alpha standards, procured from Canberra, was used to establish calibration and counting efficiencies. Samples were counted for at least 24 h and an overall recovery of ~ 70 to 95% was obtained.

Inorganic cation and anion analyses

The major ions were analyzed by a Metrohm USA 930 Compact Ion Chromatograph (IC) FLEX, while trace metal analysis was conducted using inductively coupled plasma mass spectrometers (PerkinElmer, NexION 2000). The Metrohm 930 Compact IC Flex system used for cation/anion analysis is equipped with one standard pump, one guard column, one chromatographic column, a conductivity detector, one chromatography enclosure, and an autosampler. The system is operated by a dedicated computer, using Metrohm MagIC Net® software. Only one type of analysis can be performed at a time. The "cation" system is used to analyze cations such as calcium, magnesium, potassium, sodium. Prior to performing "anion" analyses, the system was flushed and set up appropriately.

The ICP-MS were calibrated prior to performing analysis using pure standards, matrix-matched standards, or relevant certified reference materials to assure traceability of the reported results. The precision between replicates observed within the linear range of the instrument was typically < 1%. The replicate precision for the method is typically < 5%. Based on analysis of secondary source standards and method performance samples a ± 10% accuracy level can be expected. For samples with more complex matrices like oil field water, an instrument precision of < 5%, a method precision of < 20%, and an accuracy level of ± 20% are expected.

Radium measurement by gamma counting

Radium activities in the samples were measured using gamma spectroscopy with a Broad Energy Germanium detector (BeGe) (Mirion Technologies, Inc.) calibrated with matrix-specific standards obtained from Eckert & Ziegler Analytics, Inc. Each day, before the start of an analysis, background and instrument quality-control checks were performed, reviewed, and validated. Liquid samples were weighed into a new 1.5 L Marinelli and sealed with polyethylene tape. Solid samples were sealed in 300-mL tin-plated steel cans and stored for at least 21 days, to allow radon progeny to reach equilibrium with parent radionuclides, before counting. The ^{226}Ra activities in liquid samples were determined directly by measuring the 186.2 keV gamma photopeak (3.28% abundance) and indirectly by measuring the gamma photopeaks of ^{214}Pb (295 and 351 keV) and ^{214}Bi (609 keV) in solid samples. The ^{228}Ra activities were determined indirectly by measuring their immediate, short-lived daughter ^{228}Ac ($t_{1/2 =}$ 6.1 h) using 911 and 969 keV gamma photo peaks. The ^{224}Ra was determined by measuring the gamma photopeaks of ^{212}Pb (238 keV) and ^{208}Tl (583 keV). Samples were counted for 48 h to minimize statistical counting error, which was typically in the range of 10–15%.

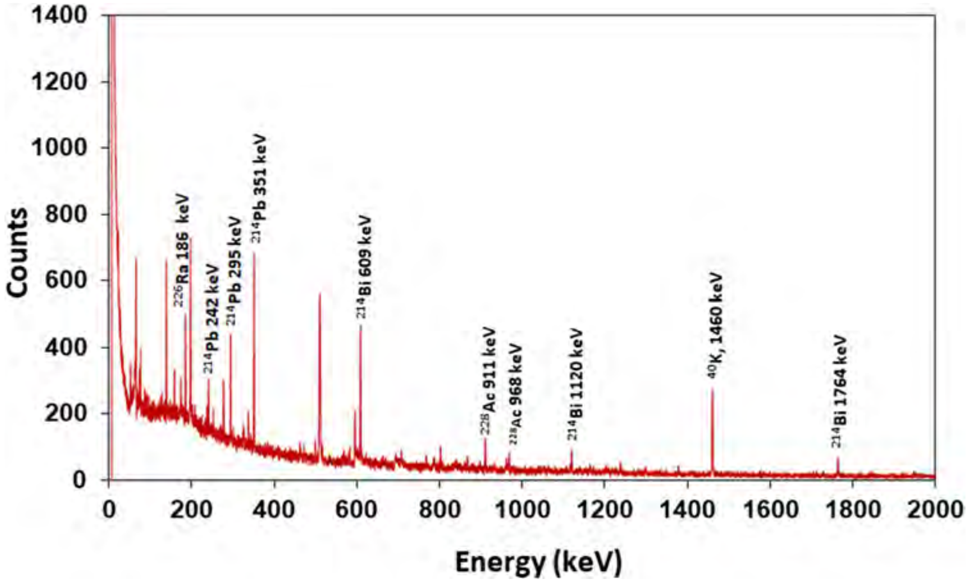
For liquid samples without U, this approach provides an accurate ^{226}Ra result. However, the presence of ^{235}U in samples such as soil, sediment, drill cuttings, and scale causes interference with direct ^{226}Ra measurement because one of its gamma lines is of similar energy, 185.7 keV (54% abundance). This could lead to an overestimation of ^{226}Ra activity. In such cases, possible contributions from ^{235}U on ^{226}Ra activities were corrected. Excess ^{226}Ra is calculated by converting the ^{235}U value to ^{226}Ra activity by a factor equal to the ratio of the gamma yields, i.e., 50.4/3.28. The gamma peaks of the ^{222}Rn daughters, ^{214}Pb (295.1 keV, 19.2% abundance and 352 keV, 37.1% abundance), and ^{214}Bi (609.3 keV, 46.1% abundance and 1120.3 keV, 15% abundance) gamma lines were also used to infer ^{226}Ra activity when ^{238}U was present in the sample. However, ^{222}Rn being a gas can escape, if the sample container is permeable to radon gas, eventually accumulating in any headspace above the bulk matrix to cause an underestimation of ^{226}Ra activity. The gamma spectra of a produced water sample from the Permian Basin are shown in Fig. 2.

Results and discussion

Inorganic constituents in the flowback and produced waters

The amount of total dissolved solids (TDS) is a measure of all inorganic and organic substances dissolved in water and is an aggregate indicator of water quality. Based on TDS, water is classified as fresh (TDS < 1000 mg/L), brackish (1000 < TDS < 10,000 mg/L), saline (10,000 < TDS < 35,000 mg/L), or hypersaline (TDS > 35,000 mg/L). The TDS of drinking water is typically < 300 mg/L. The quality of Permian Basin flowback water varied from brackish to hypersaline with TDS in

Fig. 2 A typical gamma spectra of produced water, count time = 24 h



the range of 5000 to 118,000 mg/L in this study. All produced water samples were hypersaline with TDS ranging from 40,000 to 173,000 mg/L. These values are similar to those reported for flowback and produced waters from other parts of the USA. The levels of TDS in wastewaters from various shale formations around the USA range from 120,000 in Marcellus Shale, to 13,000 in Fayetteville Shale, 30,00 in Woodford Shale, 80,000 in Barnett Shale, 110, 000 in Haynesville Shale, and 250,000 mg/L in Appalachian Shale (USDOE 2011; Rowan et al. 2011). The level of TDS in Marcellus Shale flowback water, from storage impoundments in southwestern Pennsylvania, ranged from 48,100 to 117, 500 mg/L (Zhang et al. 2015). The level of TDS in Marcellus Shale flowback from northeastern Pennsylvania was significantly higher at 278,000 mg/L (Nelson et al. 2014). Baseline characterization of groundwater in the Culebra aquifer in the vicinity of the WIPP site show TDS ranging from 17,000 to 280,000 mg/L. The pH of these waters varied in the range 7.05–7.3. The major constituents measured in Permian flowback and produced waters are listed in Table 1.

TENORM constituents in the flowback and produced waters

The activity concentrations of TENORM measured in Permian Basin flowback and produced water samples are listed in Table 2. Both ^{226}Ra and ^{228}Ra were detected in all flowback and produced water samples, whereas ^{224}Ra was detected in only one produced water sample. Permian flowback and produced waters contained ^{226}Ra, ^{228}Ra, and ^{224}Ra at activity concentrations in the range from 19.1 ± 1.2 to 35.9 ± 3.2 Bq/L, 10.3 ± 0.5 to 21.5 ± 1.2 Bq/L and 2.0 ± 0.05 to 3.7 ± 0.07 Bq/L, respectively. The range of ^{226}Ra + ^{228}Ra activity concentrations was much lower than that of Marcellus Shale-produced water (< MDC–666 Bq/L) and Gulf Coast shales (0.02–117 Bq/L) but are comparable to the range 29.1–63.7 Bq/L reported in Bakken-produced water in SD, USA (Lauer et al. 2016). However, activity concentrations of ^{226}Ra + ^{228}Ra in the Permian Shale are significantly higher than those of ^{226}Ra (0.04–8.6 Bq/L) and ^{228}Ra (0.05–3.7 Bq/L) measured in produced waters from southern San Joaquin Valley of California (McMahon et al. 2018).

Table 1 Concentration of major ions in the flowback and produced waters from the New Mexico portion of the Permian Basin

Constituents	Flowback water (mg/L)	Produced water (mg/L)
pH	7.05–7.2	7.1–7.3
TDS	5000 ± 200 to 118,000 ± 4500	40,000 ± 1900 to 173,000 ± 8234
Sodium	31,856 ± 1876 to 40,000 ± 2134	32,725 ± 1200 to 43,000 ± 1600
Magnesium	202 ± 18 to 1150 ± 157	451 ± 42 to 2430 ± 150
Calcium	668 ± 38 to 1630 ± 112	3552 ± 225 to 4123 ± 467
Potassium	148 ± 20 to 750 ± 87	165 ± 9 to 780 ± 54
Strontium	101 ± 8 to 195 ± 16	202 ± 14 to 260 ± 21
Chloride	5160 ± 765 to 37,800 ± 2033	59,400 ± 2078 to 66,700 ± 2600
Bromide	315 ± 32 to 520 ± 44	352 ± 22 to 596 ± 63
Silica	20 ± 3 to 26 ± 5	22 ± 3 to 32 ± 8
Sulfate	291 ± 15 to 785 ± 165	856 ± 60 to 1980 ± 200

Table 2 Activity concentration (Bq/L) of TENORM radionuclides measured in flowback and produced water samples from the Permian Basin

Radionuclides	Flowback water unfiltered, Bq/L	Flowback water filtered, Bq/L	Produced water unfiltered, Bq/L
^{210}Po	0.011 ± 0.007–0.014 ± 0.005	Not detected	0.03 ± 0.005–0.20 ± 0.02
^{238}U	0.021 ± 0.01–0.038 ± 0.01	0.005 ± 0.003–0.022 ± 0.009	0.001 ± 0.001–0.012 ± 0.04
^{234}U	0.041 ± 0.01–0.059 ± 0.02	0.029 ± 0.01–0.037 ± 0.02	0.008 ± 0.001–0.028 ± 0.06
^{235}U	Not detected	Not detected	0.001 ± 0.001–0.009 ± 0.001
^{228}Th	0.18 ± 0.02–1.23 ± 0.04	Not detected	0.14 ± 0.02–1.03 ± 0.04
^{232}Th	0.004 ± 0.002–0.020 ± 0.001	Not detected	0.001 ± 0.001–0.003 ± 0.001
^{230}Th	0.002 ± 0.001–0.005 ± 0.001	Not detected	0.003 ± 0.001–0.014 ± 0.005
^{226}Ra	4.6 ± 2.1–8.8 ± 3.2	2.5 ± 1.2–4.3 ± 2.3	19.1 ± 1.2–35.9 ± 3.2
^{228}Ra	2.7 ± 1.2–3.6 ± 1.5	Not detected	10.3 ± 0.5–21.5 ± 1.2
^{224}Ra	Not detected	Not detected	2.0 ± 0.05–3.7 ± 0.07
^{40} K	Not detected	Not detected	4.33 ± 2.2–33.9 ± 4.5

Measurements of ^{224}Ra in oil field waters are rare, but there have been a few reports of ^{224}Ra in produced water samples. For example, McMahon et al. (2018) reported ^{224}Ra in the range of 0.09 to 4.8 Bq/L in produced water samples from southern San Joaquin Valley, California. Levels of ^{224}Ra levels in produced water from Ukraine ranged from 1.57 to 5.51 Bq/L (Plyatsuk et al. 2017). Samples of produced water from Ghana showed ^{224}Ra in the range of 0.7–7.0 Bq/L (Kpeglo et al. 2016). These data suggest that ^{224}Ra could be an important component of the total radium ($\mathrm{Ra_{total}} = {}^{226}\mathrm{Ra} + {}^{228}\mathrm{Ra} + {}^{224}\mathrm{Ra}$) inventory in oil field waters.

Several authors have reported the presence of ^{226}Ra and ^{228}Ra in oil field wastewater. The range of radium concentrations measured in various produced and flowback waters are summarized in Table 3. There is evidence that radium activity in subsurface waters depends, to some extent, on salinity, pH, and the redox state of the water (Kraemer and Reid 1984; Vinson et al. 2013). In a critical investigation of radium data for 215 produced water samples from eight different geologic settings, Fisher (1998) reported ^{226}Ra concentrations in the range of 0.048–190.5 Bq/L. Furthermore, there was an excellent correlation ($r^2 = 0.96$, slope = 1.03) between ^{226} and ^{228}Ra concentrations. Low radium concentrations also appear to be much more common than high concentrations, where ~ 75% of produced water samples have shown ^{226}Ra concentrations less than 11.1 Bq/L, whereas only about 11% of the samples had ^{226}Ra concentrations greater than 37 Bq/L (Fisher 1998). Concentrations of ^{226}Ra in produced water vary from 62.9 to 984.2 Bq/L in unfiltered samples and 56.2 to 891.7 Bq/L in filtered samples (Barbot et al. 2013, Frazier et al. 2015). In contrast, ^{228}Ra concentrations varied from 13.5 to 70.3 (unfiltered sample) and 13.8 to 68.8 (filtered sample).

In a compilation of published data, Rowan (2011) observed significantly higher concentrations of radium in produced water from Marcellus Shale than in water from non-Marcellus shale. This database showed that produced waters from Marcellus Shale contain more radium (^{226}Ra + ^{228}Ra < MDC–666 Bq/L) than the non-Marcellus produced water (< MDC–248 Bq/L). Furthermore, radium concentrations increased with TDS. Some studies have shown that radium in produced water increases with salinity ($\mathrm{Cl^-}$ concentrations). This increase is attributed to the complexation of radium with $\mathrm{Cl^-}$ (or $\mathrm{SO_4{}^{2-}}$ or $\mathrm{CO_3{}^{2-}}$ ions) and competition with $\mathrm{Na^+}$ or other cations for ion-exchange sites. Speciation calculations in pure Ra–Cl or Ra–$\mathrm{SO_4}$ systems show that $\mathrm{RaSO_4}$ complexes are more significant than $\mathrm{Cl^-}$, even when the $\mathrm{SO_4{}^{2-}}$ concentrations are as low as 0.5% of $\mathrm{Cl^-}$ concentrations. Complexes with $\mathrm{Cl^-}$ and $\mathrm{SO_4{}^{2-}}$, particularly $\mathrm{SO_4{}^{2-}}$, can significantly

Table 3 Ranges of activity levels of ^{226}Ra and ^{228}Ra in flowback and produced waters from different shale

Location/field	Sample type	^{226}Ra Bq/L	^{228}Ra Bq/L	^{228}Ra/^{226}Ra	Reference
USA	Produced water	22.5–30.8	25.5–30.1	0.97–1.14	Zielinski and Budahn 2007
US Gulf Coast	Produced water	< 0.002–58	0.02–59	0.65–2.25	Kraemer and Reid 1984
Louisiana, USA	Produced water	< MDC–34.4	< MDC–34.3	-	Hamilton et al. 1991
Marcellus Shale, PA, USA	Flowback water	33.9–82.1	19.2–44.0	-	Frazier 2015
Bakken Shale, ND, USA	Produced water			0.42–0.49	Lauer et al. 2016
Norway	Produced water	0.5–16	0.5–21	-	Eriksen et al. 2006
Norway	Produced water	< MDC–10.4	< MDC–10.0	-	Strand et al. 1997
Tunisia	Produced water	0.37–19	-	-	Hrichi et al. 2013
Nigeria, Delta state	Produced water	3.5–10.8	3.4–9.3	0.30–2.93	Avwiri et al. 2013
Marcellus Shale, PA, USA	Flowback water	0.0–92.9	-	-	Zhang et al. 2015
Syria, Al Jafra, Attla, Qahar		9.9–111.2	8.8–67.4	-	Al-Masri 2006
Egypt	Formation water	5–40	1–59	-	Shawky et al. 2001
Egypt	Produced water	5.3–27.9	< MDC–7.7	-	Moater et al. 2010
Algeria	Formation water	5.1–14.8	-	-	
Ghanna, Salpond, Jubliee oil Field	Produced water	6.2–22.3	6.4–33.5	0.99–1.69	Kpeglo et al. 2016
Brazil, Bacia de Campos	Produced water	0.012–6.0	0.05–12.0	-	Vegueria et al. 2002
Ukraine	Produced water	27.4–39.8	3.2–5.57	0.12–0.19	Plyatsuk et al. 2017
Iraq	Produced water	20.3–67.3*	-	-	Ali 2017
Romania	Formation water	0.005–10.2	-	-	Botezatu and Grecea 2004
Indonesia, S. Java Sea	Produced water	0.3–2.1	0.02–0.66	-	Neff and Foster 1997
The Netherlands, Dutch North Sea	Produced water	< 2–302	< 1–20	-	NRPA 2004
Poland, Baltic basin Lublin Trough	Produced water	4–66	4–36	0.42–1.0	Jodłowski et al. 2017

increase radium mobility (Kraemer and Reid 1984, McMahon et al. 2018).

Reported uranium and thorium concentrations in oil field wastewater are very scarce. Typical concentrations of these radionuclides in produced water usually range from 1 to 10 Bq/L. The concentration of natural uranium (^{238}U, ^{235}U, and ^{234}U) and thorium isotopes (^{228}Th, ^{230}Th, and ^{232}Th), measured in Permian Shale flowback and produced waters, were lower than 0.06 Bq/L except for ^{228}Th (Table 2). This observation is consistent with the data from other formations. For example, Nelson et al. (2016) reported uranium and thorium concentrations <0.005 Bq/L in produced waters from Marcellus Shale. The Pennsylvania Department of Environmental Protection (PA DEP) reported concentrations of ^{238}U in Marcellus Shale in the range of 0.0003–0.10 Bq/L, with ^{232}Th ranging from 0.0003 to 0.001 Bq/L (Barbot et al. 2013, Frazier et al. 2015). Other oil-producing regions outside of the USA, such as the Bugruvate oil and gas fields in Ukraine showed concentrations in the range of 0.005–0.007 Bq/L for ^{238}U, 0.01–0.013 Bq/L for ^{234}U, and 0.058–0.19 Bq/L for ^{232}Th (Plyatsuk et al. 2017). Uranium isotopes (^{234}U and ^{238}U) in produced water from Ghana were in the range of 0.001–0.006 Bq/L, whereas thorium isotopes (^{228}Th, ^{230}Th, and ^{232}Th) ranged from 0.001 to 0.012 Bq/L (Kpeglo et al. 2016). Analysis of Permian Basin waters shows a slight enrichment of ^{234}U, relative to ^{238}U (^{234}U/^{238}U = 1.4–2.3), which is common in groundwater and is indicative of daughter recoil (Osmond et al. 1983).

Radioactivity in oil field wastes originates primarily from elements in the ^{232}Th and ^{238}U decay series. The parent isotope in the natural Th decay series, ^{232}Th ($t_{1/2} = 1.4 \times 10^{10}$ years), is insoluble in natural groundwater and brine but is known to be particle-reactive, readily sorbing on hydrous metal oxides and mineral surfaces of geomedia (Melson et al. 2012). Oxidation/reduction reactions in groundwater are also unlikely under natural conditions. As a result, the activity concentration of Th-isotopes in produced waters is expected to be very low (Langmuir and Herman 1980). Consistent with these expectations, the activity concentrations of ^{232}Th and ^{230}Th in unfiltered produced water from the Permian Basin are quite low (<0.05 Bq/L) (Table 2). However, ^{232}Th decays slowly by alpha emission to ^{228}Ra ($t_{1/2} = 5.75$ years), which is a divalent alkaline earth element that is highly soluble in low-sulfate brine. ^{228}Ra is therefore likely to have been in secular equilibrium with ^{232}Th for millions of years. Relative to ^{232}Th, produced water is therefore enriched in ^{228}Ra. ^{228}Ra decays by beta emission to the short-lived ^{228}Ac ($t_{1/2} = 6.15$ h), which is not only particle-reactive but forms insoluble complexes and decays rapidly to the low-solubility α-emitter ^{228}Th ($t_{1/2} = 1.91$ years). Similar to other Th isotopes, ^{228}Th is also insoluble in natural pore waters of shale formations, and consequently, its concentrations in produced waters are low. Ingrowth of ^{228}Th begins at a rate relative to its half-life and the decay product ^{224}Ra ($t_{1/2} = 3.63$ days), which is also soluble in the brine, rapidly grows to a steady-state radioactive equilibrium. However, ^{228}Th concentration in produced water is usually higher, relative to other thorium isotopes. This is attributed to ^{228}Ra decay rather than the leaching of thorium (Table 2).

The parent isotope in the natural U decay series, ^{238}U ($t_{1/2} = 4.47 \times 10^9$ years), like ^{232}Th, is insoluble and remains immobile in the subsurface. However, unlike ^{232}Th, ^{238}U can be redox-sensitive. The dominant forms of uranium in geologic environments are the uranous (U^{4+}) and uranyl (UO_2^{2+}) ions. In anoxic conditions, such as those found in deep shales, the stable form of uranium is U^{4+}, which is essentially insoluble in groundwater and brine. In oxic environments, uranium exists as the more soluble U(VI), which can form numerous complexes. Compared to the low solubility of ^{238}U decay series actinides in oil field waters, the ^{238}U decay product, ^{226}Ra, is highly soluble. Dissolved radium is likely to remain in secular equilibrium with its parents in brine until it decays. It may also be adsorbed onto clay particles, by ion exchange processes, and may substitute for other divalent cations such as Ba^{2+}, Ca^{2+}, and Sr^{2+} in the divalent-ion-rich brine to form minerals such as barite ($BaSO_4$), anhydrite ($CaSO_4$), and calcite ($CaCO_3$). It may also form precipitates with sulfate with which it comes in contact. Dissolved radium that is in secular equilibrium with its parents (^{238}U, ^{232}Th) at depth in a shale reservoir, may be sequestered from its parents when pumped to the surface (Rowan et al. 2011).

Radium activity ratio

The ^{228}Ra/^{226}Ra activity ratio measured in the Permian Basin produced water ranges from 0.48 to 0.65 with a mean of 0.57 ± 0.04, whereas the ^{224}Ra/^{226}Ra ratio ranges from 0.093 to 0.11 with a mean of 0.10 ± 0.02. This ^{228}Ra/^{226}Ra activity ratio is comparable to the 0.45 ratio (range 0.42–0.49) reported for Bakken produced water (Lauer et al. 2016), but higher than the ratios reported for Marcellus Shale produced water, which is generally less than 0.3 (Rowan et al. 2011) and lower than those ratios reported for produced water from southern San Joaquin Valley, California (0.14–2.3) (McMahon et al. 2018). Because ^{226}Ra is part of the ^{238}U decay series, and ^{224}Ra and ^{228}Ra are part of the ^{232}Th decay series, the ^{228}Ra/^{226}Ra activity ratio in produced water generally reflects the Th/U ratio of the reservoir lithologies, which ranges from 0.1 to 2.0. There is limited information on ^{224}Ra/^{226}Ra activity ratio in oil field waters. McMahon et al. (2018) reported ^{224}Ra/^{226}Ra activity ratios between 0.2 and 5.5 and a mean of 1.5 in produced water from San Joaquin Valley, California. The ratios in Ghanaian produced water varied from 0.11 to 0.31 with a mean of 0.22 (Kpeglo et al.

2016). The ^{224}Ra/^{226}Ra activity ratios in Ukrainian-produced water were in the range of 0.49–0.99 with a mean of 0.74 (Plyatsuk et al. 2017). ^{224}Ra/^{228}Ra ratios > 1 are common in groundwater and primarily reflect the effect of alpha-recoil release of the short-lived ^{224}Ra from solids, and adsorption of radium on solid surfaces (Hancock and Murray 1996; Vengosh et al. 2009). In the ^{232}Th decay series, ^{224}Ra is followed by two alpha decays while ^{228}Ra is followed only by one alpha decay. Therefore, ^{224}Ra shows a higher probability of migration because of the direct transfer of atoms across the solid/liquid phase boundary or by lattice destruction due to the recoil effect (Fleischer 1980). This mechanism is similar to that responsible for uranium isotope disequilibrium and ^{234}U/^{238}U activity ratios that are generally > 1 in groundwater.

Published reports of ^{210}Po in oil and gas wastewater are also limited. In this study, ^{210}Po was slightly above the detection limit in both filtered samples of flowback and produced water (Table 2). No ^{210}Po was measured above the detection limit in the filtered flowback water samples. However, produced water concentrations in the range of 0.032 ± 0.005 to 0.20 ± 0.06 Bq/L are consistent with the range 0.022 to 0.085 Bq/L reported in produced water samples from the US Gulf Coast (Lagera et al. 1999) and the 0.022 to 0.14 Bq/L reported for produced water from two offshore oil fields in Ghana (Kpeglo et al. 2016). Although ^{226}Ra is highly soluble in oil field waters, the decay product radionuclides (^{210}Pb, ^{210}Bi, and ^{210}Po) are relatively insoluble and remain mostly adsorbed to mineral phases in the subsurface environment. This is consistent with the observation of the higher concentrations of ^{210}Po found in filter residues. Residue concentrations ranged from 28.2 ± 6.5 to 78.3 ± 15.5 Bq/g, with a mean of 53.3 ± 12.6 Bq/g. This suggests that most of the ^{210}Po remain associated with the suspended particles with only a small dissolved fraction. However, it is important to keep in mind that radioactivity would continue to increase for decades as longer-lived isotopes (^{210}Pb, $t_{1/2} = 22$ years; ^{210}Po, $t_{1/2} = 138$ days) approach radioactive equilibrium with ^{226}Ra. Both ^{210}Pb and ^{210}Po are important from the perspective of risk assessment because of their bioavailability and ability to accumulate in higher organisms (Thakur and Ward 2019).

Transuranic constituents in the flowback and produced waters

None of the transuranic radionuclides ($^{239+240}$Pu, ^{238}Pu, ^{237}Np, and ^{241}Am) were detected in any of the oil field water samples. This observation is of particular significance to operations at WIPP, which is intended to serve as a permanent repository for transuranic waste. Baseline concentrations of anthropogenic radionuclides in the Carlsbad area are listed in Table 4. Air emission is recognized as the major pathway for radionuclides to the accessible environment during facility operations. After the facility is permanently closed, there is no credible, probable mechanism for radionuclide release to the surrounding environment unless the site is breached by humans. Under such a scenario, any releases would be through groundwater that is predominantly non-potable water and classified as brine (National Research Council 1996). The ability to measure TENORM and their ratios, as well as actinides, in environmental samples allows accurate identification of the source of contaminants, i.e., oil field wastes versus WIPP, should issues of regulatory compliance ever arise.

Radioactivity in proppant

The levels of radionuclides measured in samples of proppant sand used in fracking are listed in Table 5. Proppant sand contained nominal concentrations of elements from the U and Th decay series. Measured concentrations of radionuclides were in the range of 0.02 to 2.16 for ^{40}K, 0.003 to 0.017 for ^{238}U, 0.0006 to 0.01 Bq/g for ^{232}Th, < MDC to 0.061 Bq/g for ^{226}Ra, and 0.002 to 0.01 Bq/g for ^{228}Ra. Jodłowski et al. (2017) reported concentrations ranging from 0.12 to 0.27 for ^{40}K, 0.014 to 0.39 Bq/g for ^{238}U, 0.015 to 0.41 Bq/g for ^{226}Ra, and 0.008 to 0.52 Bq/g for ^{228}Ra in flowback proppant sand. Analysis of proppant sand in Pennsylvania, sampled from sand hoppers before being mixed with fluids, showed concentrations in the range of 0.001 to 0.27 Bq/L for ^{40}K, 0.0004 to 0.012 Bq/g for ^{238}U, 0.0003 to 0.004 Bq/g for ^{232}Th, 0.006–0.013 for ^{226}Ra, and 0.0005 to 0.005 for ^{228}Ra. These studies indicate that radioactivity levels in proppant sand are less than or comparable to the

Table 4 Background concentrations of anthropogenic radionuclides in the Carlsbad area. Values were taken from the CEMRC annual report (www.cemrc.org/annualreport)

Environmental media	Ground water (Bq/L)	Surface water (Bq/L)	Sediment (Bq/g)	Surface soil (Bq/g)
^{238}Pu	Not detected	Not detected	Not detected	Not detected
$^{239+240}$Pu	Not detected	Not detected	2.1×10^{-4}–2.9×10^{-4}	3.7×10^{-5}–3.1×10^{-4}
^{241}Am	Not detected	Not detected	6.9×10^{-5}–1.0×10^{-4}	1.1×10^{-5}–1.3×10^{-4}
^{137}Cs	0.3 ± 0.06–1.46 ± 0.5	Not detected	0.002 ± 0.001–0.029 ± 0.001	0.0014 ± 0.006–0.008 ± 0.003

Table 5 Activity concentration (Bq/g) of TENORM radionuclides measured in filter particulate and proppant sand samples

Radionuclides	Flowback water Filter particulate Bq/g	Proppant sand Bq/g
^{210}Po	0.028 ± 0.01–0.078 ± 0.02	Not detected
^{238}U	0.011 ± 0.006–0.03 ± 0.009	0.003 ± 0.0008–0.017 ± 0.004
^{234}U	0.026 ± 0.01- 0.046±0.02	0.002 ± 0.0004–0.02 ± 0.002
^{235}U	Not detected	< MDC (0.0001)–0.001 ± 0.0003
^{228}Th	0.12 ± 0.03–0.16 ± 0.05	0.0005 ± 0.0002–0.01 ± 0.002
^{232}Th	0.017 ± 0.003–0.034 ± 0.01	0.0006 ± 0.0001–0.01 ± 0.001
^{230}Th	0.034 ± 0.01–0.095 ± 0.03	0.001 ± 0.0004–0.018 ± 0.003
^{226}Ra	ND	< MDC (0.0084)–0.061 ± 0.008
^{228}Ra	ND	0.002 ± 0.0004–0.01 ± 0.0006
^{224}Ra	ND	Not detected
^{40} K	ND	0.024 ± 0.005–2.16 ± 0.05

ND, not determined

natural background levels of radioactivity typically found in surface soil. Thus, there is little potential for radiological exposure to workers and members of the public from proppant sand. It is worth noting that some proppant sands incorporate radioactive tracers with different half-lives to allow downhole mapping of the injection profile and fracture propagation during fracking (Scott 1995;1997). The radionuclides used as tracers are regulated by the Nuclear Regulatory Commission (USNRC 2018) and typically have different half-lives that may range from 40.2 h (^{140}La) to 28.90 years (^{90}Sr) depending on the stage of fracking in which they are used (Gadeken 1989). Tracer concentrations are regulated to ensure that air emissions of radioactive material to the environment, excluding ^{222}Rn and its daughters, will not result in exposures to individual members of the public above 0.1 mSv in a year from those emissions (USNRC 2018).

Flux of radium in the Permain-produced water

As discussed in the preceding section, the dominant radionuclide in oil and gas wastewater is radium. Therefore, the annual flux of radium in the produced water was calculated by taking into account the average concentrations of ^{226}Ra measured in the produced waters and the volume of produced water generated each year since 2011. The data for the annual generation of produced water was taken from the Center for Western Priorities. Figure 3 shows the volume of produced water generated and the estimated concentrations of ^{226}Ra in tetra becquerel (TBq = 1 × 10^{12} Bq) that could be expected in produced water.

Baseline concentrations of NORM/TENORM in the Carlsbad region of the Permian Basin

Although the ability to measure TENORM and actinides in the same sample is essential for accurate source identification, perhaps more important is knowledge of the radiological baseline. A comprehensive radiological baseline study, completed before WIPP disposal operations began, provides the basis for comparison of operations and post-closure compliance monitoring (DOE/WIPP 1992). Herczeg et al. (1988) also quantified naturally occurring isotopes of uranium and radium in freshwater, springs, and saline groundwater in the Delaware Basin of southeastern New Mexico, a subprovince of the greater Permian Basin. These data are invaluable for interpreting any fluctuations in radionuclide concentrations in environmental samples in the Permian Basin.

High concentrations of radium, similar to those found in produced water, have been reported in groundwater samples collected from saline springs (Herczeg et al. 1988). Historical data from the monitoring of groundwater in the Culebra aquifer at WIPP (WIPP Site Report 1995) show ^{226}Ra concentrations in the range of 1.23 to 9.1 Bq/L and ^{228}Ra in the range of 0.2 to 1.41 Bq/L (Table 6). Concentrations of ^{234}U and ^{238}U in the groundwater vary from 0.3 to 1.46 Bq/L and

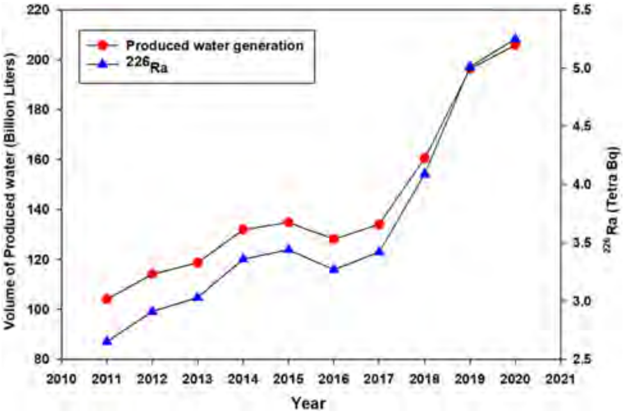


Fig. 3 Uranium concentrations in natural and oil field waters in the Permian Basin. Data for drinking and surface waters were taken from the CEMRC report 1998 and that of groundwater were from the WIPP site report 1995

0.056–0.25 Bq/L, respectively. All of the groundwater samples show a radioactive disequilibrium between ^{234} and ^{238}U isotopes with a ^{234}U/^{238}U activity ratio in the range of 4.9 to 8.1. This disequilibrium is attributed mostly to the higher solubility of ^{234}U, relative to ^{238}U, and preferential leaching. Other contributing factors include ^{234}U recoil and crystal damage. In groundwater from the Culebra aquifer, ^{226}Ra activity varied from < MDC to 10.4 Bq/L, whereas ^{238}U concentrations were in the range of 0.1 to 7.4 Bq/L (Chapman 1988). Marked disequilibrium also exists between ^{238} and ^{234}U activities in Culebra groundwater with ^{234}U/^{238}U activity ratios ranging from 1.5 to 18 and TDS ranging from 17,000 to 280,000 mg/L (Chapman 1988).

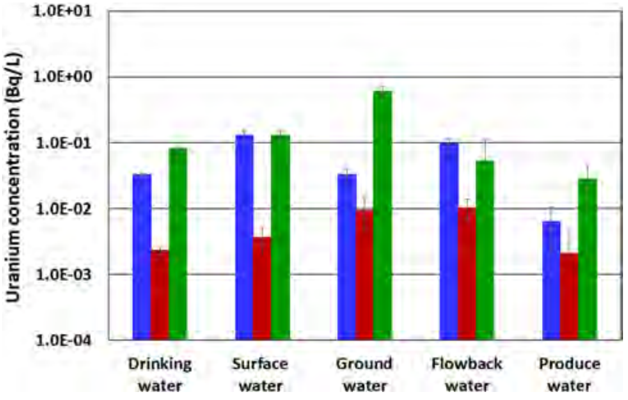


Fig. 4 Produced water volume and estimated concentrations of ^{226}Ra in these waters. Data for the volume of produced water generation were from ref. Center for Western Priorities. ^{226}Ra content was calculated using the average ^{226}Ra concentration measured in this study

The NORM concentrations in surface waters, sediments, and soils in the vicinity of WIPP were also evaluated, as they are more directly linked to human exposure and environmental contaminations. The ^{226}Ra and ^{228}Ra concentrations in surface water were all < 0.1 Bq/L, whereas concentrations of uranium and thorium isotopes were < 2 Bq/L (Table 6). The ^{234}U/^{238}U activity ratios in surface water samples are in the range of 0.87 to 3.66 and are very similar among the different reservoirs (CEMRC report 1998). All of the reservoirs appeared to be slightly enriched in ^{234}U compared to ^{238}U (CEMRC report 1998).

Baseline soil concentrations of NORM in this area are also listed in Table 6. Levels of ^{234}U were in the range 0.005–0.14 Bq/g compared to a range of 0.005–0.093 Bq/g for ^{238}U. Isotopes of thorium were in the range of 0.008–0.02 Bq/g for ^{230}Th and 0.006–0.021 Bq/g for ^{232}Th, whereas ^{40} K ranged from 0.13 to 0.28 Bq/g. Natural background concentrations of these radionuclides in the US soil are in the range of 0.004 to 0.14 Bq/g, with a mean of 0.035 Bq/g for ^{238}U; 0.004 to 0.13 Bq/g, with a mean of 0.035 Bq/g for ^{232}Th; 0.008 to 0.16 Bq/g, with a mean of 0.041 Bq/g for ^{226}Ra; and 0.1 to 0.7 Bq/g, with a mean of 0.37 Bq/g for ^{40} K (UNSCEAR 2000). A typical concentration of uranium isotopes in various natural and oil field waters is shown in Fig. 4. Concentrations in oil field waters are consistent with natural background levels found in surface soils. However, radium concentrations are elevated above background levels for soil and groundwater.

Radiological dose assessment to the workers and the public

More than 80% of the radiation dose received by humans comes from natural radiation sources (NRC-BEIR-IV 2006; USNRC 2010), which are comprised primarily of primordial radionuclides such as ^{40} K and the progenies of ^{238}U and ^{232}Th decay series. Human exposure to radionuclide releases from transuranic waste disposed at WIPP is likely to be low compared to the USA and international standards (National Research Council 1996). However, handling, transportation, and storage of oil field waste that include TENORM can expose workers to high levels of radiation. Similarly, disposal of oil field wastes by burial, land spreading, injection

Table 6 Background concentrations of NORM in the Carlsbad area. Values were taken from the CEMRC annual report 1999–2018 (www.cemrc.org/annualreport)

Radionuclides	Ground water (Bq/L)	Surface water (Bq/L)	Sediment (Bq/g)	Surface soil (Bq/g)
^{226}Ra	1.23–9.07	0.004–0.05	0.017–0.048	0.003–0.043
^{228}Ra	0.2–1.41	< MDC–0.03	0.013–0.039	0.007–0.02
^{238}U	0.056–0.25	0.001–0.20	0.013–0.062	0.005–0.093
^{234}U	0.3–1.46	0.002–0.57	0.013–0.091	0.005–0.14
^{235}U	0.003–0.082	0.00015–0.006	0.0011–0.0081	0.0002–0.0009
^{228}Th	0.03–0.214	0.002–0.008	0.013–0.042	0.15–0.17
^{232}Th	Not detected	Not detected	0.014–0.048	0.006–0.021
^{230}Th	0.016–0.040	0.02–0.10	0.004–0.07	0.008–0.020
^{210}Po	0.009–0.10	< MDC	0.007–0.036	0.016–0.032
^{40} K	8.1–63.1	0.81–2.72	0.31–0.51	0.13–0.28

Values have an uncertainty of about 10–20%

into deep wells, or dumping into shallow trenches or the sea can increase the likelihood of human exposure to high levels of radioactivity and toxic metals.

The radiation dose from radionuclides in the oil field wastes can be inferred from three different dose indices, which include (1) the radium equivalent radioactivity (Ra_{eq}), (2) the gamma dose rate (D (nGy/h)), and (3) the effective annual dose rate (D_{eff}). These three indices are representative of reference doses in the outdoor air at a height of 1 m above the ground surface and can be calculated using the activity-to-dose conversion model adopted by the UNSCEAR (2000) and modified by Tufail (2012). Because 98.5% of the radiological effects from uranium-series elements are produced by radium and its daughter products, the contribution from ^{238}U and other ^{226}Ra precursors are normally ignored. Rather than calculate the dose of every radionuclide in the produced water, a single annual effective dose (mSv/year) is calculated from the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40} K, according to Tufail (2012) as

$$D_{eff} = \left(0.463A_{\mathrm{Ra}} + 0.604A_{\mathrm{Th}} + 0.0417A_{\mathrm{K}}\right) \times 6.136 \times 10^{-3} \quad (1)$$

In Eq. (1), A_{Ra}, A_{Th}, and A_{K} are the activity concentrations in Bq/L of ^{226}Ra (can be assumed to be the concentration of ^{238}U), ^{232}Th, and ^{40} K, respectively. The annual effective doses calculated by Eq. (1) from the activity concentrations in oil field waters (Table 2) and groundwater near the WIPP site (Table 6) would be 0.1–0.2 mSv/year from the oil field waters and 0.01–0.05 mSv/year from the groundwater. Zhang et al. (2015) evaluated health risks associated with NORM generated from Marcellus Shale gas exploration and concluded that total effective dose equivalent (TEDE) would be well below the NRC limit for the general public of 1 mSv/year even under the worst-case scenario assumptions. Workers in the centralized waste treatment facilities might receive excessive TEDE; however, appropriate measures such as a safety distance of 5 m can reduce TEDE to an acceptable level.

This and previous studies showed that there is little or limited potential for radiation exposure to the public and workers from the oil and gas development. However, there are potential radiological environmental impacts from oil field wastes if spilled. Therefore, these waste materials must be handled, stored, and disposed of in compliance with regulations that ensure the safety of workers and the public. There should also be site-specific circumstances and situations where the use of personal protective equipment by workers or other controls should be evaluated. According to the Nuclear Regulatory Commission (USNRC 2010), an average American receives a radiation dose of about 6.2 mSv per year from all sources of radiation (3.1 mSv) from naturally occurring sources and about 3.1 mSv from man-made sources and applications. The radiation dose from the oil and gas development is much lowered than the natural background level of radiation.

Conclusion

The objectives of this study were to quantify background levels of radium in the Permian Basin and quantify the concentration range and dose associated with oil field wastes. The quality of oil field water varied from brackish to hypersaline with TDS > 5000 mg/L. Radium, the major TENORM of interest in hydraulic fracturing wastes were in the range of 19.1 ± 1.2 to 35.9 ± 3.2 Bq/L for ^{226}Ra, 10.3 ± 0.5 to 21.5 ± 1.2 Bq/L for ^{228}Ra, and 2.0 ± 0.05–3.7 ± 0.07 Bq/L for ^{224}Ra. In addition to elevated concentrations of radium, these wastewaters also contain elevated concentrations of dissolved salts (Na, Cl, Br), divalent cations (Ca, Mg, Sr) compared to background waters. The ^{228}Ra/^{226}Ra activity ratios (0.48–0.65) in Permian-produced water were consistent with the ratios measured in other US Shale-produced waters such as Bakken and Marcellus shales.

These elevated levels are of radiological significance and represent a major source of Ra in the environment. However, the risk assessment study indicates that there is little or limited potential for radiation exposure to the public and workers from the oil and gas development. The resulting dose from the activity concentrations in oil field waters and groundwater near the WIPP site was around 0.1–0.2 mSv/year from the oil field waters and 0.01–0.05 mSv/year from the groundwater, which are well below the natural background radiation dose of 3.1 mSv and the NRC limit effective dose limit of 1 mSv/year for the general public.

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