Chapter 5

Chemical Mixing

5. Chemical Mixing

5.1. Introduction

This chapter addresses the potential for on-site spills of chemicals used in the chemical mixing process to affect the quality of drinking water resources. Chemical mixing is a complex process that requires the use of specialized equipment and a range of different additives to produce the hydraulic fracturing fluid that is injected into the well. The number, type, and volume of chemicals used vary from well to well based on site- and company-specific factors. Spills may occur at any point in the hydraulic fracturing process. Chemicals may spill from on-site storage and containment units; from interconnected hoses and pipes used to transfer chemicals to and from mixing and pumping units, and tanker trucks; and from the equipment used to mix and pressurize chemical mixtures that are pumped down the well. The potential for a spill to affect the quality of a drinking water resource is governed by three overarching factors: (1) fluid characteristics (e.g., chemical composition and volume), (2) chemical management and spill characteristics, and (3) chemical fate and transport (see Figure 5-1). This chapter is organized around the three factors.

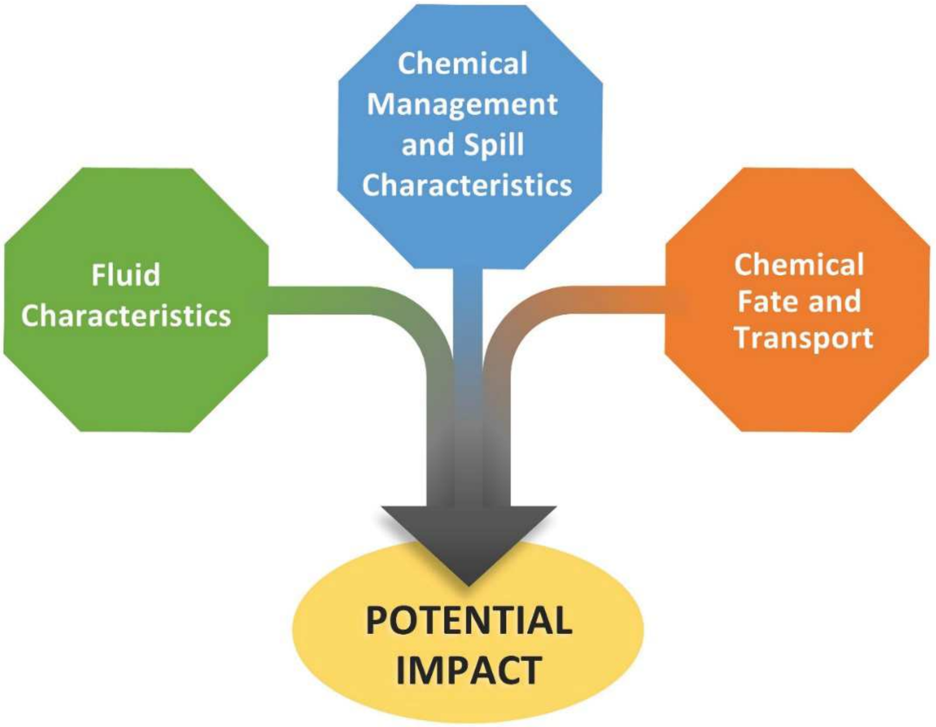

Figure 5-1. Factors governing potential impact to drinking water resources.

Factors include (1) fluid characteristics (e.g., chemical composition and volume), (2) chemical management and spill characteristics, and (3) chemical fate and transport.

Section 5.2 provides an introductory overview of the chemical mixing process. The number and volume of chemicals used and stored on-site are affected by such variables as the type, size, and goals of the operation; formation characteristics; depth of the well; the length of the horizontal leg; and the number of fracturing phases and stages.

Section 5.3 describes the different components of the hydraulic fracturing fluid, generally comprised of the base fluid, proppant, and additives, which may be either individual chemicals or mixtures. The composition of the hydraulic fracturing fluid is engineered to meet specific criteria. The total amount and types of additives vary according to the characteristics of the well, site geology, economics, availability, and the production goals (e.g., Maule et al., 2013). Section 5.4 presents the wide range of different chemicals used and their classes, the most frequently used chemicals nationwide and from state-to-state, and volumes used.[1] Appendix A provides a list of chemicals that the EPA identified as being used in hydraulic fracturing fluids based on eight sources.

Sections 5.5 to 5.7 discuss how chemicals are managed on-site, how spills may occur, and the different approaches for addressing spills. Section 5.5 describes how the potential impact of a spill on drinking water resources depends upon chemical management practices, such as storage, on-site transfer, and equipment maintenance. Section 5.6 discusses spill prevention, containment, and mitigation. A summary analysis of reported spills and their common causes at hydraulic fracturing sites is presented in Section 5.7.

Section 5.8 discusses the fate and transport of spilled chemicals. Spilled chemicals may react and transform into other chemicals, travel from the site of release to a nearby surface water, or leach into the soils and reach ground water. Chemical fate and transport after a release depend on site conditions, environmental conditions, physicochemical properties of the released chemicals, and the volume of the release.

Section 5.9 provides an overview of on-going changes in chemical use in hydraulic fracturing, with an emphasis on efforts by industry to reduce potential impacts from surface spills by using fewer and safer chemicals. A synthesis and a discussion of limitations are presented in Section 5.10.

Factors affecting the frequency and severity of impacts to drinking water resources from surface spills include size and type of operation, employee training and experience, standard operating procedures, quality and maintenance of equipment, type and volume of chemical spilled, environmental conditions, proximity to drinking water resources, spill prevention practices, and spill mitigation measures. Due to the limitations of available data and the scope of this assessment, it is not possible to provide a detailed analysis of all of the factors listed above. Data limitations also preclude a quantitative analysis of the likelihood or magnitude of chemical spills or impacts. Spills that occur off-site, such as those during transportation of chemicals or storage of chemicals in staging areas, are out of scope. This chapter qualitatively characterizes the potential for impacts to

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[1] Chemical classes are groupings of different chemicals based on similar features, such as chemical structure, use, or physical properties. Examples of chemical classes include hydrocarbons, pesticides, acids, and bases.

drinking water resources given the current understanding of overall operations and specific components of the chemical mixing process.

5.2. Chemical Mixing Process

An understanding of the chemical mixing process is necessary to understand how, why, and when spills that may affect drinking water resources might occur. This description provides a general overview of chemical mixing in the context of the overall hydraulic fracturing process (Carter et al., 2013; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008).

Figure 5-2 shows a hydraulic fracturing site during the chemical mixing process. The discussion focuses on the types of additives used at each phase of the process. While similar processes are used to fracture horizontal and vertical wells, a horizontal well treatment is described here because it is likely to be more complex and because horizontal hydraulic fracturing has become more prevalent over time with advances in hydraulic fracturing technology. A water-based system is described because water is the most commonly used base fluid, appearing in more than 93% of FracFocus disclosures between January 1, 2011 and February 28, 2012 (U.S. EPA, 2015a).

Figure 5-2. Hydraulic fracturing site showing equipment used on-site during the chemical mixing process.

Source: Industry source.

While the number and types of additives may widely vary, the basic chemical mixing process is similar across sites. The on-site layout of hydraulic fracturing equipment is also similar from site to site (BJ Services Company, 2009). Equipment used in the chemical mixing process typically consists of chemical storage trucks, water supply tanks, proppant supply, slurry blenders, a number of high-pressure pumps, a manifold, surface lines and hoses, and a central control unit. Detailed descriptions of specific additives and the equipment used in the process are provided in Sections 5.3 and 5.5, respectively.

The chemical mixing process begins after the drilling, casing, and cementing processes are finished and hydraulic fracturing equipment has been set up and connected to the well. The process can generally be broken down into sequential phases with specific chemicals added at each phase to achieve a specific purpose (Knappe and Fireline, 2012; Fink, 2003). Phases may overlap. The process for water-based hydraulic fracturing is outlined in Figure 5-3 below.

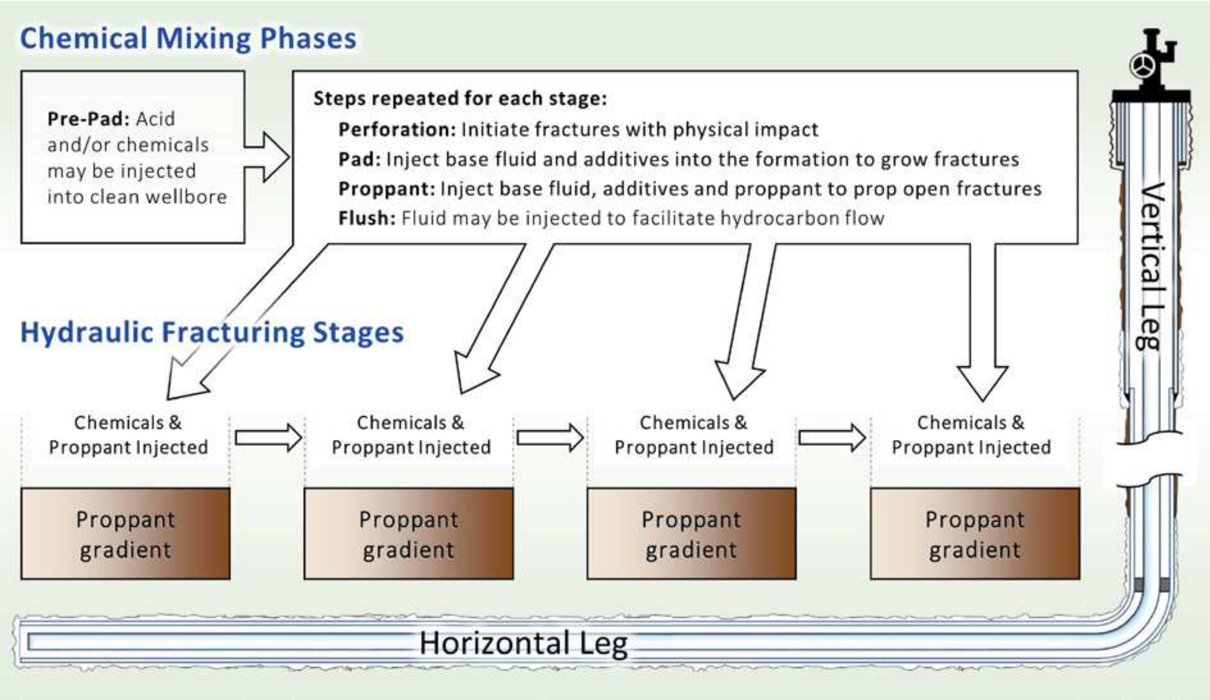

Figure 5-3. Overview of a chemical mixing process of the hydraulic fracturing water cycle.

This figure outlines the chemical mixing process for a generic water-based hydraulic fracture of a horizontal well. The chemical mixing phases outline the steps in the overall fracturing job, while the hydraulic fracturing stages outline how each section of the horizontal well would be fractured beginning with the toe of the well, shown on left-side. The proppant gradient represents how the proppant size may change within each stage of fracturing as the fractures are elongated. The chemical mixing process is repeated depending on the number of stages used for a particular well. The number of stages is determined in part by the length of the horizontal leg. In this figure, four stages are represented, but typically, a horizontal fracturing treatment would consist of 10 to 20 stages per well (Lowe et al., 2013). Fracturing has been reported to be done in as many as 59 stages (Pearson et al., 2013).

The first phase of the process consists of the cleaning and preparation of the well. The fluid used in this phase is often referred to as the pre-pad fluid or pre-pad volume. Acid is typically the first chemical introduced. Acid, with a concentration of 3%–28% (typically hydrochloric acid, HCl), is used to adjust pH, clean any cement left inside the well from cementing the casing, and dissolve any pieces of rock that may remain in the well and could block the perforations. Acid is typically pumped directly from acid storage tanks or tanker trucks, without being mixed with other additives. The first, or pre-pad, phase may also involve mixing and injection of additional chemicals to facilitate the flow of fracturing fluid introduced in the next phase of the process. These additives may include biocides, corrosion inhibitors, friction reducers, and scale inhibitors (Carter et al., 2013; King, 2012; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008).

In the second phase, a hydraulic fracturing fluid, typically referred to as the pad or pad volume, is mixed, blended, and pumped down the wellbore to create fractures in the formation. The pad is a mixture of base fluid, typically water, and additives. The pad is designed to create, elongate, and enlarge fractures along the natural channels of the formation when injected under high pressure (Gupta and Valkó, 2007). A typical pad consists of, at minimum, a mixture of water and friction reducer. The operator may also add other additives (see U.S. EPA (2015a) and Table 5-1) used to facilitate flow and kill bacteria (Carter et al., 2013; King, 2012; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008). The pad is pumped into the formation through perforations in the well casing (see Text Box 5-1).

Text Box 5-1. Perforation.

Prior to the injection of the pad, the well casing is typically perforated to provide openings through which the pad fluid can enter the formation. A perforating gun is typically used to create small holes in the section of the wellbore being fractured. The perforating gun is lowered into position in the horizontal portion of the well. An electrical current is used to set off small explosive charges in the gun, which creates holes through the well casing and out a short, controlled distance into the formation (Gupta and Valkó, 2007).

In the third phase, proppant, typically sand, is mixed into the hydraulic fracturing fluid. The proppant volume, as a proportion of the injected fluid, is increased gradually until the desired concentration in the fractures is achieved. Gelling agents, if used, are also mixed in with the proppant and base fluid in this phase to increase the viscosity and carry the proppant. Additional chemicals may be added to gelled fluids, initially to maintain viscosity and later to break the gel down into a more readily removable fluid. (Carter et al., 2013; King, 2012; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008).

A final flush or clean-up phase may be conducted after the stage is fractured, with the primary purpose of maximizing well productivity. The flush is a mixture of water and chemicals that work to aid the placement of the proppant, clean out the chemicals injected in previous phases, and prevent microbial growth in the fractures (Knappe and Fireline, 2012; Fink, 2003).

The second, third, and fourth phases are repeated multiple times in a horizontal well, as the horizontal section, or leg, of the wellbore is typically fractured in multiple segments referred to as stages. For each stage, the well is typically perforated and fractured beginning at the end, or toe, of the wellbore and proceeding backwards toward the vertical section. Each fractured stage is isolated before the next stage is fractured. The number of stages corresponds directly to the number of times the chemical mixing process is repeated at the site surface (see Figure 5-3). The number of stages depends upon the length of the leg (Carter et al., 2013; King, 2012; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008).

The number of stages per well can vary, with several sources suggesting between 10 and 20 is typical (GNB, 2015; Lowe et al., 2013).[1] The full range reported in the literature is much wider, with one source documenting between 1 and 59 stages per well (Pearson et al., 2013) and others reporting values within this range (NETL, 2013; STO, 2013; Allison et al., 2009). It also appears that the number of stages per well has increased over time. For instance, in the Williston Basin the average number of stages per horizontal well rose from approximately 10 in 2008 to 30 in 2012 (Pearson et al., 2013).

In each of these phases, water is the primary component of the hydraulic fracturing fluid, though the exact composition of the fluid injected into the well changes over the duration of each stage. In water-based hydraulic fracturing, water typically comprises between 90% and 94% of the hydraulic fracturing fluid, proppant comprises 5% to 9%, and additives comprise the remainder, typically 2% or less (Carter et al., 2013; Knappe and Fireline, 2012; SWN, 2011). The exception to this typical fluid composition may be when a concentrated acid is used in the initial cleaning phase of the fracturing process.

5.3. Overview of Hydraulic Fracturing Fluids

Hydraulic fracturing fluids are formulated to perform specific functions: create and extend the fracture, transport proppant, and place the proppant in the fractures (Montgomery, 2013; Spellman, 2012; Gupta and Valkó, 2007). The hydraulic fracturing fluid generally consists of three parts: (1) the base fluid, which is the largest constituent by volume, (2) the additives, which can be a single chemical or a mixture of chemicals, and (3) the proppant. Additives are chosen to serve a specific purpose in the hydraulic fracturing fluid (e.g., friction reducer, gelling agent, crosslinker, biocide) (Spellman, 2012). Throughout this chapter, "chemical" is used to refer to individual chemical compounds (e.g., methanol). Proppants are small particles, usually sand, mixed with fracturing fluid to hold fractures open so that the target hydrocarbons can flow from the formation through the fractures and up the wellbore. The combination of chemicals, and the mixing and injection process, varies based on a number of factors as discussed below. The chemical combination determines the amount and what type of equipment is required for storage and, therefore, contributes to the determination of the potential for spills and impacts of those spills.

The particular composition of hydraulic fracturing fluids is selected by a design engineer based on empirical experience, the formation, economics, goals of the fracturing process, availability of the

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[1] The number of stages has been reported to be 6 to 9 in the Huron in 2009 (Allison et al., 2009), 25 and up in the Marcellus (NETL, 2013), and up to 40 by STO (2013).

desired chemicals, and preference of the service company or operator (Montgomery, 2013; ALL Consulting, 2012; Klein et al., 2012; Ely, 1989). No single set of specific chemicals is used at every site. Multiple types of fracturing fluids may be appropriate for a given site and any given type of fluid may be appropriate at multiple sites. For the same type of fluid formulation, there can be differences in the additives, chemicals, and concentrations selected. There are broad criteria for hydraulic fracturing fluid selection based on the fracturing temperatures, formation permeability, fracturing pressures, and formation water sensitivity, as shown in Figure 5-4 (Gupta and Valkó, 2007; Elbel and Britt, 2000). One of the most important properties in designing a hydraulic fracturing fluid is the viscosity (Montgomery, 2013).[1]

Figure 5-4 provides a general overview of which fluids can be used in different situations. As an example, crosslinked fluids with 25% nitrogen foam (titanate or zirconate crosslink + 25% N_2) can be used in both gas and oil wells with high temperatures with variation in water sensitivity.

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[1] Viscosity is a measure of the internal friction of fluid that provides resistance to shear within the fluid, informally referred to as how “thick” a fluid is. For example, custard is thick and has a high viscosity, while water is runny with a low viscosity. Sufficient viscosity is needed to create a fracture and transport proppant (Gupta and Valkó, 2007). In lower-viscosity fluids, proppant is transported by turbulent flow and requires more hydraulic fracturing fluid. Higher-viscosity fluids allows the fluid to carry more proppant, requiring less fluid but necessitating the reduction of viscosity after the proppant is placed (Rickman et al., 2008; Gupta and Valkó, 2007).

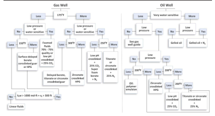

Figure 5-4. Example fracturing fluid decision tree for gas and oil wells.

Adapted from Elbel and Britt (2000).

Table 5-1 provides a list of common types of additives, their functions, and the most frequently used chemicals for each purpose based on the EPA's analysis of disclosures to FracFocus 1.0 (hereafter EPA FracFocus report; U.S. EPA (2015a)), the EPA's project database of disclosures to FracFocus 1.0 [hereafter EPA FracFocus database; U.S. EPA (2015b)], and other literature sources. Additional information on more additives can be found in U.S. EPA (2015a).

Table 5-1. Examples of common additives, their function, and the most frequently used chemicals reported to FracFocus for these additives.

The list of examples of common additives was developed from information provided in multiple sources (U.S. EPA, 2015a, b; Stringfellow et al., 2014; Montgomery, 2013; Vidic et al., 2013; Spellman, 2012; GWPC and ALL Consulting, 2009; Arthur et al., 2008; Gupta and Valkó, 2007; Gidley et al., 1989). The additive functions are based on information the EPA received from service companies (U.S. EPA, 2013a).

Additives	Function	Chemicals reported in ≥20% of FracFocus disclosures for additive[a,b]
Acid	Dissolves cement, minerals, and clays to reduce clogging of the pore space	Hydrochloric acid
Biocide	Controls or eliminates bacteria, which can be present in the base fluid and may have detrimental effects on the fracturing process	Glutaraldehyde; 2,2-dibromo-3-nitrilopropionamide
Breaker	Reduces the viscosity of specialized treatment fluids such as gels and foams	Peroxydisulfuric acid diammonium salt
Clay control	Prevents the swelling and migration of formation clays in reaction to water-based fluids	Choline chloride
Corrosion inhibitor	Protects the iron and steel components in the wellbore and treating equipment from corrosive fluids	Methanol; propargyl alcohol; isopropanol
Crosslinker	Increases the viscosity of base gel fluids by connecting polymer molecules	Ethylene glycol; potassium hydroxide; sodium hydroxide
Emulsifier	Facilitates the dispersion of one immiscible fluid into another by reducing the interfacial tension between the two liquids to achieve stability	2-Butoxyethanol; polyoxyethylene(10)nonylphenyl ether; methanol; nonyl phenol ethoxylate
Foaming agent	Generates and stabilizes foam fracturing fluids	2-Butoxyethanol; Nitrogen, liquid; isopropanol; methanol; ethanol

Additives	Function	Chemicals reported in ≥20% of FracFocus disclosures for additive[a,b]
Friction reducer	Reduces the friction pressures experienced when pumping fluids through tools and tubulars in the wellbore	Hydrotreated light petroleum distillates
Gelling agent	Increases fracturing fluid viscosity allowing the fluid to carry more proppant into the fractures and to reduce fluid loss to the reservoir	Guar gum; hydrotreated light petroleum distillates
Iron control agent	Controls the precipitation of iron from solution	Citric acid
Nonemulsifier	Separates problematic emulsions generated within the formation	Methanol; isopropanol; nonyl phenol ethoxylate
pH control	Affects the pH of a solution by either inducing a change (pH adjuster) or stabilizing and resisting change (buffer) to achieve desired qualities and optimize performance	Carbonic acid, dipotassium salt; potassium hydroxide; sodium hydroxide; acetic acid
Resin curing agents	Lowers the curable resin coated proppant activation temperature when bottom hole temperatures are too low to thermally activate bonding	Methanol; nonyl phenol ethoxylate; isopropanol; alcohols, C12-14-secondary, ethoxylated
Scale inhibitor	Controls or prevents scale deposition in the production conduit or completion system	Ethylene glycol; methanol
Solvent	Controls the wettability of contact surfaces or prevents or breaks emulsions	Hydrochloric acid

[a] Chemicals (excluding water and quartz) listed as reported to FracFocus in more than 20% of disclosures for a given purpose when that purpose was listed as used on a disclosure. These are not necessarily the active ingredients for the purpose, but rather are listed as being commonly present for the given purpose. Chemicals may be disclosed for more than a single purpose (e.g., 2-butoxyethanol is listed as being used as an emulsifier and a foaming agent).

[b] Analysis considered 32,885 disclosures and 615,436 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; valid concentrations; and valid purpose. Disclosures that did not meet quality assurance criteria (5,645) or other, query-specific criteria were excluded from analysis.

A general description of typical hydraulic fracturing fluid formulations nationwide is difficult because fracturing fluids vary from well to well. Based on the FracFocus report, the median number of chemicals reported for each disclosure was 14, with the 5th to 95th percentile ranging from four to 28. The median number of chemicals per disclosure was 16 for oil wells and 12 for gas wells (U.S. EPA, 2015b). Other sources have stated that between three and 12 additives and chemicals are used (Schlumberger, 2015; Carter et al., 2013; Spellman, 2012; GWPC and ALL Consulting, 2009).[1]

Water, the most commonly used base fluid for hydraulic fracturing, is inferred to be used as a base fluid in more than 93% of FracFocus disclosures. Alternatives to water-based fluids, such as hydrocarbons and gases, including carbon dioxide or nitrogen-based foam, may also be used based on formation characteristics, cost, or preferences of the well operator or service company (ALL Consulting, 2012; GWPC and ALL Consulting, 2009). Non-aqueous base fluid ingredients were identified in 761 (2.2%) of FracFocus 1.0 disclosures (U.S. EPA, 2015a). Gases and hydrocarbons may be used alone or blended with water; more than 96% of the disclosures identifying non-aqueous base fluids are blended (U.S. EPA, 2015a). There is no standard method to categorize the different fluid formulations (Patel et al., 2014; Montgomery, 2013; Spellman, 2012; Gupta and Valkó, 2007). Therefore, we broadly categorize the fluids as water-based or alternative fluids.

5.3.1. Water-Based Fracturing Fluids

The advantages of water-based fracturing fluids are low cost, ease of mixing, and ability to recover and recycle the water. The disadvantages are low viscosity, the narrowness of the fractures created, and they may not provide optimal performance in water-sensitive formations (see Section 5.3.2) (Montgomery, 2013; Gupta and Valkó, 2007). Water-based fluids can be as simple as water with a few additives to reduce friction, such as “slickwater,” or as complex as water with crosslinked polymers, clay control agents, biocides, and scale inhibitors (Spellman, 2012).

Gels may be added to water-based fluids to increase viscosity, which assists with proppant transport and results in wider fractures. Gelling agents include natural polymers, such as guar, starches, and cellulose derivatives, which requires the addition of biocide to minimize bacterial growth (Spellman, 2012; Gupta and Valkó, 2007). Gels may be linear or crosslinked. Crosslinking increases viscosity without adding more gel. Gelled fluids require the addition of a breaker, which breaks down the gel after it carries in the proppant, to reduce fluid viscosity to facilitate fluid flowing back after treatment. (Spellman, 2012; Gupta and Valkó, 2007). The presence of residual breakers may make it difficult to reuse recovered water (Montgomery, 2013).

5.3.2. Alternative Fracturing Fluids

Alternative hydraulic fracturing fluids can be used for water-sensitive formations (i.e., formations where permeability is reduced when water is added) or as dictated by production goals (Halliburton, 1988). Examples of alternative fracturing fluids include acid-based fluids; non-aqueous-based fluids; energized fluids, foams or emulsions; viscoelastic surfactant fluids; gels;

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[1] Sources may differ based on whether they are referring to additives or chemicals.

methanol; and other unconventional fluids (Montgomery, 2013; Saba et al., 2012; Gupta and Hlidek, 2009; Gupta and Valkó, 2007; Halliburton, 1988).

Acid fracturing removes the need for a proppant and is generally used in carbonate formations. Fractures are initiated with a viscous fracturing fluid, and the acid (gelled, foamed, or emulsified) is added to irregularly etch the wall of the fracture and prop open the formation for a higher conductivity fracture (Spellman, 2012; Gupta and Valkó, 2007).

Non-aqueous fluids are used in water-sensitive formations. Non-aqueous fluids may also contain additives, such as gelling agents, to improve performance (Gupta and Valkó, 2007). The use of non-aqueous fluids has decreased due to safety concerns, and because water-based and emulsion fluid technologies have improved (Montgomery, 2013; Gupta and Valkó, 2007). Methanol, for example, was previously used as a base fluid in water-sensitive reservoirs beginning in the early 1990s, but was discontinued in 2001 for safety concerns and cost (Saba et al., 2012; Gupta and Hlidek, 2009; Gupta and Valkó, 2007). Methanol is still used as an additive or in additive mixtures in hydraulic fracturing fluid formulations.

Energized fluids, foams, and emulsions minimize fluid leakoff, have high proppant-carrying capacity, improve fluid recovery, and are sometimes used in water-sensitive formations (Barati and Liang, 2014; Gu and Mohanty, 2014; Spellman, 2012; Gupta and Valkó, 2007; Martin and Valko, 2007).[1] However, these treatments tend to be expensive, require high pressure, and pose potential health and safety concerns (Montgomery, 2013; Spellman, 2012; Gupta and Valkó, 2007). **Energized fluids** are mixtures of liquid and gas (Patel et al., 2014; Montgomery, 2013). Nitrogen (N_2) or carbon dioxide (CO_2), the gases used, make up less than 53% of the fracturing fluid volume, typically ranging from 25% to 30% by volume (Montgomery, 2013; Gupta and Valkó, 2007; Mitchell, 1970). **Energized foams** are liquid-gas mixtures, with N_2 or CO_2 gas comprising more than 53% of the fracturing fluid volume, with a typical range of 70% to 80% by volume (Mitchell, 1970). **Emulsions** are liquid-liquid mixtures, typically a hydrocarbon (e.g., condensate or diesel) with water, with the hydrocarbon typically 70% to 80% by volume.[2] Both water-based fluids, including gels, and non-aqueous fluids can be energized fluids or foams.

Foams and emulsions break easily using gravity separation and are stabilized by using additives such as foaming agents (Gupta and Valkó, 2007). Emulsions may be used to stabilize active chemical ingredients or to delay chemical reactions, such as the use of carbon dioxide-miscible, non-aqueous fracturing fluids to reduce fluid leakoff in water-sensitive formations (Taylor et al., 2006).

Other types of fluids not addressed above include viscoelastic surfactant fluids, viscoelastic surfactant foams, crosslinked foams, liquid carbon dioxide-based fluid, and liquid carbon dioxide-based foam fluid, and hybrids of other fluids (King, 2010; Brannon et al., 2009; Curtice et al., 2009;

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[1] Leakoff is the fraction of the injected fluid that infiltrates into the formation (e.g., through an existing natural fissure) and is not recovered during production (Economides et al., 2007). See Chapter 6, Section 6.3 for more discussion on leakoff.

[2] Diesel is a mixture typically of C8 to C21 hydrocarbons.

Tudor et al., 2009; Gupta and Valkó, 2007; Coulter et al., 2006; Boyer et al., 2005; Fredd et al., 2004; MacDonald et al., 2003).

Alternative fluids have been developed to work in tight formations, shales, and coalbeds, where production is based on desorption of the natural gas, or in formations where the fracturing fluid must displace a fluid that is already in place.

5.3.3. Proppants

Proppants are small particles carried down the well and into fractures by fracturing fluid. They hold the fractures open after hydraulic fracturing fluid has been removed (Brannon and Pearson, 2007). The propped fractures provide a path for the hydrocarbon to flow from the reservoir. Sand is most commonly used, but other proppants include man-made or specially engineered particles, such as resin-coated sand, high-strength ceramic materials, or sintered bauxite (Schlumberger, 2014; Brannon and Pearson, 2007). Proppant types can be used individually or in combinations.

5.4. Frequency and Volume of Hydraulic Fracturing Chemical Use

This section highlights the different chemicals used in hydraulic fracturing and discusses the frequency and volume of use. Based on the U.S. EPA analysis of the FracFocus 1.0 database (see Text Box 5-2), we focus our analysis on individual chemicals rather than mixtures of chemicals used as additives. Chemicals are reported to FracFocus by using the chemical name and the Chemical Abstract Services Registration Number (CASRN), which is a unique number identifier for every chemical substance.[1] The information on specific chemicals, particularly those most commonly used, can be used to assess potential impacts to drinking water resources. The volume of chemicals stored on-site provides information on the potential volume of a chemical spill.

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[1] A CASRN and chemical name combination identify a chemical substance, which can be a single chemical (e.g., hydrochloric acid, CASRN 7647-01-0) or a mixture of chemicals (e.g., hydrotreated light petroleum distillates (CASRN 64742-47-8), a complex mixtures of C9 to C16 hydrocarbons). For simplicity, we refer to both pure chemicals and chemical substances that are mixtures, which have a single CASRN, as "chemicals."

Text Box 5-2. The FracFocus Registry and EPA FracFocus Report.

The Ground Water Protection Council (GWPC) and the Interstate Oil and Gas Compact Commission (IOGCC) developed a national hydraulic fracturing chemical registry, FracFocus (www.fracfocus.org). Well operators can use the registry to disclose information about chemicals they use during hydraulic fracturing. The EPA accessed data from FracFocus 1.0 from January 1, 2011 to February 28, 2013, which included more than 39,000 disclosures from 20 states that had been submitted by operators prior to March 1, 2013.

Submission to FracFocus was initially voluntary and varied from state to state. During the timeframe of the EPA's study, six of the 20 states with data in the project database began requiring operators to disclose chemicals used in hydraulic fracturing fluids to FracFocus (Colorado, North Dakota, Oklahoma, Pennsylvania, Texas, and Utah). Three other states started requiring disclosure to either FracFocus or the state (Louisiana, Montana, and Ohio), and five states required or began requiring disclosure to the state (Arkansas, Michigan, New Mexico, West Virginia, and Wyoming). Alabama, Alaska, California, Kansas, Mississippi, and Virginia did not have reporting requirements during the period of the EPA's study.

Disclosures from the five states reporting the most disclosures to FracFocus (Texas, Colorado, Pennsylvania, North Dakota, and Oklahoma) comprise over 78% of the disclosures in the database; nearly half (47%) of the disclosures are from Texas. Thus, data from these states are most heavily represented in the EPA's analyses. The EPA's analysis may or may not be nationally representative.

The EPA summarized information on the locations of the wells in the disclosures, water volumes used, and the frequency of use and concentrations (% by mass, reported as maximum ingredient concentration) of the chemicals in the additives and the hydraulic fracturing fluid. Additional information can be found in the EPA FracFocus report (U.S. EPA, 2015a).

The EPA compiled a list of 1,076 chemicals known to be have been used in the hydraulic fracturing process (see a full list, methodology, and the source citations in Appendix A). The chemicals used in hydraulic fracturing fall into different chemical classes and include both organic and inorganic chemicals. The chemical classes of commonly used hydraulic fracturing chemicals include but are not limited to:

- Acids (e.g., hydrochloric acid, peroxydisulfuric acid, acetic acid, citric acid).
- Alcohols (e.g., methanol, isopropanol, ethylene glycol, propargyl alcohol, ethanol).
- Aromatic hydrocarbons (e.g., benzene, naphthalene, heavy aromatic petroleum solvent naphtha).
- Bases (e.g., sodium hydroxide, potassium hydroxide).
- Hydrocarbon mixtures (e.g., petroleum distillates).
- Polysaccharides (e.g., guar gum).
- Surfactants (e.g., poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy, 2-butoxyethanol).
- Salts (e.g., sodium chlorite, dipotassium carbonate).

Text Box 5-3. Confidential Business Information (CBI)

This assessment relies in large part upon information provided to the EPA or to other organizations. The submitters of that information (e.g., businesses that operate wells or perform services to hydraulically fracture the well) may view some of the information as confidential business information (CBI), and accordingly asserted CBI claims to protect such information. Information deemed to be CBI may include information such as trade secrets or other proprietary business information, entitled to confidential treatment under Exemption 4 of the Freedom of Information Act (FOIA) and other applicable laws. FOIA and the EPA's CBI regulations may allow for information claimed as CBI provided to the EPA to be withheld from the public, including in this document.

The EPA evaluated data from FracFocus 1.0, a national hydraulic fracturing chemical registry used and relied upon by some states, industry groups and non-governmental organizations. A company submitting a disclosure to FracFocus may choose to not report the identity of a chemical it considers CBI. As part of the EPA's analysis, more than 39,000 FracFocus 1.0 disclosures over the period January 1, 2013 to March 1, 2013 were analyzed and more than 70% of disclosures contained at least one chemical designated as CBI. Of the disclosures containing CBI chemicals, there was an average of five CBI chemicals per disclosure (U.S. EPA, 2015a). The prevalence of CBI claims in FracFocus 1.0 limits completeness of the data set.

Consistent with the hydraulic fracturing study plan, data were submitted by nine service companies to the EPA regarding chemicals used in hydraulic fracturing from 2005 to 2009. Because this submission was to the EPA, the EPA was given the actual names and CASRNs of any chemicals the company considered CBI. This included a total of 381 CBI chemicals, with a mean of 42 CBI chemicals per company and a range of 7 to 213 (U.S. EPA, 2013a).

5.4.1. National Frequency of Use of Hydraulic Fracturing Chemicals

The EPA reported that 692 chemicals were reported to FracFocus 1.0 for use in hydraulic fracturing from January 1, 2011, to February 28, 2013, with a total of 35,957 disclosures (U.S. EPA, 2015a).[1]

Table 5-2 presents the 35 chemicals (5% of all chemicals identified in the EPA's study) that were reported in at least 10% of the FracFocus 1.0 disclosures for all states reporting to FracFocus during this time. This table also includes the top four additives that were reported to include the given chemical in FracFocus disclosures from January 1, 2011 to February 28, 2013.

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[1] The EPA reported that 692 chemicals were reported to FracFocus 1.0 for use in hydraulic fracturing from January 1, 2011, to February 28, 2013, with a total of 35,957 disclosures. Chemicals may be pure chemicals (e.g., methanol) or chemical mixtures (e.g., hydrotreated light petroleum distillates), and they each have a single CASRN. Of these 692 chemicals, 598 had valid fluid and additive concentrations (34,675 disclosures). Sixteen chemicals were removed because they were minerals listed as being used as proppants. This left a total of 582 chemicals (34,344 disclosures).

Table 5-2. Chemicals reported to FracFocus 1.0 from January 1, 2011 to February 28, 2013 in 10% or more disclosures, with the percent of disclosures for which each chemical is reported and the top four reported additives for the chemical.

For chemicals with fewer than four reported additives, the table presents all additives (U.S. EPA, 2015b).

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Chemical used in these additives (four most common, FracFocus database)[c]
1	Methanol	67-56-1	72%	corrosion inhibitors, surfactants, non-emulsifiers, scale control
2	Hydrotreated light petroleum distillates[d]	64742-47-8	65%	friction reducers, gelling agents and gel stabilizers, crosslinkers and related additives, viscosifiers
3	Hydrochloric acid	7647-01-0	65%	acids, solvents, scale control, clean perforations
4	Water	7732-18-5	48%	acids, biocides, clay control, scale control
5	Isopropanol	67-63-0	47%	corrosion inhibitors, non-emulsifiers, surfactants, biocides
6	Ethylene glycol	107-21-1	46%	crosslinkers and related additives, scale control, corrosion inhibitors, friction reducers
7	Peroxydisulfuric acid, diammonium salt	7727-54-0	44%	breakers and breaker catalysts, oxidizer, stabilizers, clean perforations
8	Sodium hydroxide	1310-73-2	39%	crosslinkers and related additives, biocides, pH control, scale control
9	Guar gum	9000-30-0	37%	gelling agents and gel stabilizers, viscosifiers, clean perforations, breakers and breaker catalysts
10	Quartz[e]	14808-60-7	36%	breakers and breaker catalysts, gelling agents and gel stabilizers, scale control, crosslinkers and related additives
11	Glutaraldehyde	111-30-8	34%	biocides, surfactants, crosslinkers and related additives, sealers
12	Propargyl alcohol	107-19-7	33%	corrosion inhibitors, inhibitors, acid inhibitors, base fluid
13	Potassium hydroxide	1310-58-3	29%	crosslinkers and related additives, pH control, friction reducers, gelling agents and gel stabilizers
14	Ethanol	64-17-5	29%	surfactants, biocides, corrosion inhibitors, fluid foaming agents and energizers

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Chemical used in these additives (four most common, FracFocus database)[c]
15	Acetic acid	64-19-7	24%	pH control, iron control agents, acids, gelling agents and stabilizers
16	Citric acid	77-92-9	24%	iron control agents, scale control, gelling agents and gel stabilizers, pH control
17	2-Butoxyethanol	111-76-2	21%	surfactants, corrosion inhibitors, non-emulsifiers, fluid foaming agents and energizers
18	Sodium chloride	7647-14-5	21%	breakers/breaker catalysts, friction reducers, scale control, clay control
19	Solvent naphtha, petroleum, heavy arom.[f]	64742-94-5	21%	surfactants, non-emulsifiers, inhibitors, corrosion inhibitors
20	Naphthalene	91-20-3	19%	surfactants, non-emulsifiers, corrosion inhibitors, inhibitors
21	2,2-Dibromo-3-nitrilopropionamide	10222-01-2	16%	biocides, clean perforations, breakers and breaker catalysts, non-emulsifiers
22	Phenolic resin	9003-35-4	14%	proppants, biocides, clean perforations, base fluid
23	Choline chloride	67-48-1	14%	clay control, clean perforations, base fluid, biocides
24	Methenamine	100-97-0	14%	proppants, crosslinkers and related additives, biocides, base fluid
25	Carbonic acid, dipotassium salt	584-08-7	13%	pH control, proppants, acids, surfactants
26	1,2,4-Trimethylbenzene	95-63-6	13%	surfactants, non-emulsifiers, corrosion inhibitors, inhibitors
27	Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides[g]	68424-85-1	12%	biocides, non-emulsifiers, corrosion inhibitors, scale control
28	Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)[h]	127087-87-0	12%	surfactants, friction reducers, non-emulsifiers, inhibitors
29	Formic acid	64-18-6	12%	corrosion inhibitors, acids, inhibitors, pH control
30	Sodium chlorite	7758-19-2	11%	breakers/breaker catalysts, biocides, oxidizer, proppants
31	Nonyl phenol ethoxylate	9016-45-9	11%	non-emulsifiers, resin curing agents, activators, friction reducers

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Chemical used in these additives (four most common, FracFocus database)[c]
32	Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8	11%	biocides, scale control, clay control
33	Polyethylene glycol	25322-68-3	11%	biocides, non-emulsifiers, surfactants, clay control
34	Ammonium chloride	12125-02-9	10%	friction reducers, crosslinkers and related additives, scale control, clay control
35	Sodium persulfate	7775-27-1	10%	breakers and breaker catalysts, oxidizer, pH control

[a] Chemical refers to chemical substances with a single CASRN, these may be pure chemicals (e.g., methanol) or chemical mixtures (e.g., hydrotreated light petroleum distillates).
[b] Analysis considered 34,675 disclosures and 676,376 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (3,855) or other, query-specific criteria were excluded from analysis.
[c] Analysis considered 32,885 disclosures and 615,436 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; valid concentrations; and valid purpose. Disclosures that did not meet quality assurance criteria (5,645) or other, query-specific criteria were excluded from analysis.
[d] Hydrotreated light petroleum distillates (CASRN 64742-47-8) is a mixture of hydrocarbons, in the C9 to C16 range.
[e] Quartz (CASRN 14808-60-7) the proppant most commonly reported, was also reported as an ingredient in other additives U.S. EPA (2015a).
[f] Heavy aromatic solvent naphtha (petroleum) (CASRN 64742-94-5) is mixture of aromatic hydrocarbons, in the C9 to C16 range.
[g] Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides (CASRN 68424-85-1) is a mixture of benzalkonium chloride with carbon chains between 12 and 16.
[h] Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture) (CASRN 127087-87-0) is mixture with varying length ethoxy links.

There is no single chemical used at all wells across the nation. Methanol is the most commonly used chemical, reported at 72.1% of wells in FracFocus 1.0, and is associated with 33 types of additives, including corrosion inhibitors, surfactants, non-emulsifiers, and scale control (U.S. EPA, 2015b). Table 5-2 also shows the variability in different chemicals reported to FracFocus 1.0. The percentage of disclosures reporting a given chemical suggests the likelihood of that chemical's use at a site. Only three chemicals (methanol, hydrotreated light petroleum distillates, and hydrochloric acid) were used at more than half of the sites nationwide, and only 12 were used at more than one-third.

In addition to providing information on frequency of use, FracFocus 1.0 data provides the maximum concentration by mass of a given chemical in an additive. For example, for the most frequently used chemical, methanol, the median maximum additive concentration reported in FracFocus disclosures is 30%, by mass, with a range of 0.44% to 100% (5th to 95th percentile). This suggests that methanol is generally used as part of a mixture of chemicals in the hydraulic fracturing fluid, and may be stored in a mixture of chemicals or as pure methanol. This wide range of possible concentrations of methanol further complicates assessing the potential impact of spills, as the properties of the fluid will depend on the different chemicals present and on their concentrations. For all chemicals, spills of a highly concentrated chemical can have different potential impacts than spills of dilute mixtures.

5.4.2. Nationwide Oil versus Gas

FracFocus 1.0 data also can elucidate the differences between the chemicals used for oil production and those used for gas production, providing a better understanding of potential spill impacts from each. Table C-1 and C-2 in Appendix C present the chemicals reported in at least 10% of all gas (34 chemicals) and oil (39 chemicals) disclosures nationwide.

Many of the same chemicals are used for oil and gas, but some chemicals are used more frequently in oil production and others more frequently in gas.[1] For example, hydrochloric acid is the most commonly reported chemical for gas wells (73% of disclosures); it is the fifth most frequently reported chemical for oil wells (58% of disclosures). However, both oil and gas operators each reports using methanol in 72% of disclosures. Methanol is the most common chemical used in hydraulic fracturing fluids at oil wells and the second most common chemical in hydraulic fracturing fluids at gas wells.

5.4.3. State-by-State Frequency of Use of Hydraulic Fracturing Chemicals

We conducted a state-by-state analysis of chemical use based on FracFocus 1.0 disclosures (U.S. EPA, 2015b). Some states reported more disclosures than other states, because they have relatively more hydraulic fracturing activity and/or greater numbers of disclosures to FracFocus 1.0. Reporting can bias national numbers towards those states with a disproportionate number of disclosures. For example, the EPA (2015a) reported that Texas had 16,405 of the 34,675 disclosures with parsed ingredients and valid CASRNs and concentrations, making up almost half (47%) of all disclosures for the 20 states reporting to FracFocus 1.0. We attempt to account for the possible effect of having a large number of disclosures in Texas by looking at a compilation of the top 20 chemicals reported to FracFocus for all states.

Table 5-3 presents and ranks chemicals reported most frequently to FracFocus 1.0 for each state (U.S. EPA, 2015b). There are 94 unique chemicals comprising the top 20 chemicals for each state, indicating similarity in chemical usage among states.

Methanol is reported in 19 of the 20 (95%) states. Alaska is the only state in which methanol is not reported (based on the state's 20 disclosures to FracFocus). The percentage of disclosures reporting use of methanol ranges from 38% (Wyoming) to 100% (Alabama, Arkansas).

Ten chemicals (excluding water) are among the 20 most frequently reported in 14 of the 20 states. These chemicals are: methanol; hydrotreated light petroleum distillates; ethylene glycol;

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[1] This separation was done solely based on whether it was an oil or gas disclosure. The analysis did not separate out reservoir factors, such as temperature, pressure, or permeability, which may be important factors for which chemicals are used.

isopropanol; quartz; sodium hydroxide; ethanol; guar gum; hydrochloric acid; and peroxydisulfuric acid, diammonium salt.[1] These 10 chemicals are also the most frequently reported chemicals nationwide.

By performing this analysis by state, we observed that methanol is used across the continental U.S. (not Alaska), and there are 9 other chemicals that are frequently used across the U.S. Beyond those, however, there are a number of different chemicals that are used in one state more commonly than others and many may not be used at all in other states. This suggests that there is regional variability in some chemicals and a common set of the same chemicals that are frequently used.

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[1] Quartz was the most commonly reported proppant and also reported as an ingredient in other additives (U.S. EPA, 2015a).

Table 5-3. The percentage of disclosures of the 20 most commonly reported chemical by state, where a chemical is reported in at least three states.

The 20 most frequently reported chemicals were identified for all 20 states that reported to FracFocus 1.0 (U.S. EPA, 2015b). The chemicals were ranked by counting the number of states where that chemical was in the top 20. Chemicals were then ranked so that chemicals used most widely among the most states come first. Methanol is reported in 19 of 20 states, so methanol is ranked first. A chemical was only presented on the list if it were reported in at least three states, resulting in 33 chemicals. The full table of top 20 chemicals (91 chemicals) is presented in Appendix C.

		Percentage of disclosures per state[a]																			
Chemical name	**CASRN**	**AL**	**AK**	**AR**	**CA**	**CO**	**KS**	**LA**	**MI**	**MS**	**MT**	**NM**	**ND**	**OH**	**OK**	**PA**	**TX**	**UT**	**VA**	**WV**	**WY**
Methanol	67-56-1	100%		100%	39%	63%	79%	59%	93%	75%	63%	91%	53%	52%	70%	69%	78%	79%	61%	64%	38%
Distillates, petroleum, hydrotreated light	64742-47-8		45%	56%	55%	74%	90%	84%	100%	100%	60%	63%	47%	84%	70%	60%	66%	75%		82%	51%
Ethylene glycol	107-21-1	100%	100%	22%	60%		63%	34%	71%	75%	49%	45%	36%	57%	47%	34%	59%	85%	28%	59%	
Isopropanol	67-63-0	100%	65%	44%		57%	25%	51%	79%		64%	62%	37%	49%	42%	31%	48%	53%	54%	31%	43%
Quartz	14808-60-7		100%		89%	23%	23%	37%		50%	64%	68%	46%	45%	27%		43%	40%		22%	30%
Sodium hydroxide	1310-73-2		100%	21%	69%	22%	28%	53%		50%	54%	30%	52%		27%	17%	46%	37%			57%
Ethanol	64-17-5			45%		50%	80%	42%		100%		47%	27%	60%	46%	16%	21%		63%	54%	25%
Guar gum	9000-30-0		50%		93%			49%		50%	43%	63%	55%	51%	25%	23%	43%	43%		23%	69%
Hydrochloric acid	7647-01-0	100%		99%		53%	85%	57%			23%	79%		99%	76%	96%	71%	85%	86%	96%	
Peroxydisulfuric acid, diammonium salt	7727-54-0		50%		83%		22%	27%	57%		62%	75%	55%	64%	39%		54%	39%		54%	64%
Propargyl alcohol	107-19-7			61%			71%	30%	36%			68%		49%	41%	58%	39%	36%	28%	58%	
Glutaraldehyde	111-30-8			55%			75%	36%		50%		57%		72%	55%	34%	40%			71%	22%
Naphthalene	91-20-3	100%				30%	42%	29%	86%		49%		43%		25%			38%	9%		
2-Butoxyethanol	111-76-2	100%	100%						79%			37%				21%	24%	53%	89%	26%	

Chemical name	CASRN	Percentage of disclosures per state[a]																			
		AL	AK	AR	CA	CO	KS	LA	MI	MS	MT	NM	ND	OH	OK	PA	TX	UT	VA	WV	WY
Citric acid	77-92-9						46%					40%		66%	36%	29%	24%	79%	80%	41%	
Sodium chloride	7647-14-5					35%		41%		50%			25%				21%		9%	22%	23%
Solvent naphtha, petroleum, heavy aromatics	64742-94-5					33%	43%				70%		49%		31%		17%		9%		35%
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1			28%			54%			50%				37%	33%	16%				22%	
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	100%				49%			71%		36%					34%			28%		
Potassium hydroxide	1310-58-3							34%		100%	60%		59%	73%			39%				
Acetic acid	64-19-7					21%		28%							24%		31%				31%
Choline chloride	67-48-1					27%						34%		38%				52%	57%		
Polyethylene glycol	25322-68-3	100%							50%		36%		29%			29%					
1,2,4-Trimethylbenzene	95-63-6					27%	40%						25%						9%		
Ammonium chloride	12125-02-9			21%		28%										31%				21%	
Diatomaceous earth, calcined	91053-39-3		100%		71%							38%						35%			
Didecyl dimethyl ammonium chloride	7173-51-5			24%						50%				32%						21%	
Sodium chlorite	7758-19-2							35%		100%			24%								23%
Sodium erythorbate	6381-77-7			33%			30%												13%	32%	
N,N-Dimethylformamide	68-12-2													47%	20%			33%			

This document is a draft for review purposes only and does not constitute Agency policy.

Chemical name	CASRN	Percentage of disclosures per state[a]																			
		AL	AK	AR	CA	CO	KS	LA	MI	MS	MT	NM	ND	OH	OK	PA	TX	UT	VA	WV	WY
Nonyl phenol ethoxylate	9016-45-9											30%						36%	32%		
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0					25%	40%												9%		
Sodium persulfate	7775-27-1									100%						16%					26%
Tetramethylammonium chloride	75-57-0										44%		29%								26%

[a] Analysis considered 34,675 disclosures and 676,376 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (3,855) or other, query-specific criteria were excluded from analysis.

5.4.4. Volumes of Chemicals Used

Understanding the volume of chemicals used at each hydraulic fracturing site is important for understanding potential impacts of chemicals to drinking water resources, because the chemical volume governs how much will be stored on-site, the types of containers required, and the total amount that could spill. While the on-site operator has precise knowledge of the composition and volume of chemicals stored on-site, this information is generally not publicly available. We conducted a comprehensive review of publicly available sources and found two sources (OSHA, 2014a, b; Sjolander et al., 2011) that identify specific chemicals used at a hydraulic fracturing site and provide information on volumes. These are presented in Table 5-4. The volume of chemicals totaled 7,500 gal (28,000 L) and 14,700 gal (56,000 L) for the two sources, with a mean volume for an individual chemical of 1,900 gal (7,000 L) and 1,225 gal (4,600 L), respectively. The range of volumes for each chemical used is 30 to 3,690 gal (114 to 14,000 L).

Table 5-4. Example list of chemicals and volumes used in hydraulic fracturing.

Volumes are for wells with and unknown number of stages and at least one perforation zone. Every well and fluid formation is unique. Volumes may be larger for longer horizontal laterals and with a greater number of stages.

		Sjolander et al. (2011)[a]		Occupational Safety and Health Administration (OSHA, 2014a, b)[b]	
Ingredient	**Examples**	**Volume (gal) or mass (lbs)**	**Percent overall[c]**	**Volume (gal)**	**Percent by volume**
Water		4,000,000 gal	94.62	2,700,000	90
Proppant	Sand	~ 1,500,000 lbs[d]	5.17	285,300	9.51
Acid	Hydrochloric acid or muriatic acid	1,338 gal	0.03	3,690	0.123
Friction reducer	Polyacrylamide, mineral oil	2,040 gal	0.05	2,640	0.088
Surfactant	Isopropanol			2,550	0.085
Potassium chloride				1,800	0.06
Gelling agent	Guar gum or hydroxymethyl cellulose	-[e]	-[e]	1,680	0.056
Scale inhibitor	Ethylene glycol, alcohol, and sodium hydroxide			1,290	0.043

		Sjolander et al. (2011)[a]		Occupational Safety and Health Administration (OSHA, 2014a, b)[b]	
Ingredient	**Examples**	**Volume (gal) or mass (lbs)**	**Percent overall[c]**	**Volume (gal)**	**Percent by volume**
pH buffer	Carbonate			330	0.011
Preservative	Ammonium persulfate			300	0.01
Crosslinker	Borate salts	-[e]	-[e]	210	0.007
Iron control	Citric acid	-[e]	-[e]	120	0.004
Corrosion inhibitor	n,n-Dimethyl formamide	-[e]	-[e]	60	0.002
Biocide / antimicrobial agent	Glutaraldehyde, ethanol, methanol	2,040 gal	0.05	30	0.001
Gel-breaker	Ammonium persulfate	-[e]	-[e]		
All chemicals		7,458 gal	0.21	14,700	0.49
Chemical Volume: Mean (full range)		1,864.5 gal (1,338 – 2,040 gal)		1,225 (30 – 3,690)	

[a] Adapted from Penn State "Water Facts" publication entitled "Introduction to Hydrofracturing" (Sjolander et al., 2011). Composite from two companies: Range Resources, LLC, and Chesapeake Energy, which released in July 2010 the chemistry and volume of materials typically used in their well completions and stimulations.

[b] Adapted from a table generated by the OSHA for use in a training module (OSHA, 2014a, b).

[c] As presented in Sjolander et al. (2011); does not explicitly state percent by mass or by volume.

[d] The Penn State publication presented proppant in pounds instead of gallons.

[e] Listed as an ingredient, but no information on volume or percentage.

Because of the limited information on chemical volumes publicly available, we estimated chemical volumes used across the nation based on the information provided in the FracFocus database. Figure 5-5 plots median estimated chemical volumes, ranked from high to low, with the range of 5th to 95th percentiles.[1] Volumes used are presented for the 74 chemicals that were reported to FracFocus in at least 100 disclosures and for which density data were available.[2] The estimated median volumes vary widely among the different chemicals, covering a range of near zero to 27,000 gal (98,000 L). The mean of the estimated median volumes was 650 gal (2,500 L).[3]

With the median chemical volume, we can estimate total chemical volume for all chemicals used. Based on the above mean of median chemical volumes of 650 gal (2,500 L) per chemical, and given that the median number of chemicals used at a site is 14 (U.S. EPA, 2015a), an estimated 9,100 gal

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[1] Volumes were estimated using FracFocus disclosures. The total hydraulic fracturing fluid volume reported was used to calculate the total fluid mass by assuming the fluid has a density of 1 g/mL. This is a simplifying assumption based on the fact that more than 93% of disclosures are inferred to use water as a base fluid. Water had a median concentration of 88% by mass in the fracturing fluid. Some disclosures reported using brine, which has a density between 1.0 and 1.1 g/mL. This would introduce at most an error of 10% for the fluid calculation (the difference of a chemical being present at 10 versus 9 gal, 1,000 versus 900 gal). We also assume that the mass of chemicals present in calculating the total fluid mass is negligible. Given that ≤2% of the fluid volume is non-water chemicals, and assuming the density of which is 3 mg/L, the error introduced is approximately 6%. For reference, for the chemicals we are calculating volumes, chlorine dioxide is the densest at 2.757 mg/L. Chemical with densities less than 1 mg/L introduce approximately <1% error.
Next, the mass of each chemical per disclosure was calculated. Each chemical is reported to FracFocus 1.0 as a maximum concentration by mass in the hydraulic fracturing fluid. This introduces error, as we only know that it is equal to or less than this mass fraction. In the U.S. EPA (2015a) EPA's analysis of the FracFocus 1.0 database, an additive is comprised of three chemicals with maximum ingredient concentration of 60% in the additive and a maximum concentration of 0.22% in the hydraulic fracturing fluid. Each of the three chemicals cannot be present at 60%. We have no way to know the actual proportions of each chemical in the additive and thus must calculate chemical mass based on the given information. Therefore, our calculations likely overestimate actual volumes. However, in some cases, the concentration in the additive that is given is less than 100% and only one chemical is listed in the additive. In these cases, it appears that the disclosure is reporting the concentration of that chemical in water. Hydrogen chloride is listed as the sole ingredient in the acid additive, and the maximum concentration is 40% by mass. In this case, the HCl is diluted down to 40%, so the total volume would be underestimated.
After all the chemical masses are calculated, the volume is calculated by dividing chemical mass by density.
Given the limited information available, due to the limits of the FracFocus database and general lack of publicly available data, and despite the errors associated with these calculations, these calculations provide context for the general magnitude of volumes for each of the chemicals used on-site. These calculations are used to calculate median volumes for each chemical. These volume calculations are for the chemicals themselves, not the additives.
Analysis considered 34,495 disclosures and 672,358 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; criteria for water volumes; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (4,035) or other, query-specific criteria were excluded from analysis.

[2] Density data were gathered from Reaxys® and other sources as noted. Reaxys® (http://www.elsevier.com/online-tools/reaxys) is an online database of chemistry literature and data. Direct density source, as provided by Reaxys®, is provided in Table C-7 in Appendix C.

[3] Reporting records to FracFocus 1.0 was required in six of the 20 states between January 1, 2011 and February 28, 2013. An additional three states required disclosure to either FracFocus or the state, and five states required reporting to the state. Reporting to FracFocus 1.0 was optional in other states. Some states changed their reporting requirements during the course of the study. The FracFocus 1.0 database therefore does not encompass all data on chemicals used in hydraulic fracturing. As stated in Text Box 4-2, this mix of voluntary versus mandatory disclosure requirements limits the completeness of data extracted from FracFocus 1.0 for estimating hydraulic fracturing fluid. According to a comparison between FracFocus reported fluid volumes and literature values, water use per well was reported to be about 86% of the actual used (median of estimated values. See Chapter 4, Text Box 4-1). If the fluid volume is underreported, then estimated chemical volumes based on fluid volume would be similarly underestimated. Using the underreporting of 86%, then the estimated median chemical volume would be 760 gal.

(34,000 L) of chemicals may be used per well. Given that the number of chemicals per well ranges from 4 to 28 (U.S. EPA, 2015a), the total volume of chemicals per well may range from 2,600 to 18,000 gal (9,800 to 69,000 L).

Another way to estimate total volume of chemicals per well is to use the estimated median volume of 1.5 million gal (5.7 million L) of fluid used to fracture a well (see Chapter 4) (U.S. EPA, 2015a) and assume that up to 2% of that volume are chemicals added to base fluid (Carter et al., 2013; Knappe and Fireline, 2012), resulting in up to 30,000 gal (114,000 L) of chemicals used per well.

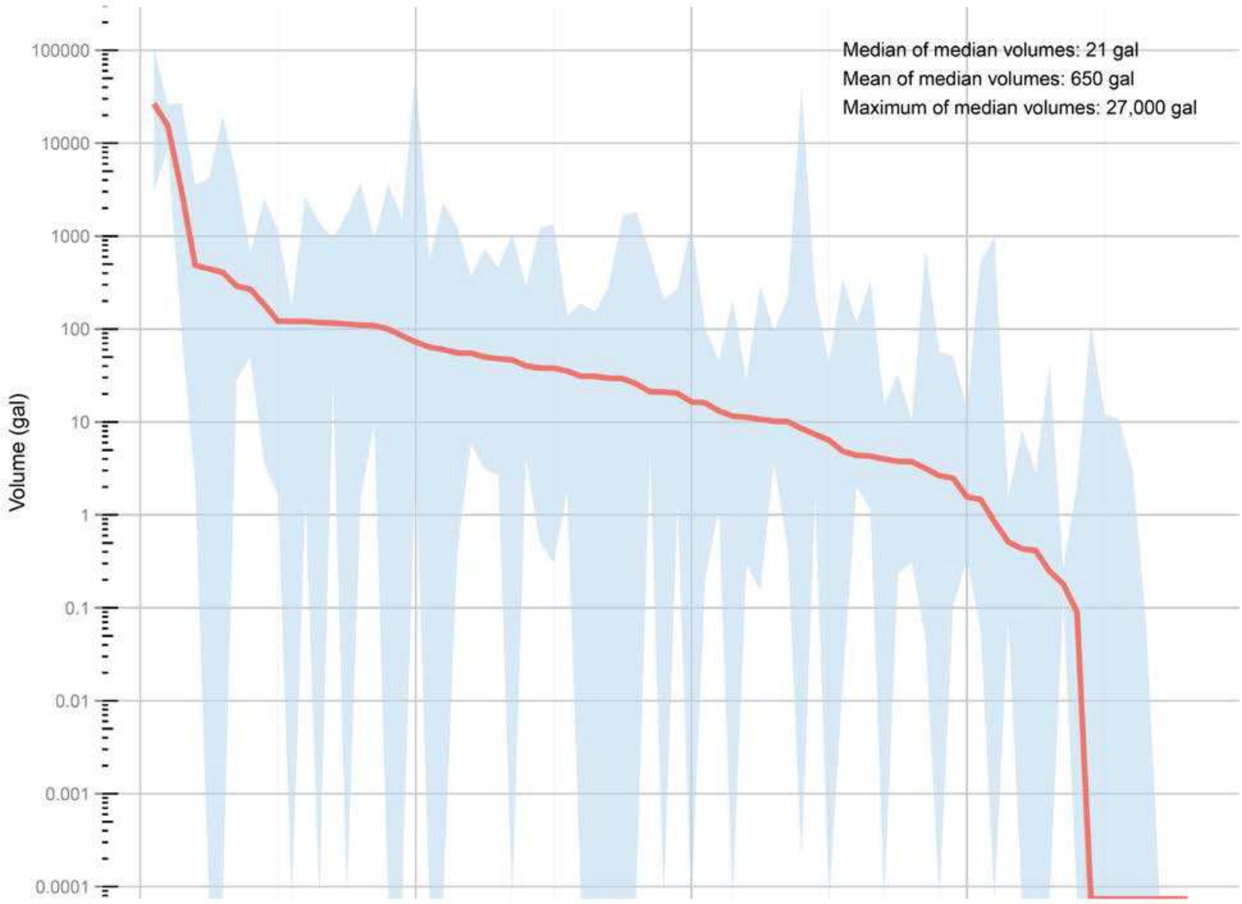

Figure 5-5. Estimated median volumes for chemicals reported in at least 100 FracFocus disclosures by February 28, 2013 for use in hydraulic fracturing from January 1, 2011 to February 28, 2013.

Shaded area represents the zone of 5% and 95% confidence limits. Derived from (U.S. EPA, 2015b).

Using the mean of the median chemical volumes from disclosures in FracFocus 1.0, we can also estimate volume per additive and extrapolate to estimate on-site chemical storage. If we assume three to five chemicals per additive, then total volume per additive stored on-site would approximate 1,900 to 3,200 gal (7,400 to 12,000 L). On-site containers generally store 20% to

100% more additive volume than needed (Houston et al., 2009; Malone and Ely, 2007). This would suggest that 2,300 to 6,500 gal (8,800 to 25,000 L) per additive are stored on-site.

The volume that may be released during a spill depends on where in the chemical mixing process the spill occurs. Spills from chemical or additive containers may result in higher volume spills than the estimated volumes in Figure 5-5 suggest. However, if the spill is of the hydraulic fracturing fluid downstream of the blender, then the total volume of chemical spilled may be less than the estimated total volumes held on site.

5.5. Chemical Management and Spill Potential

This section provides a description of the primary equipment used in the chemical mixing and well injection processes, along with a discussion of the spill vulnerabilities specific to each piece of equipment. Equipment breakdown or failure can trigger a spill itself, and it can also lead to a suspension of activity and the disconnection and reconnection of various pipes, hoses, and containers. Each manipulation of equipment poses additional potential for a spill. The EPA found that approximately one-third of chemical spills on or near the well pad related to hydraulic fracturing resulted from equipment failure (U.S. EPA, 2015n). When possible, we describe documented spills associated with or attributed to specific pieces of equipment, in text boxes in the relevant subsections.

Hydraulic fracturing operations are mobile and must be assembled at each well site, and each assembly and disassembly presents a potential for spills. Equipment used in the chemical mixing and well injection processes typically consists of chemical storage trucks, oil storage tanks/tanker trucks; a slurry blender; one or more high-pressure, high-volume fracturing pumps; the main manifold; surface lines and hoses; and a central control unit. There are many potential sources for leaks and spills in this interconnected system.

Equipment varies in age and technological advancement depending upon service company standards and costs associated with purchase and maintenance. Older equipment may have experienced wear and tear, which may be a factor in spills caused by equipment failure. New equipment may be more automated, reducing opportunities for human error. Information detailing the extent of technological and age differences in fracturing equipment across sites and operators is limited. Table 5-5 provides a description of typical hydraulic fracturing equipment.

Table 5-5. Examples of typical hydraulic fracturing equipment and their functions.

Equipment	Function
Acid transport truck	Transports acids to job sites, the truck has separate compartments for multiple acids or additives.
Chemical storage truck	Transport chemicals to the site in separate containment units or totes. Chemicals are typically stored on and pumped from the chemical storage truck.
Base fluid tanks	Store the required volume of base fluid to be used in the hydraulic fracturing process.
Proppant storage units	Hold proppant and feed it to the blender via a large conveyor belt.
Blender	Takes fluid (e.g., water) from the fracturing tanks and proppant (e.g., sand) from the proppant storage unit and combines them with additives before transferring the mixture to the fracturing pumps
High-pressure fracturing pumps	Pressurize mixed fluids received from the blender and injected into the well.
Manifold trailer with hoses and pipes	A transfer station for all fluids. Includes a trailer with a system of hoses and pipes connecting the blender, the high-pressure pumps, and the fracturing wellhead.
Fracturing wellhead or frac head	A wellhead connection that allows fracture equipment to be attached to the well.

While the primary equipment and layout is generally the same across well sites, the type, size, and number of pieces of equipment may vary depending on a number of factors (Malone and Ely, 2007):

- The size and type of the fracture treatment;
- The number of wells drilled per well pad;
- The location, depth, and length of the fractures;
- The volumes and types of additives, proppants, and fluids used; and
- The operating procedures of the well operator and service company (e.g., some companies require backup systems in case of mechanical failure, while others do not).

Figure 5-6 provides a schematic diagram of a typical layout of hydraulic fracturing equipment.