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Review

Grand Challenges and Opportunities for Greener Chemical Alternatives in Hydraulic Fracturing: A Perspective from the ACS Green Chemistry Institute Oilfield Chemistry Roundtable

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ABSTRACT: Formulated products used in hydraulic fracturing are designed to address specific subsurface challenges during oil and gas well completion and are intended for the treatment of a myriad of issues in a wellbore; however, there are public concerns regarding the use of certain chemical ingredients in hydraulic fracturing. Public perception of hydraulic fracturing and concerns regarding water and chemical usage provide the industry with a unique opportunity to review current chemistries and water management practices with the aim being to identify more environmentally acceptable alternatives or replacements. Herein, we describe what the industry considers to be the greatest challenges, what is currently being done, and potential opportunities to provide alternatives that lead to a more sustainable industry.

INTRODUCTION

The ability to economically extract hydrocarbons through hydraulic fracturing has increased oil and gas production in several markets, and this increase in production is also directly linked to the growth of oilfield water and chemical utilization. Understanding how and why chemicals are used in hydraulic fracturing is vital to a thoughtful review of existing practices and a consideration of potential replacements designed to have fewer or reduced environmental, safety, and health hazards. Increased public awareness and particular concerns related to leaks from field chemical storage containment, leaks, or spills during transfer from transports to field storage, and during treatment at the fracturing site has prompted the development and use of more environmentally preferred products and benefits many stakeholders.

In 2014, the ACS Green Chemistry Institute partnered with companies in the hydraulic fracturing value chain to create a roundtable with the mission to integrate green chemistry and engineering into the chemical supply chain for hydraulic fracturing. The roundtable provides member companies with a scientifically focused organization well-positioned to prioritize research needs, inform the research agenda, and improve cost effectiveness of investment in the design and implementation of green chemistry and engineering tools specific to the industry.[1]

The hydraulic fracturing industry is interested in the reduction or elimination of the handling, storage, and transport of hazardous (e.g., flammable, corrosive, toxic, etc.) substances. It is also interested in concerted efforts to ensure chemicals are used in a responsible manner to reduce risk of human and environmental exposure to potential hazards. In addition to chemical selection and/or reduction, the hydraulic fracturing industry strives to use efficient treatment processes to enhance the recovery and utilization of the produced water for fracturing reuse.

It is also true that for hydraulic fracturing practices to be more sustainable, new chemicals and processes must be economically viable and have performance that is equal to or better than the materials to be replaced. Chemicals developed for the oilfield have a specific purpose and possess certain qualities that allow them to work under demanding surface and subsurface conditions. These same qualities may also prevent the use of alternate chemistries. For example, suspending a water-soluble polymer in a hydrocarbon fluid to facilitate the metered addition of the polymer during a hydraulic fracturing process is likely to preclude the use of water as a less expensive and less hazardous alternative because the water would hydrate the polymer and form a fluid that is too viscous to pump. The alternative to the hydrocarbon carrier fluid may be to use a hydrotreated mineral oil, or possibly alternate metering methods could be considered to eliminate the use of a carrier oil altogether. In addition, physical constraints such as subsurface temperatures, pressure, and geological formation fluid complexity may also affect the chemical additive and hydraulic fracturing fluid performance.

Proposed alternatives must undergo a robust review to determine whether they reduce potential public and environmental hazards and risks including evaluation of intrinsic

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molecular and physical properties. Additional performance testing must be conducted to determine the efficacy and compatibility of the chemical alternative with other naturally occurring formation chemistries and common conditions. If an alternative chemical meets the demands for performance and is more environmentally acceptable than the current chemical, a final review that considers chemical manufacture at scale and the commercial cost of the alternative must be conducted. This paper will outline the general classes of chemicals used in hydraulic fracturing, the history of improvements in the profile of these chemistries, and opportunities for further improvements in the context of green chemistry.

■ WATER USED IN HYDRAULIC FRACTURING

The industry trend is to use larger quantities of water to fracture longer horizontal wells in unconventional oil and gas wells.[2] The U.S. Geological service notes that water use varies depending on rock formation, the operator, and the number of horizontal stages or portions being fractured, and therefore, water requirements for a well can vary from about 1.5 million to 16 million gallons per well.[3] From the standpoint of the oilfield worker and the environment, if there was a spill of hydraulic fracturing fluid (i.e., preinjection water and chemicals), the safest, highest quality water to use is potable water. Close seconds would be freshwater from wells, ponds, irrigation canals, streams, rivers, and lakes. Freshwater for hydraulic fracturing is becoming a less acceptable water source in areas where precipitation may be no more than about 20 in. of rainfall per year, especially if the area is suffering from drought conditions. In those areas, produced water is being treated for use/reuse as fracturing makeup water, where it might comprise as little as 10−15% of the total water used to fracture with, and as much as 100% of the fracturing makeup water. Although produced water use/reuse is viewed as more environmentally acceptable than fresh water consumption for oilfield applications, the worker-related risks and potential for environmental damage are greater than they would otherwise be when using freshwater. Produced water, even treated produced water suitable for fracturing use, can contain very high total dissolved solids (TDS; i.e., 10 000 to 250 000 mg/L TDS is not uncommon; some areas, such as portions of the Delaware Basin in West Texas and Southeastern New Mexico and the Bakken in North Dakota, can possess TDS amounts of 250 000+ mg/L) and naturally occurring radioactive materials (NORM). Produced waters before being treated for fracture reuse can contain liquid hydrocarbons (i.e., from as little as 10 mg/L to as much as 100 000 mg/L), volatile organics (i.e., methane), and hydrogen sulfide (H_2S), which require removable or substantial mitigation during the pretreatment process. Produced water treatment and storage practices must continue to improve to maximize worker safety and minimize the potential for environmental damage in the event of a spill or contact with wildlife.

■ CHEMICALS USED IN HYDRAULIC FRACTURING

Hydraulic fracturing is a method by which the production of a well is enhanced. For example, it is used in well remediation practices that prolong the productive life of the well and the completion of new horizontal wells as part of the well completion process to "bring them online." Water and sand make up 98 to 99.5% of a slickwater hydraulic fracturing fluid, with the exact formulation varying from well to well. Typically, between two and 14 different types of chemicals are deployed in hydraulic fracturing practices in controlled concentrations to address specific formation, fracturing and production challenges in the subsurface environment.[4] Each chemical used has a specific purpose and may include friction reducers (FR) and gelling agents, breakers, biocides, iron control additives, scale inhibitors, and flowback surfactants.

Hydraulic fracturing chemical additives are mixed with a carrier fluid, typically water, at ratios that are generally less than 1 % (w/v) of the overall fluid mixture.[5] Many slickwater fractures, which are the fracture fluid of choice for most unconventional shale oil and gas wells, use nothing more than 0.5 to 1 gallon of friction reducer per 1000 gallons of water. Therefore, as a percent by weight of the fracturing fluid, the FR typically comprises no more than about 0.12% (w/v) and the polyacrylamide polymer no more than about 0.04% (w/v). Dunn-Norman[6] reference two sources which estimate 1900 and 1225 gallons of chemical additives being added to the base fluid. By whatever method one uses to determine the volumes of chemical additives being used in fracturing fluids, the trend is not only to use fewer different chemicals but less of them. Hydraulic fracturing fluids are then delivered to the subsurface through a series of metal (steel) casings and cement designed to separate the well, fracturing fluids, and the subsequent production of hydrocarbons from potential public and environmental risks.

Approximately 700 different chemicals were identified by the U.S. EPA[7] as being used in hydraulic fracturing fluids from January 2011 to March 2013. Dunn-Norman[8] et al., in their evaluation of the U.S. EPA 2015 report, found that only about 5% of the chemicals had been reported as ingredients in at least 10% of the fracturing treatments reviewed, and that only 12 of these chemicals were used more than a third of the time. No single chemical additive was reported as being used in all fracturing fluids in the U.S. The study supports the trend by operators and their fracturing service providers to use fewer chemicals in hydraulic fracturing operations.

The public perception that there is a paucity of information regarding the chemicals used in the formulation of fracturing fluids is simply mistaken. While there is certainly a great deal of proprietary information on the precise formulation of some chemical additives, and with some of the formulated frac fluids, there are excellent references on chemicals used in well stimulation practices, including matrix acidizing, acid fracturing, gravel packing, and fracture-n-pack stimulation treatments. Useful references on chemicals and their general usage in well stimulation applications listed chronologically include Howard and Fast,[9] Williams et al.,[10] Ely,[11,12] Schechter,[13] Economides and Martin,[14] Gupta and Valko,[15] Ghalambor et al.,[16] Kelland,[17] Dusterhoft et al.,[18] Fink,[19] Frenier and Ziauddin,[20] Drogos,[21] King and Durham,[22] Smith and Montgomery,[23] Ali et al.,[24] Nasr-El-Din,[25] Dunn-Norman et al.,[26] and Miskimins,[27] not to mention the plethora of patents held by fracturing service companies which make considerable chemical disclosures about their fracturing fluids.

Generally, chemicals used in hydraulic fracturing fall into different categories and these are described in the order of widest use.[28]

1. Friction reducers (FRs). *1.1. Use.* FRs are chemical compounds that "slick the water" to minimize friction and reduce surface treating pressures at the wellhead. At present, FRs are the single most widely used fracturing chemical additive. Only water and sand are used in greater volume/

weight, and these are not typically regarded as "chemical" additives. Slickwater fluids are typically used in horizontal well applications and utilize fracturing fluids that are considerably less viscous than guar-based fluids. In the absence of high viscosity, Slickwater fractures require high pump rates (often 2 to 5 times greater than pump rates used in classic vertical-well fracturing) to suspend the proppant during the fracturing treatment. As a result of the need for higher fluid velocity to suspend the proppant, any reduction in the amount of friction pressure created means the surface treating pressure and the attending horsepower required to pump the fracturing treatment are substantially reduced. Pumping at higher rates allows fracturing fluids to carry more sand into the fractures making them wider and more conductive, which in turn, stimulates the production of more oil and gas.

Friction reduction on the order of 70–80% by the inclusion of friction reducers is not uncommon. FRs are typically sold at 20–30% active polymer with most of the remainder of the product being a hydrotreated (non-BETX, where BETX is benzene, ethylbenzene, toluene, and xylenes) mineral oil. Although polyacrylamides, which are copolymers with slightly anionic character, have been in use in the fracturing industry since the 1970s, it has only been in the past 15–18 years that they have seen such widespread use in unconventional gas and oil production and have become the fracturing fluid of first choice.

1.2. Green Progression. Lower cost, dry-powdered materials with no oil phase that do not require the use of surfactants, have one-third the volume, have lower VOC emissions, and are less inherently hazardous are being developed. With dry-powdered materials, however, there may be potential inhalation risks that need to be managed. There are also EPA-DFE (Design for Environment)-listed and drinking water approved polymers.[29]

1.3. Gaps, Challenges, and Opportunities. Currently, the raw materials for friction reducers come from nonrenewable sources. An opportunity exists to explore the use of renewable resources for the manufacture of these products. The molecular weight of the polymer is the property that has the greatest impact on friction reduction, so an opportunity may exist for the use of very high molecular weight polysaccharides to provide the same effect. There is also the attending logistical cost of using dry versus liquid polymers at fracturing sites. While liquid polymers may be transported, metered, and utilized with relative ease with the current complement of fracturing equipment, powders, can be difficult to transfer and require the use offield-based hydration and metering equipment. This adds an extra "manufacturing-burden" to already at high capacity field locations where the focus has to be managing a safe high pressure (to 10 000 psi), high rate (4200 gpm) fracturing "factory" assembled in no more than about 48 h. Nevertheless, several operators are now using powder polymer with hydration units. The economics of having fewer truckloads of FR, the reduced cost of not needing to process the dry powder into a slurry, or savings on surfactant and mineral in emulsion polymers, can result in lower cost than the costs of having a dry hydration unit on site.

2. High Viscosity FRs (HVFRs). *2.1. Use.* The development of slickwater fracturing fluids was in response to the need to fracture unconventional shales differently than conventional oil and gas reservoirs. Conventional reservoirs have very high permeabilities (0.1+ milliDarcies) relative to the unconventional shales, possessing nanoDarcy permeabilities, and so have high potential fluid loss controlled by comparatively high viscosity cross-linked fracturing fluids. In response to the absence of fluid loss in low permeability unconventional fracturing regimes requiring high viscosity to optimize efficiency, the trade-off was to pump the fracturing fluids at a much higher rate to transport the proppant. Still, the much higher pump rate brought with it much higher surface treating pressure and a much higher hydraulic horsepower requirement. The addition of an FR provided for a reduction in the friction pressure as well as a reduction in horsepower. Slickwater fracturing was born of unconventional gas wells.

All formations are different, and while it is an oversimplification to simply state that unconventional oil wells are different from unconventional gas wells, it can be said that oil is more viscous than gas, and so more difficult to produce oil from nanodarcy shales. The response from operators and their fracturing service providers was to use higher proppant concentrations and/or higher proppant mesh sizes to produce a higher permeability contrast between the formation and the propped fracture. To achieve this required a greater pumping fracture width and better proppant transport in even longer horizontal wells, and the route to achieving this was to enhance the viscosity of the FR with the development of high-viscosity friction reducers (HVFR).[30] At first, simply higher FR loadings (8–10 gallons per 1000 gallons of water) were used to achieve higher viscosities, but with time, improved HVFRs became available.

2.2. Green Progression. At first, simply higher FR loadings (8–10 gallons FR per 1000 gallons of water) were used to achieve higher viscosities, but with time, improved HVFRs requiring lower concentrations were developed. The HVFR itself typically has a higher activity at 40 to 50% by weight of the product than the FRs, but like the FRs, most of the remainder of the product is a hydrotreated (non-BETX) mineral oil. HVFRs are the most recent development in fracturing fluid chemistry and have already found just about as much use in the industry as FRs and guar slurries. Many companies (e.g., SNF, Kemira, Nuoer etc.) are using dry polymers for high-viscosity friction reduction. These may be applied in a dry add unit, or alternatively combined with mineral oil and a dispersing surfactant to make a slurry. For emulsion polymer, it is possible to create HVFR without increasing polymer loading, simply by increasing the molecular weight of the acrylamide co-polymer. This has been common practice in acrylamide manufacture for many years, predating its use in hydraulic fracturing. Indeed many of the powder materials that are used for HVFR rely on the same principle, higher molecular weight.

2.3. Gaps, Challenges, Opportunities. The transition from freshwater fracturing fluids to the use of some, and then substantial, treated produced water as the fracturing fluid makeup water revealed a gap in HVFR technology. HVFRs are typically anionic polyacrylamides which are found to be particularly susceptible to total dissolved solids (TDS), specifically to the presence of hardness ions (Ca, Mg, Sr, Ba) and especially iron (Fe), almost universally present in produced waters. This applies to FR's as well; it is the acrylate group in the polyacrylamide co-polymer that is the impediment, not the molecular weight. Although produced waters are highly variable, and it may seem less costly to remove the problem ions from the water than it would be to develop HVFRs which are suitable for use in a wide variety of waters, it is not, especially given the transitory nature of drilling and fracturing and the accompanying requirement for water treatment to be flexible and mobile. The inclusion of 2-Acrylamido-2-methylpropane sulfonic acid into the co-polymer backbone ameliorates the negative effects of the presence of calcium and magnesium for the purposes of friction reduction. In produced waters, often the ionic strength of the solution prevents the polymer from uncoiling as it does in a low TDS environment. This uncoiling is necessary for development of viscosity. There is also the ongoing development of methods which the evaluation of HVFRs must address, such as viscosity vs shear rate (what is required at what pump rate) or formation damage (since an increase in viscosity is an inherently greater concern with HVFRs vs FRs)[31−33]

3. Guar Slurries. *3.1. Use.* In hydraulic fracturing, sand in a fluid mixture is pushed at great pressures to crack the rock surrounding a bore hole. To effectively deliver sand into the cracks within the well, it must be suspended in a fluid. A fluid system comprised of gel, often made from natural guar materials, is used to suspend the sand or proppant, especially where higher viscosity fracturing fluids are required to achieve wider fracture widths and/or higher proppant concentrations. Guar and derivatized guar slurries form the backbone for "linear gels," where "linear gels" include hydrated and non-cross-linked polymer solutions. Linear and cross-linked gel systems are used in conventional and unconventional wells. Guar slurries are typically 40 to 45% active polymer, with the remainder of the product being a hydrotreated (non-BETX) mineral oil. Where guar slurries are added to water and the hydrated polymer solution is cross-linked, the most widely used cross-linker is currently some kind of boron-containing compound. Borate cross-linked water-based fracturing fluids have been in use since about 1960[34] and have proven to be highly adaptable to changes in fracturing treatment needs, such as the transition from batch fracturing treatments to fracture-on-the-fly, to fracturing high temperature (to 400 °F) wells, and to the need for low-polymer cross-linked fluid systems for some types of unconventional fracturing treatments.[32]

Although guar slurries are used in hybrid and cross-linked fluid fracturings at an annual volume almost equal to that of FRs, because they are typically used at higher concentrations (at up to about 5 gallons of guar slurry per 1000 gallons of water) to provide for a more highly viscous fracturing fluid, not as much water is pumped with a guar slurry-based fluid as with an FR.

Once proppants are in place, a breaker must be introduced to break the polymer chains in the gel allowing the fluid to become less viscous and flow back out of the fractured rock while leaving the sand behind to support the new opening. Breaker chemicals range from oxidizing agents to enzyme concentrates. The availability, shelf life, hazards, and downhole performance should be considered when developing greener alternatives for breakers.

3.2. Green Progression. Guars, either natural or modified, are inherently nontoxic with good biodegradation properties so there is not great concern or need to develop alternatives. Cross-linkers historically may have been transition metal ions, such as antimony and chromium, but these have been displaced by some kind of boron-containing compound, aluminum, titanium, and zirconium.

3.3. Gaps, Challenges, and Opportunities. Dry on-the-fly guar systems are becoming more commonplace. It is a challenge to produce a base fluid reproducibly using dry blending methods, but progress is being made on this front. Dry on-the-fly systems reduce the volume of guar-based chemicals added to the fracturing fluid by over 50%. However, dry-on-the-fly fluid systems, whether guar or FR based, place an additional burden on field operations in terms of product handling, additional process equipment, and hydration than metering a liquid polymer slurry, and the cost-benefit may go to whether or not the equipment is on hand or not. Enzymatic hydrolysis of guar can replace degradation of the guar by oxidative means; however, enzymes are sensitive to both pH and temperature and typically do not represent an inhalation hazard. Consequently, development of enzymes that work at both higher pH and higher temperature and are effective with synthetic polymers such as those used in the manufacture of FRs and HVFRs are desirable.

4. Breakers. *4.1. Use.* When fracturing operations are complete, the viscosifying agent or friction reducer often needs to be removed from the fracture to avoid impairment of production. The chemistries which remove the viscosifying agent or friction reducer are referred to as breakers. The breakers will react with the target chemical and effect a break, typically by reducing the molecular weight of the target chemical. If the target chemical is a polysaccharide such as guar, both oxidizing breakers and enzymatic breakers are effective. If the target chemical is a synthetic polymer such as an acrylamide copolymer, then oxidizing agents are generally the only chemistries found to be effective, although new chemistries are becoming available.

4.2. Green Progression. Oxidizers were the main mechanism for viscosity reduction until the advent of enzymatic degradation. Enzymes such as hemicellulase have been developed that function over a broad pH range and higher temperatures. With polysaccharide-based systems, enzymatic degradation is the typical method for breaking the fracturing fluid. Enzymes are ineffective in breaking acrylamide copolymers. For these systems, oxidizing breakers such as persulfate or peroxides are the most common break mechanism.[35−37]

4.3. Gaps Challenges and Opportunities. While the useful range of temperature and pH for enzymes continues to expand, further work to provide improved efficacy at alkaline pH and higher temperatures will extend the usefulness of these chemistries. For acrylamide copolymers, a way to get around the use of oxidizing agents is perhaps to incorporate hydrolyzable bonds into the backbone of the polymer or some other form of readily degradable bond that provides chain scission.

5. Solvents. *5.1. Use.* Carrier oils may be the most widely used chemical additive in fracturing fluids since 70−80% of FRs, 55−60% of guar slurries, and 50−60% of VFRs contain a hydrotreated mineral oil. Diesel was, for years, the primary carrier fluid for FRs and guar-based slurries, but there has been an effort to reduce the amount of BETX going back into the well, and since 2010, diesel has been replaced with a light hydrotreated hydrocarbon oil as the best compromise between toxicity and cost.

Solvents are utilized for several applications in oil and gas production and may be used to aid in removal of heavy hydrocarbon deposits, to create and break emulsions, and for increasing wettability of surfaces. Common solvents include ethylene glycol monobutyl ether (EGMBE), xylene, methanol, and isopropanol. Opportunities to develop or employ the use of greener materials with lower toxicity and fewer volatile emissions for widespread solvent use should be considered.

Work has been done by the American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable (ACS GCIPR),[38] which has developed a publicly available guide on solvents. Solvents in this guide are ranked for various hazard categories including safety, health, and environment pathways such as air, water, and waste. Solvents are scored based on these parameters and are assigned two numbers from 1 to 10, with the lower number indicating fewer concerns as well as color coding to allow users to quickly compare solvents.

5.2. Green Progression. Base solvents/carrier chemistry has evolved substantially over the past 20 years. Diesel, which was once a popular carrier, was replaced with hydrotreated distillate streams. The hydrotreated distillate streams were then narrowed down to streams which had improved health and safety profiles. Currently, most carrier solvents are based on severely hydrotreated light distillates which have no detectable BTEX chemistries and extremely low aromatic content. In recent years, renewable streams from various seed oils have, in some cases, been incorporated as a portion of the carrier chemistry.

5.3. Gaps, Challenges, and Opportunities. Biobased solvents from seed oils and seed oil derivatives are generally less cost-effective than distillate-based materials. Rheological properties of biobased solvents are more challenging to modify than distillate-based materials. An opportunity exists to replace the distillate-based solvents with biobased solvents if the cost differential can be reduced and the rheological properties can be adequately modified.

6.0. Biocides. *6.1. Use.* Biocides are chemicals designed to control populations of bacteria and other microorganisms. A recent critical review of biocides use, mobility, degradation, and toxicity in hydraulic fracturing fluids has been published.[39] Current biocidal solutions rely primarily on inducing cell death, though future alternatives may have more subtle modes of action. Biocides are often used in hydraulic fracturing because bacteria at the surface and in the reservoir can cause corrosion of the piping in the well, leading to operational shutdown and, at worst, large-scale spills. Bacteria can also form extensive biofilms or proliferate to an extent that fluid conductivity through the fractured reservoir significantly reduces. Additionally, some species of chemotrophic bacteria produce highly toxic, corrosive metabolic byproducts such as hydrogen sulfide, which leads to reservoir souring. Common biocides used in oil and gas operations are often deployed as an aqueous solution containing the active biocide. Early biocides, such as bromine-based biocides, tributyl tetradecyl phosphonium chloride (TTPC), and halogenated oxidizers, are now considered inferior for oilfield use due to the lack of versatility in a broad range of treatment environments and/or lower sustainability scores in ratings such as the Offshore Chemical Notification Scheme (OCNS).[40] All current biocides are highly regulated in the United States by the Environmental Protection Agency (EPA) under the Federal Insecticide Fungicide Rodenticide Act (FIFRA)[41] and require robust documentation of toxicity to mammals and nontarget organisms, degradation, fate, and transport of the material for these chemicals to be registered for oilfield use. Current commonly used biocidal chemicals are listed below, in rough order of frequency of use:

6.1.1. Glutaraldehyde or Mixtures of Glutaraldehyde and Quaternary Ammonium. OCNS Gold Band rated, with great cost performance and friction reducer compatibility.

6.1.2. Tetrakis(hydroxymethyl)phosphonium Sulfate (THPS) and 2,2-Dibromo-3-nitrilopropionamide (DBNPA). Also OCNS Gold Band rated, though each possesses a more concerning sustainability profile than glutaraldehyde. Specifically, THPS is a known formaldehyde releaser.[42] DBNPA—though able to decompose to the natural products that include CO_2, H_2O, NH_3, and bromide[43]—has recently been classed as an endocrine disruptor by the European Chemicals Agency (ECHA),[44] and additional decomposition intermediates are themselves hazardous.

6.1.3. Oxidants. Oxidants such as chlorine dioxide, sodium hypochlorite, hydrogen peroxide, and peracetic acid are finding targeted use in surface operations to provide effective biocidal activity while reducing concerns about surface contamination in the event of leaks or spills. However, due to chemical compatibility issues, oxidants may only be used for surface water treatment prior to adding other chemicals when formulating fracturing fluids.

6.1.4. Nonchemical Methods. Ultraviolet light may be used for bacterial control but is limited to relatively transparent fluids. Other mechanical methods are under trial, although these mechanical methods, by nature, will have no lingering efficacy on organisms that cause problems in the reservoir.

6.2. Green Progression. In the short term, biocides that are currently registered by the EPA are the only alternatives from which to choose. In the longer term, biocide alternatives may be identified, but these will require registration, and registering a new biocide requires extensive testing and time, both of which translate into significant cost. When considering biocide options or evaluating new biocidal solutions for hydraulic fracturing, there are many aspects of biocide safety from a hazard, exposure, and fate perspective that should be considered. Many industry organizations refer to the OCNS rating scheme for hydraulic fracturing due to it being the best available assessment, but it should be noted that the risk assessments performed in the OCNS are for conventional oilfield operations, not hydraulic fracturing.

6.3. Gaps, Challenges and Opportunities. Biocides are inherently hazardous to many organisms including humans, as the intent of a biocide is to kill living microorganisms. As such, chronic and acute toxicity should be considered when attempting to develop a biocide alternative; however, the use of a less potent alternative in place of a more potent biocide usually requires the use of a higher loading volume to achieve the same level of control and thereby could potentially negate the positive toxicity attributes of the experimental material, resulting in equal or greater risk.

6.4. Potential Opportunities. 6.4.1. Nitrogen Reducing, Sulfate Oxidation (NRSOB) Bioexclusion Technology. This technology is borderline commercial and has been trialed in the Marcellus Shale and the Permian formation in the Wolfcamp. While this may be a more sustainable direction for the industry, continuous dosing of bioexclusion technologies is generally required for efficacy and is more difficult to operationalize in unconventional wells.

6.4.2. Phage Bio-Control. Phages are generally highly specific to certain species or even strains of microbes. Therefore, to be effective, phages must be designed to target a wide variety of species that cause problems in the oilfield. Preliminary studies are underway for the health, food safety, veterinary, agriculture, aquaculture, and fermentation industries.

6.4.3. Enzymes May Be Used to Control, Disperse, or Prevent Biofilm Formation. Enzymes must be evolved to be stable during shipment and formulation into fracturing fluid and must also be effective under a variety of subsurface conditions.

7. Scale Inhibitors. *7.1. Use.* Water is the principal carrier fluid for hydraulic fracturing treatments today. The water used in these treatments may be surface waters having comparatively low total dissolved solids (TDS) content, or they may be treated formation waters with high TDS contents approaching saturation. Fracturing operations often incorporate blended waters to facilitate treatment. The waters used in fracturing applications may not be compatible with each other, or they may not be compatible with the formation waters with which they ultimately come into contact. Such incompatibilities may result in the formation of carbonate or sulfate precipitates which may plug formation fractures or foul wellbores or surface production equipment. More particularly, some of these precipitates, such as calcium carbonate, calcium sulfate, and barium sulfate, can cause scale to form and inhibit oil and gas flow. To treat for the development of scale in a well, scale inhibitor chemicals are introduced. Most scale inhibitors are a combination of phosphonates, for example diethylenetriaminepentamethylene phosphonic acid or other phosphonomethylated amines or phosphorus-containing compounds, formulated in methanol, and more recently, low molecular weight anionic polymers possessing lower toxicity although still formulated with methanol or ethylene glycol.

7.2. Green Progression. Greener alternatives formulated as a dry product are available and reduce or eliminate some chemical hazards found in the liquid counterparts. Additional benefits include the reduction in overall volume (1/8 the volume), reduced risk and cost for transport of dry materials (1/3 the logistics risk), and lowered VOC emissions (1/3 the VOC), also EPA-DFE listed. The use of synthetic polymers has been partially replaced with the use of biobased polymers such as carboxymethylinulin and polyaspartic acid.[45]

7.3. Gaps, Challenges, and Opportunities. Biobased scale inhibitors are not as robust as synthetic polymers or phosphonate chemistry. At higher temperatures, these products hydrolyze, reducing their efficacy. A gap exists for higher-temperature biobased scale inhibitors, and further work needs to be performed in this area.

8.0. Surfactants. *8.1. Use.* Frac jobs typically start with a small acid job which consists of a few thousand gallons of hydrochloric acid to dissolve near a wellbore formation and excess cement and ensure that the perforations in the casing are clear for the fracturing stage. The additives for this acid job include corrosion inhibitors and surfactants. The surfactants are similar to the surfactants used in the fracturing fluid itself. These chemicals reduce the surface tension between oil and water and thereby have a detergency effect that mobilizes contaminants in the well that can impede or reduce the production of oil and gas. Surfactants are typically evaluated by an interfacial tension reduction test or through column flow testing. The major uses of surfactants in hydraulic fracturing are listed in Figure 1.

8.2. Green Progression. In the past, benzene, toluene, ethylbenzene, and xylene-based (BTEX) surfactants were used along with cationic surfactants like oxalkylated amines and quaternary ammonium salts in water with methanol. Currently, nonionic organic compounds like oxyalkylated alcohols in water and methanol or anionics such as sulfonates in water and methanol or IPA/propylene glycol are used. The development of alternatives, including biobased surfactants, has been attempted. The prohibitive cost of production, sustainability, and the ability to scale production to meet the needs of a high-volume industry have limited the adoption of these alternatives.

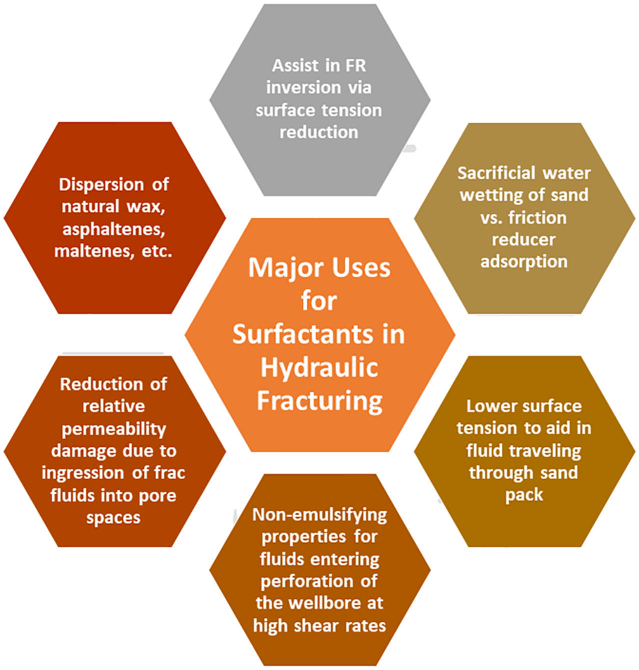

Figure 1. Major uses of surfactants in hydraulic fracturing.

8.3. Gaps, challenges, and opportunities. Attributes such as lower toxicity, improved biodegradation rates, and the ability to scale production to adequate volumes should be considered when selecting potential alternatives.

9. Acid Additives Include the Following. *9.1. Corrosion Inhibitors. 9.1.1. Use.* Corrosion inhibitors are used in conjunction with acids that are introduced into the well. The corrosion inhibitors work to counteract negative effects of acid and other corrosive materials on the metal pipe in the well. Corrosion inhibitors are generally hazardous materials. The continued use of these materials is often based on the aid the materials provide in defending against corrosion of pipes and potentially offsetting impacts and the need for additional resources to counter corroded pipes. However, recent studies reviewing the use of natural materials including plant extracts and other less hazardous materials as corrosion inhibitors may offer viable alternatives to the current selection.

9.1.2. Green Progression. Historically, acetylenic organics like propargyl alcohol (2-propyn-1-ol) and alkylpyridine quaternary ammonium salts or fatty amines and fatty quaternary amines were used. Greener acid corrosion inhibitors have been developed and are in use in the U.S. Propoxylated propargyl alcohol has a comparably smaller environmental, safety, and health profile and is much safer than propargyl alcohol itself.

9.1.3. Gaps, Challenges, and Opportunities. While safer alternatives to propargyl alcohol have been developed and are used in the industry, higher temperature inhibition often requires the use of other chemistries such as pyridine and quinoline quaternized amines. Intensifiers often need to be added to the high temperature inhibitors including compounds such as potassium iodide, antimony compounds, and certain aldehydes; e.g., cinnamaldehyde. Ideally replacements for the metals and halide-based intensifiers will be developed.

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9.2. Iron Reducing Agents. 9.2.1. Use. Acids like hydrochloric acid (HCl) are frequently used to remove iron containing scales from the well, and the concentration of the HCl typically ranges from 5% to 20% (W/V). Concentrated 32% hydrochloric acid may be present at oilfield sites, but acid of this strength is rarely used in the wellbore. HCl is corrosive to iron and will dissolve iron scales such as iron carbonate or iron sulfide that may be present in the wellbore. Dissolution of any iron during an acidizing operation may result in reprecipitation of the iron as the pH of the spent acidizing fluid rises.

9.2.2. Green Progression. Additives to prevent the oxidation of Fe^{2+} (ferrous) to Fe^{+3} (ferric) salts that will precipitate out of solution have included tin(II) compounds, phosphite compounds, and various mercaptans catalyzed with copper catalysts. Today metals such as tin(II) are rarely if ever used. A large portion of iron control agents in use today are based on mercaptans such as mercaptoacetic acid.

9.2.3. Gaps, Challenges, and Opportunities. Mercaptan chemistry, while effective, has its own drawbacks due to the noxious odor created by these compounds. The next generation of iron reducing agents should incorporate the chemical reduction potential of the mercaptan chemistry with chemistries that are not odorous and that are easier for personnel to apply.

10. Chelating Agents. *10.1. Use.* The largest volume of material introduced into a well during hydraulic fracturing operations is water. The hydraulic fracturing fluid has historically been largely composed of fresh water. With increased concerns over the use of freshwater and associated costs, many operators choose to use produced water as the carrier. Produced water is a natural consequence of drilling and fracturing and is generated along with hydrocarbons in oil and gas extraction. Produced water typically contains elevated concentrations of total dissolved solids (TDS) and can impact the other additives in the carrier fluid mixture such as cross-linkers used for the polymers that produce the gel which suspends the proppant. To reduce the effect of TDS in produced water, chelating agents are introduced to bind dissolved ions in the water that would otherwise negatively affect the gelling agent performance. Chelating agents are also frequently used in conjunction with reducing agents for iron control.

10.2. Green Progression. Chelating agents based on amine substituted carboxylic acids, such as ethylenediaminetetraacetic acid (EDTA) and nitrilotrisacetic acid (NTA), have historically provided the most cost-effective performance for chelation. EDTA suffers from a lack of biodegradability, while NTA suffers from undesirable health effects. These chemistries have been widely replaced with products such as citric acid both by itself and in conjunction with other naturally occurring carboxylic acids. Chemistries that are more effective than citric acid/carboxylic acid combinations have been developed such as iminodisuccinic acid (IDS). All of these latter compounds show improved biodegradability and are benign from a health perspective. The increased use of slickwater systems has substantially reduced the consumption of these chemistries over the past decade.

10.3. Gaps, Challenges, and Opportunities. The development of greener alternatives to some widely used chelating agents such as ethylenediaminetetraacetic acid (EDTA) is necessary, as some studies have shown persistence in the environment and poor biodegradation with increased potential for bioavailability of some heavy metals bound by the agent. Green alternatives to historical additives have been developed and are widely used throughout the industry. The performance of the alternative chemistries is not always equal to the amine substituted chemistries. The challenge going forward will be to develop chemistries with the HSE profile of the naturally occurring carboxylic acids or IDS.

11. pH Adjusting Agents. *11.1. Use.* Depending on the type of system, the pH of a hydraulic fracturing fluid frequently needs to be adjusted. Water used in slickwater hydraulic fracturing operations is typically kept between a pH of about 6 and 8. In cross-linked borate fracturing fluids, the pH is adjusted to a mildly alkaline pH, and derivatized cross-linked borate systems are adjusted to either mildly alkaline or mildly acidic pH's depending on the system of interest. When water is found to have a pH out of the range of the desired pH, adjusting agents may be used to bring the pH to the range of interest. Price and availability determine the most commonly used chemical additives for pH adjustment, and these are hydrochloric acid, acetic acid, sodium hydroxide, sodium carbonate, and sodium bicarbonate.

11.2. Green Progression. Chemistry used for adjusting pH has remained unchanged for several years. The increased use of slickwater systems has substantially reduced the consumption of these chemistries over the past decade.

11.3. Gaps, Challenges, and Opportunities. Chemistry used for pH adjustment is likely as optimized as can be achieved, but the industry is always open to low cost opportunities having superior performance and environmental, health, and safety profiles.

12. Clay Control Additives and Formation Stabilizers. *12.1. Use.* Migration of swelling and migrating clays has been accomplished by incorporating potassium chloride into the fracturing fluid. In the early 1980s, a quaternized amine polymer, polydiallyldimethylammonium chloride (DADMAC), was found to be an effective clay stabilizer at lower concentrations of chemicals (mass/mass), making the DADMAC substitution significantly less costly as well as a means by which significantly less chemical additive had to be employed to achieve protection from clay swelling. Shortly thereafter, it was discovered that monomeric quaternized amines such as tetramethylammonium chloride[46,47] and choline chloride functioned effectively as clay stabilizers at similar low concentrations. In the 1990s, several alternate chemistries were incorporated including quaternized and nonquaternized amines. Perhaps the most widely used clay stabilizer used in the industry today is choline chloride. Choline chloride is also referred to by its common name, vitamin B4.

12.2. Green Progression. Industry moved from using large volumes of potassium chloride to lesser amounts of synthetic polymers and then moved from the synthetic polymers to simpler chemicals such as choline chloride and salts of biodegradable simple amines for use as temporary clay stabilizers.

12.3. Gaps, Challenges, and Opportunities. The chemistries used for clay stabilization have recently focused on the use of choline chloride. Choline is produced metabolically by many organisms. The main synthetic method for manufacturing choline, however, is based on petrochemical feedstocks. An opportunity exists to examine whether there is potential for production via a biochemical reaction pathway.

GENERAL REQUIREMENTS FOR CHEMICAL REPLACEMENTS

Chemicals utilized in hydraulic fracturing applications can be generally categorized by the service they provide during the application and include salts and buffers, friction reducers, polymeric viscosifiers, cross-linkers, gel stabilizers, surfactants and nonemulsifiers, scale and corrosion inhibitors, clay control additives, formation stabilizers, breakers, energizing gases, acids, and biocides. Postfracturing well maintenance operations may include the use of many of the same chemistries used to formulate fracturing fluids, as well as solvents and other wellbore cleaning aides.

Any proposed replacement for a hydraulic fracturing chemical must successfully meet and usually beat a range of requirements, and these requirements may differ substantially from other applications where a new, more sustainable chemical may already be actively used in other industrial sectors.

Proposed chemical alternatives have always needed to meet technical specifications set forth by operators and service companies and be shown to work in conditions with differing levels of salinity, heat, pressure, and other parameters which may change from basin to basin. For instance, surface operating conditions may range from −40 °F to 125 °F, and downhole conditions may range from 40 °F to 400 °F. A viable chemical product replacement must match or exceed the technical performance of the material it is replacing and should have a wide range of applicability for utilization in multiple geographic areas. In addition to technical performance and environmental, safety, and health properties, the total efficacy of the material based on loading volume should be considered, as this impacts not only the cost to treat but also the sustainability profile of using the product.

There are key areas of concern that can be addressed by offering alternative chemicals. The energy industry and chemical manufacturers can mitigate some of these concerns by eliminating hazardous chemical ingredients by using less toxic chemistries, introducing targeted volume reductions for certain chemicals, and giving preference to modified delivery methods such as dry additives in place of slurry mixtures.

To reduce the number of products containing hazardous chemicals, chemical manufacturers should avoid the use of ingredients that are listed on inventories for hazardous materials, such as the U.S. Toxic Release inventory[48] and the Hazardous Air Pollutants (HAPS) list.[49] Persistent, bioaccumulative, and toxic chemicals (PBT), as defined by both the OSPAR Commission for the North Sea[50] and the United States Environmental Protection Agency (U.S. EPA),[51] and Persistent Organic Pollutants (POP), as defined by the United Nations Environment Programme (UNEP),[52] should be avoided in the selection of chemical ingredients. Materials on these lists have been documented to persist in the environment, bioaccumulate in the food chain, and demonstrate toxic effects on a variety of flora and fauna. Accepted levels of toxicity, biodegradation, and bioaccumulation factors can vary globally. It is advised to consult multiple authorities including the U.S. EPA, OSPAR Commission, and European Union based on geographic market for the materials. Potential cost savings in the development of a single product for global use should also be considered, employing ingredients which meet the most restrictive requirements versus the costs associated with developing, manufacturing, and marketing a product that meets the minimum standards for a given region. While all authorities have suggested limits, some are stricter and may result in necessary modifications to ensure applicability in a specific area. In addition to a purely hazard-based approach, as is generally used to form these lists, risk should also be considered. A risk-based assessment should account for (1) the amount of a compound required to perform its required function and (2) if a hazard cannot be reduced or eliminated, exposure management activities such as manufacturing engineering controls and personal protective equipment (PPE), which can limit worker and environmental exposure, are included. Information on combining hazard and exposure variables to develop a risk-based approach can be found within the framework designed by the National Academy of Sciences Committee on the Design and Evaluation of Safer Chemical Substitutions.[53]

CHEMICAL USE REDUCTION STRATEGIES

Operators and service companies work to lower the volumes of chemicals used, use chemicals that are less toxic to human health and the environment, and use chemicals that are not persistent or bioaccumulative. Reduction strategies are shown in Figure 2.

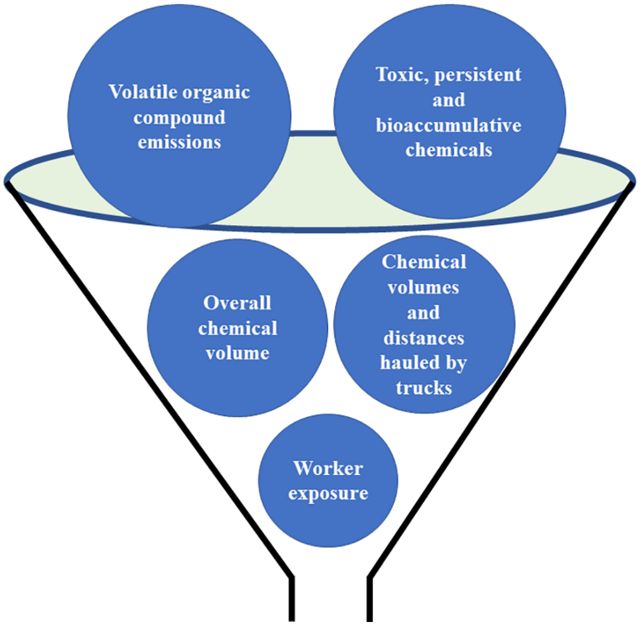

Figure 2. The desire is to adopt strategies to enable a reduction in each sphere and thereby reduce environmental, safety, and health impacts associated with the process of hydraulic fracturing.

Fewer chemical additives are being used to form hydraulic fracturing fluids. Where chemical additives are being used, efforts are being made to use less of them and to find alternatives to those which are toxic.

CONCLUSIONS AND OPPORTUNITIES

The hydraulic fracturing industry has enabled the extraction of hydrocarbons from a variety of geological formations that heretofore have not been economically extracted and which give the U.S. the potential for energy independence. Historically, the practice of horizontal hydraulic fracturing has raised significant public and regulatory concern over impacts to the environment and to human health. The hydraulic fracturing industry has worked over the past 10 years or more to develop hydraulic fracturing technology while decreasing the variety of chemicals, the volume used in a typical slickwater fracturing fluid, and the toxicity of the chemicals that have been employed to stimulate oil and gas production from previously unavailable reserves. While these efforts are laudable, there continue to be opportunities for improvement in several key chemical classes as outlined in this paper. The minimization of chemicals with less desirable environmental, safety, and health concerns and the adoption of greener chemical alternatives will continue to improve the industry's collective chemical footprint. Innovation is essential to finding new alternatives and can be driven by a careful review of current offerings and collaboration among academia, chemical manufacturers, end users, and nonindustry members.

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Notes

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