Water Management for Hydraulic Fracturing in Unconventional Resources—Part 2

Properties and Characteristics of Flowback Fluids

John M. Walsh, GHD Group

In this second article of a series covering water management in hydraulic fracturing (HF) in unconventional resources, the properties and characteristics of the flowback fluids are discussed, together with the general categories of technologies that are best suited to treat them.

As discussed in the June column, the water quality required to make up the HF fluid is a key criterion for selecting the recycle water treatment technology. In some cases, fresh water is required. If the HF flowback water has high salinity, then some form of desalination must be applied. In other cases where salinity can be tolerated, then removal of suspended material is sufficient for recycle.

In addition to the recycle water quality, the properties and characteristics of the flowback fluids are important in the selection of water treating equipment. While this may seem like an obvious statement, it requires some justification. There is a need in the oil and gas industry to find a single, flexible, and multipurpose water treatment technology that is capable of handling most flowback fluid types. This would simplify the selection, purchase, deployment, and operation of equipment in the field. From an operations standpoint, the search for a multipurpose technology is justified.

However, such a technology has not yet been identified, although there are technologies that come close to meeting the need. In general, the operating envelope of most technologies is not yet well-established.

The term "operating envelope" is borrowed from facilities and process engineering. It is a set of conditions, such as temperature, pressure, and composition, for which the technology works well. Once the operating envelope for a technology is known, it can be selected for a given application with confidence that it will work.

HF Flowback Variability

Identifying or developing a universal water treatment technology is important because of the high variability of HF flowback water characteristics, which is not entirely understood. Some variation is explained in terms of zone-to-zone differences in penetration, soak time, and the pressure variation along the well. Other causes of variation are the fraction of produced water, and well-to-well and region-to-region differences within a shale development. In some cases, the variation can be extreme.

Perry and Bosch (2013) report a standard deviation in total dissolved solids (TDS) of 50,000 mg/L in a dataset of more than 500 samples taken from the Bakken development. Such a large standard deviation is not unique. For the Wolfcamp development, the dataset contained nearly 200 samples, and the standard deviation was close to 50,000 mg/L. The standard deviation for gas wells in the Marcellus play was 77,000 mg/L in a dataset of close to 1,000 samples.

For such large sample sets, these are enormous standard deviations. Perhaps some of the variation can be attributed to sampling error and/or analysis error. Some of the variation can be attributed to the nearly saturated concentrations of dissolved minerals. To date, the variations have not been explained.

Such findings present a challenge to production chemists, whose jobs are to prevent scaling and solids precipitation. Selection of the appropriate chemical and effective dosage is difficult. Rather than consider the individual characteristics of each job, the chemist must bracket the potential outcome and treat for the worst case. A different treating program is applied only where the most probable scenario requires it.

This approach to treatment is neither a universal application across all variations nor a fine-grained application tailored to each variation; it lies in between and is sensible.

Another seemingly random variable is load recovery, the fraction of HF fluid produced on flowback.

John M. Walsh is SPE Technical Director for Projects, Facilities, and Construction and principal engineer of water treating for oil and gas at the GHD Group. He can be reached at John.Walsh@ghd.com.

In most HF operations, there is insufficient information to accurately predict the behavior of HF fluids in the rock. The flow of the HF fluid into the rock depends on many factors that are relatively well understood in the laboratory, but are difficult to quantify for any given well in the field. Nevertheless, as with the scale inhibitor discussion, there are discernible differences from one cluster, region, or field to another. Provided that variation is recognized, different technologies can be selected.

While the Perry and Bosch example relates to scale inhibitor treatment, it could equally be applied to the broader problem of water treatment to remove dispersed and dissolved components. It suggests that treatment strategies can be customized, provided that variability is accounted for. Water treatment systems can be designed or selected based on broad, significant differences from one field to another (or one type of HF fluid to another), and must include the possibility of large variation from the average.

Taking stock of the discussion above, we need to proceed cautiously if we are to advocate the idea that water treating equipment should be selected on the basis of fluid properties and characteristics. Although there are logistics and operational incentives to develop a flexible and standard treatment technology, no such universal technology has yet emerged. Empirical evidence demonstrates the high variability of flowback fluid, but there is experience showing that the variability can be accounted for.

How do we select water treatment equipment on the basis of significant differences from one field to another, or from one fluid type to another, while taking into account large variation? As many of us in the business will admit, no one has the answers.

HF flowback fluids can be characterized using broad categories, and technologies can be identified to treat the broad categories of fluid types. More well-established industries with similar fluid types can be investigated to see what types of technologies have been proven useful.

First, let us consider the typical components of HF fluids.

Types of HF Fluids

Economides and Martin (2008) and King (2010) reported that the main fluid additives are friction reducer, biocide, oxygen scavenger, scale inhibitor, wetting agent, breaking agent, and proppant. The fluids and their concentrations are selected on the basis of the petrophysics of the formation (Rickman et al. 2008). The mineralogy (clay, quartz, or carbonate content), brittleness, permeability, and the closure stress are factors that help determine the optimum fluid type. The selection of the fluid type(s) and concentration(s) vary depending on the properties of the shale.

Assuming that biological control has been carried out competently, the major determinants of flowback fluid properties are the friction reducer/polymers. The three types of HF polymers are:

- Polysaccharides—including guar, guar derivatives, xanthan, and hydroxyethyl cellulose
- Cross-linked polysaccharides—such as borate or metal cross-linked guar
- HPAM (partially hydrolyzed polyacrylamide)—slickwater

Combinations of the above are also used.

Flowback Fluid Characteristics

If recycling of the flowback fluid is to be carried out, then the characteristics of the fluid that flows out of the well should be taken into account when selecting the type of water treatment technology to be used.

As a general rule, the fluids pumped into the ground do not necessarily determine the fluids that flow back out of the ground. In some cases, there is a correlation; in other cases, there is not. In the Marcellus development, for example, freshwater injected fluids typically become highly saline through contact with the shale. Load recovery can be as low as 10%, or as high as 60%.

HF flowback fluid contains a combination of produced water, HF fluids, hydrocarbon liquids, and dissolved minerals from contact of the injected fluids with the reservoir rock, proppant, and solids from the reservoir, and solids resulting from mineral precipitation. Polymers in the flowback fluid can be in different states of solution and have significantly different molecular weights from the polymers that were pumped downhole. In many cases, a breaking agent is used to reduce polymer viscosity, which promotes HF fluid flow from the fracture and helps the proppant stay in place during flowback.

From a water treating perspective, the following are the critical components of HF flowback fluids in unconventional resources:

- Dispersed light oil
- Dissolved polymer
- Organic solids (mostly dispersed/suspended polymer)
- Inorganic solids (sand, clay, precipitated mineral, and proppant)
- Surfactant (wetting agent)
- Dissolved salt

The presence of the surfactant reduces the interfacial tension between dispersed oil and water, thereby increasing the sensitivity of the oil drops to becoming sheared into smaller drops. The surfactant also increases the coalescence energy barrier to prevent small drops from combining into larger drops. Much of the surfactant wetting agent

The ROVER mobile clarification system was developed for heavy oil applications and is used in treating hydraulic fracturing flowback fluids. ***Photo courtesy of Fountain Quail Water Management.***

adsorbs on the formation and does not flow back.

The presence of the polymer increases the viscosity of the flowback fluid. By itself, higher fluid viscosity increases the potential for fouling of the water treating equipment because it promotes the tendency of other solids to stick to surfaces. Higher viscosity also reduces the settling rate of dispersed oil and solids. In many cases, a fraction of the polymer has precipitated in the form of organic solids, further increasing the fouling potential.

All things considered, a high concentration of polymer, and organic and inorganic suspended solids loading are the main components that make HF flowback fluids difficult to treat.

Slickwater Polymer

HPAM, or slickwater polymer, is added to HF fluids to decrease the high-shear viscosity, which reduces the pumping costs. It also increases the low-shear viscosity to between 2 cp and 5 cp, which improves the fracturing performance. The concentrations of polymer range from a few hundred to 1,000 mg/L. The polymer is available in anionic, cationic, and nonionic forms. The nonionic form is the least sensitive to water salinity.

Typically HPAM is broken (i.e, its molecular weight is reduced) at the end of the fracturing job with a breaking agent (e.g., bleach). Much of the HPAM that flows back contributes to the concentration of suspended solids. The fouling potential of HPAM is moderate, but not particularly high when compared with that of the polysaccharides (discussed below). This is because of the nature of the polymer and the lower concentration of HPAM used when compared with the concentrations of polysaccharides used.

The polymer used in the polymer flooding method of enhanced oil recovery is a variety of HPAM. Another variety is used as a viscosity reducer in water flooding, and at low concentrations, HPAM is used in water treatment as a flocculating agent.

The effect of HPAM on conventional water treating equipment, which is used for separation of oil and suspended solids, is well-known. The higher low-shear viscosity reduces the settling rate, and the effectiveness of hydrocyclones and flotation by about 50% at typical HF dosages. The effect of this higher viscosity can be modeled accurately for settling tanks and separators. For hydrocyclones, it can also be modeled accurately using the original Coleman-Thew correlation (Coleman and Thew 1983; Walsh and Henthorne 2012), which accounts for viscosity. Modeling of the effect of the higher viscosity provides assurance that a water treatment system can be designed.

The shear thinning effect causes flotation bubbles to cluster, which reduces separation efficiency. The diminished effectiveness significantly affects offshore operations, where space and weight are a limitation. For onshore operations, where all HF of unconventional resources is practiced, the effect of higher viscosity can be accounted for by increasing the system's capacity.

Other water treatment technologies effective in

HPAM contaminated fluids are discussed below.

Guar Polymer and Other Polysaccharides

The gelation polymers are cross-linked forms of polysaccharides. The cross-linking agents include boron and multivalent metallic ions. When gelled, guar, for example, has an elasticity similar to that of Jell-O gelatin (elastic modulus ~100 Pa). Guar is typically used in dosages from 10 lb/1,000 gal to 30 lb/1,000 gal (from 1,200 mg/L to 3,600 mg/L). Some applications are as high as 40 lb/1,000 gal (4,800 mg/L).

Guar is one of the most effective HF polymers and has a good rate of hydration, low high-shear (shear thinning) viscosity, low coil overlap concentration, and high low-shear viscosity. It is easily cross-linked and easily broken. But it also has a tendency to precipitate, particularly after a breaker has been added.

Guar is a naturally occurring polysaccharide. It has a linear backbone made of mannose units connected by β-1,4 acetal linkages. The β designation indicates the orientation of the linkage, and the 1,4 designation indicates that the first and fourth carbon of each monomer unit is bonded to form a polymeric chain. It contains single-unit branches of galactose connected to the mannose backbone by α-1,6 acetal linkages. Not all of the mannose backbone units have a galactose unit attached. In guar, the galactose to mannose ratio is 1:1.6. Without the galactose side units, guar would be insoluble in water. The mannose backbone (without galactose units attached) is similar to the glucose backbone of cellulose. Like cellulose, the mannose backbone is insoluble in water.

Enzyme and chemical hydrolysis are used to degrade the guar at the end of the fracturing treatment. The objective of the hydrolysis is to cleave the β (backbone) linkage, which lowers the molecular weight and reduces the viscosity. However, most hydrolyzing agents indiscriminately cleave both the α (side branch) and the β (backbone) linkage. Breakage of the side chains has little effect on viscosity. However, when the galactose side chains are cleaved from the backbone, the solubility decreases because of the drop in the galactose-to-mannose ratio. Sticky, organic suspended solids with high fouling potential are created, and the solids combine with small inorganic particles, creating a water treating challenge.

The most successful polysaccharides, from an evolutionary standpoint, are the biopolymers, cellulose, and starch (amylopectin and amylose). Cellulose is a structural biopolymer and is insoluble in water. Starch, however, is at the opposite end of the spectrum. Amylopectin (a starch component) is completely soluble in water and has no strength. Thus, it is an effective material for storing and transporting chemical energy in plants.

Although guar, cellulose, and starch have different properties, they are chemically similar. This is true of many of the polysaccharides and provides a clue to their chemical sensitivity. In oilfield terminology, guar has low chemical stability, which directly affects the quality of water required in HF and the characteristics of the flowback water. Guar-based HF flowback fluids have high organic suspended solids and a high fouling potential.

Controlling the behavior of the polymer is a primary objective in controlling the quality of water used in HF for slickwater and polysaccharide-based fluids.

Fouling—A Major Challenge

A challenge in developing a multipurpose technology is to provide effective water treating without causing rapid fouling of the equipment. Guar has high fouling tendency, but fouling is not new or unique in oilfield water treating applications.

A rule of thumb in equipment design for the prevention of fouling is to eliminate internal surfaces. The most broadly applicable and successful water treating equipment (separators, hydrocyclones, and flotation units) have simple internals. The lack of internal complexity reduces fouling and is one of the reasons why such technologies are so widely applied. These technologies are helpful in treating HF flowback fluids, particularly as pretreatment, but are generally inadequate by themselves.

Another rule of thumb in equipment design for the enhancement of performance is to add internal elements. The goal of the design for several technologies is to maximize contact and surface area, for example, the corrugated plate interceptor (CPI) and reverse osmosis (RO). Fouling is the number one problem with a CPI. RO has been used for HF flowback and is effective for treating up to roughly 65,000 mg/L salinity. Unless extensive pretreatment is used (for example, media filtration), RO membrane life is short because of fouling.

The objectives of design for the prevention of fouling and enhancement of performance are at odds with each other, thus making difficult the development of a universally applicable and multipurpose technology.

As discussed below, media filtration has been used effectively for years in oilfield water treatment, including for conventional HF flowback. However, it is expensive for the volumes of fluid involved in unconventional HF applications.

Conventional HF Flowback

HF fluids for conventional and unconventional formations are formulated from the same list of ingredients and have significant overlap. There are cases of conventional or tight reservoirs being fractured with heavy loadings of cross-linked guar and proppant, while a nearby shale reservoir is fractured with a light loading of slickwater and little or no proppant.

Two differences between conventional and unconventional HF are:

- Fluid volumes used differ by a factor between 50 and 100. Whereas a conventional HF may unload from 200 to 500 bbl of water per well, an unconventional HF may unload from 10,000 to 50,000 bbl of water per well.
- Conventional HF flowback typically contains emulsified oil, and often contains other stimulation fluids, such as aromatic solvent and/or spent acid. While acid is sometimes used at the front end of a shale HF, the acid volumes and pH do not typically compare with those used in a conventional HF. Thus, conventional HF flowback tends to involve lower fluid volumes, but tighter oil/water emulsions.

These differences affect the selection of water treating technology. In a conventional HF flowback, the fluid composition transitions from injected fluids to produced fluids. In all cases, when the oil emerges, it is emulsified from mixing with stimulation fluids. Breaking the emulsion is not possible with standard facility water treating equipment. Separators, hydrocyclones, and gas flotation are inadequate to break the oil-in-water emulsion resulting from a conventional HF stimulation. In a typical offshore HF operation, the flowback fluids from a stimulated well are routed through specialized rental equipment.

The type of equipment used depends on the fluid types and on the service company employed. Pretreatment involves a settling tank, coarse filtration, flotation unit, or decanting centrifuge. Typically, a form of media-based tertiary treatment is used.

The use of media filtration offers advantages in conventional HF flowback operations. First, it provides an ultimate barrier. Whether the media is activated clay or activated carbon, the effluent that emerges is typically pristine with the dispersed contaminants removed. Dissolved organics may also be removed, depending on the media material, but only some of the organic dissolved ions are removed.

Media arranged in series assures the operator that the discharged effluent water meets the environmental requirements. This assurance that clean water will be discharged is a major part of the value proposition of hiring a specialized services company.

Another feature of using media is perhaps both a blessing and a curse. The use of media implies the generation of a waste. It is a blessing that it is a compact solid waste and not another fluid stream that must be treated. But consumption and disposal of the waste adds to the cost of the operation.

The final and perhaps most significant advantage is that media provides flexibility and represents the multipurpose universal technology that the industry is seeking. Whether the flowback fluids contain spent acid, sludge from acidified asphaltenes, clay, oil-coated solids, emulsified heavy oil, precipitated polymer, or corrosion-inhibitor stabilized emulsions, the effluent will be clean enough to discharge overboard.

Why then, is media not used in shale HF flowback?

Media would seem to be the ideal choice for the water treating of HF fluids. However, to my knowledge, it is not used. Because of the cost of media, staff, and solids disposal, it appears to be too expensive for unconventional HF, given the high fluid volumes.

High fluid volume is a game changer, and perhaps media filtration is an overkill since HF makeup fluids are not generally required to be absolutely free of dispersed components.

Other Industries' Experience in Water Treating

Water treatment in the pulp and paper industry involves high concentrations of starch, cellulose, and other polysaccharides. The dissolved and suspended solids must be removed prior to water disposal. The food and beverage industry is faced with similar challenges.

Pokhrel and Viraraghavan (2004) reported that the chemical oxygen demand (COD) of pulp and paper mill effluents typically range from 1,000 mg/L to 5,000 mg/L. The COD is largely attributable to the polysaccharides and tends to be higher than that for slickwater HF flowback fluids. The range is spot on for HF flowback fluids containing a moderate to high loading of guar.

At the lower end of this range, typical pulp and paper mill treatment systems involve chemical oxidation followed by coagulation and filtration, achieving approximately a 50% removal of COD. The application of chemical oxidation is specific to the type of effluent that is generated in the mills and is used because of the ultimate effluent discharge into surface waters such as rivers. The waste water tends to have a high concentration of colored material, which is formed from the chemical digestion of wood. Typical surface water discharge permits require the removal of turbidity and color. However, chemical oxidation has a dual purpose in that it improves the efficiency of subsequent water treatment processes, such as coagulation and filtration. Thus, chemical oxidation is expected to be effective at moderate COD loadings in HF and, indeed, it has been used with success.

To treat the midrange of COD levels, paper mills use dissolved air flotation followed by chemical precipitation and filtration. The process results in a 60% removal of COD. A well-established technology, it is known as "floc and drop." Chemicals are used to precipitate the suspended solids, followed by settling or filtration of the solids. It is a flexible technology in that it can be used to treat any type of HF fluid. The higher the concentration of suspended solids, the higher the chemical cost and the greater the volume of generated waste.

Electrocoagulation is an intensified form of coagulation. Instead of using chemicals, it employs sacrificial anodes (aluminum and/or iron) and involves electrolysis to generate flotation bubbles. When operated properly, it can provide effective flowback cleanup.

At the high end of the COD range, typical paper mill treatment schemes involve activated sludge (anaerobic followed by aerobic) treatment. The result is approximately 90% removal of COD.

Biological treatment in large basins is the workshop of the municipal water treatment industry. Such technology is flexible, once the microbial colony has been established. It is sensitive to variation in salinity and requires a fixed or centralized facility and in many cases, a water conveyance flowline network. Such centralized treatment plants have been installed and are successfully running in the Pinedale and Marcellus developments in the United States (Boschee 2012).

Mobile and modular systems based on biological treatment have been developed, but they tend to be expensive because of the relatively low flow rate capacity. Mobile membrane bioreactor systems have also been developed (not for HF to my knowledge), but are still not compact enough to handle the high volumes economically.

Produced Water Treatment in Heavy Oil

While the steamflooding operations of the tar sands may not seem a likely place to find water treatment technology for HF flowback, there are two reasons why they are. In most steamfloods, produced water containing an emulsion of heavy oil is recycled for generating the steam. Drops of heavy oil are sticky, have high viscosity, and quickly accumulate on equipment surfaces. HF fluids containing guar behave similarly. The second reason why heavy oil experience is relevant is because heavy oil involves steamflooding, which requires desalination of recycled water.

In heavy oil operations, the most successful and widespread desalination technologies are those that are based on some form of mechanical or thermal evaporation, such as mechanical vapor recompression. It has been applied successfully in heavy oil and successfully pilot tested in unconventional HF applications. GE, Aquatech, Veolia, and Fountain Quail are among the companies that provide mobile/modular desalination units (Halldorson 2013; Veil 2012). These systems are designed to minimize fouling and can handle nearly any type of HF fluid. The cost is dependent on the throughput and the number of staffers required to operate the unit.

Chemical flocculation and chemical precipitation followed by filtration is also used extensively in recycling produced water for steamflooding of fields with heavy oil. The Fountain Quail's ROVER clarification system, for example, was developed originally for this application and helps to explain its success in treating HF flowback fluids.

Summary and Conclusions

Diving into the details of fluid properties is complex. Nevertheless, this is what a water treatment specialist does when faced with a seemingly new application. The important components are identified (polymer and organic and inorganic solids) and analog industries are identified where similar fluids have been treated with success.

In the case of shale HF, the polymers and organic and inorganic solids are the determining components. The same components are used in conventional HF. Offshore flowback has a similar stranded water challenge as in shale HF. However, media is the workhorse of the offshore application, which would be too expensive for the high volumes of fluid encountered in shale HF.

HPAM (slickwater) is used in polymer EOR where a range of conventional oilfield and industrial water treating equipment is applied, albeit with lower, but known efficiency. A challenge in slickwater is the capability to deploy the equipment in remote and isolated regions. For this purpose, mobile technologies have been developed and centralized facilities using biological treatment are being operated successfully.

The polysaccharides (for example, guar) are more challenging because of their properties and the concentrations needed. Given the high COD and the high concentrations of total suspended solids, the pulp and paper, and the food and beverage industries are close analogs. In those industries, oxidation, floc and drop, and biological treatment are being used. Oxidation and floc and drop have been successfully modularized for shale HF. Biological treatment is more suited to centralized facilities. In the heavy oil (steamflood) industry, evaporative desalination is used extensively. Mobile and modular units have been developed for shale. Electrocoagulation, as an intensified variation of coagulation, works well when properly operated.

I hope this analysis helps explain the diversity of technologies available in the market. As always, your comments are welcome. OGF

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