Water Management for Hydraulic Fracturing in Unconventional Resources—Part 3

Water Treatment Technologies: Coagulation/Flocculation and Electrocoagulation

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This is the third article of a series covering water management in hydraulic fracturing (HF) in unconventional resources. In the first article, published in June, water management and planning was discussed. Fluid properties and characterization were discussed in the second article, published in August.

This month, water treatment technologies are introduced, beginning with the removal of suspended solids by coagulation/flocculation and electrocoagulation for recycling HF flowback fluids. Water treatment for HF includes desalination of aquifer water, biological and corrosion control, control of mineral precipitation, treatments to break the polymer gel, and a number of technologies for recycling the HF flowback fluid. Technologies developed for these applications (American Water Intelligence 2013) such as ozone generation and treatment, chlorine and hypochlorite generation and treatment, ultraviolet radiation, oxygen scavengers, and scale inhibitors will be discussed in future articles.

Regardless of the technology that occurs downstream, it is almost always advantageous to apply coarse filtration as an initial treatment step. This pretreatment step is usually carried out with coarse screens or sock filters to remove the large particles and reduce the load on downstream units.

After coarse filtration has been carried out, the removal of mineral and organic suspended solids is carried out. These solids are composed of quartz, carbonate, and clay particles, and broken and unbroken polymer. The objective of the treatment is to remove suspended matter down to a few tens of parts per million.

When a proppant is used to support the fracture, it may seem counterintuitive to require the removal of suspended solids in the recycle water. After all, if thousands to a few million pounds of proppant are injected, why must suspended solids be removed?

It turns out that the size, shape, and mechanical strength of the proppant solids is critical to achieving high fracture conductivity. Small particles, also referred to as fines, do not stabilize the fracture and, instead, can form pads that restrict the flow of HF fluid into the rock. Fines can also clog the small pores of the rock, restricting flow of hydrocarbons to the wellbore.

Drilling and completions engineers prefer to use makeup water that is as clean as possible. Despite the fact that recycling has been carried out successfully with a wide range of contaminated makeup water, there will always be a preference for clean water.

The relation between HF performance and water chemistry is complex. There are many variables that are difficult to characterize in the field. An HF job is expensive and anything that can increase the likelihood of production success has strong economic justification.

Removing suspended solids from the recycle water has the added advantage that it helps to return the fluid to baseline characteristics. The quality may be higher than necessary, but establishing a consistent and reproducible baseline is helpful in understanding the performance of HF operations.

Often the productivity performance of an HF job is analyzed in terms of the variables that differ from one job to the next. If water quality is a poorly characterized variable that changes from one job to another, the analysis becomes more complicated. This is true for both the dissolved and suspended solids content of the makeup water. Dissolved solids will be the subject of a future article. For now, the focus is on suspended solids.

Two important technologies for the removal of suspended solids are coagulation/flocculation and electrocoagulation. These related technologies are being applied successfully now, and are likely to become more widely applied in the future.

The discussion of coagulation/flocculation and electrocoagulation is

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intended to provide an understanding of why these technologies are suitable for HF flowback treatment, and the similarities and differences between these technologies.

However, before these technologies are discussed, general considerations of any recycling technology must first be discussed to provide context and a better understanding of why these technologies are emerging as successful.

Cost and Operational Considerations

The technologies themselves are only a part of the picture. Equally important are the logistics, services, on-site support, reliability, and troubleshooting capabilities of the service companies.

It must be kept in mind that the delivery of HF flowback technology to a site is a challenge. The operators must plan for the job and make sure that they bring with them the needed material, equipment, and chemicals. Planning for contingencies is not straightforward. They must arrive safely, communicate with the multidisciplinary teams on site, rig up the equipment, start and operate the equipment, troubleshoot problems, take samples and make measurements, record observations, rig down, clean the site, demobilize, and report out.

Water treatment technologies that are most suitable for HF flowback are universal, robust, inherently safe, and cost-effective.

A universal technology is capable of treating a wide range of fluid properties. As discussed in the August column, HF flowback fluids have a wide variation in fluid properties, both in terms of well-to-well variation and within a well over time. There do not appear to be any magic bullet technologies, since they all have limitations. The technologies described here can be applied over a wide range of fluid types. In other words, they are technically feasible. However, the cost tends to rise as the loading of guar increases, as discussed below.

A robust technology is reliable, easy to operate, and easy to troubleshoot. Repairing broken equipment is difficult in remote locations. If the equipment is simple, and if every member of a crew can handle all the tasks involved, there is maximum scheduling flexibility—a major advantage for a service company. If expertise is required, it becomes more difficult to maintain a high level of quality services.

Another factor that contributes to robustness is that the process does not generate waste streams that are difficult to handle. In selecting the best process for a given application, consideration of all process streams is required. At the end of a job, all waste must be disposed of in a manner that does not require extensive involvement of the operating company.

The concept of an inherently safe process is well developed in the upstream oil and gas industry and involves application of design standards and tools, such as hazard identification studies, and hazard and operability studies. An inherently safe process is one in which hydrocarbon containment and operator safety does not depend to any great extent on operator training or intervention.

A cost-effective technology requires relatively few operators, takes relatively little time to mobilize and demobilize, and allows treatment at a fairly high rate such that the number of days on site is minimized. On-site treatment of HF flowback is a manual batch operation. Thus, cost models for industrial and municipal water treatment do not apply. However, consulting companies are available with expertise in HF flowback cost models.

In conventional water treatment technology, the capital cost of the technology together with economy of scale and process optimization play important roles. In HF treatment, capital and operating costs play a role, and process optimization is important to the extent that manual operations can be minimized. As discussed in the June column, economy of scale only becomes important—after the mobile and modular phase—when centralized facilities become economically feasible. Thus, it is not surprising that the technologies that emerge have roots in industrial water treatment and in oilfield services.

Coagulation/Flocculation: Background

Coagulation and flocculation (also known as floc-n-drop) are classic water treatment processes used in the treatment of surface and groundwater for drinking. In those applications, the suspended solids loadings are relatively low. Coagulation and flocculation are also used to treat industrial wastewater containing high concentrations of suspended solids, such as from a pulp and paper mill. Paper mill effluent can contain a high concentration of starch and cellulose components, which is analogous to an HF flowback fluid in which guar is used.

The main mechanism of coagulation/flocculation is the aggregation of suspended solids to promote separation. Once the solids have formed aggregates, separation can be carried out by settling, filtration, or flotation. When flotation is used, flocculation of the suspended solids improves separation by creating a larger target for the collision of flotation bubbles.

The term "coagulation" can be misleading since it is a common and broadly used term outside of water treating. In biology, it describes blood clotting. In cheese making, it describes the process of making curd from milk. Both of these processes imply aggregation of suspended material.

In water treating, coagulation does include aggregation. However, the important aspect is the earlier step of chemically modifying the surface of the suspended particles to reduce the inherent electrostatic repulsion between particles. Without this step, flocculation and aggregation in water treatment would be limited.

In produced water treatment, the surfaces of most suspended solids have a negative charge. This is true whether the solids are made of mineral, clay, or organic material. The natural abundance of anions in minerals such as clays, carbonates, silicates, and metal oxides, the effect of lattice imperfections, and the abundance of negatively charged functional groups in organic chemistry contribute to the negative charge.

The negatively charged suspended solids repel each other, making separation more difficult because the particles are so small that they tend to stay suspended. According to the DLVO theory (Derjaguin and Landau 1941; Verwey and Overbeek 1948), the charge-charge repulsion can be reduced by increasing the salinity or by adding a relatively small amount of trivalent cations. Most HF flowback fluids have high salinity, which is a good start. The Schultz-Hardy rule indicates that trivalent cations are more than 700 times more effective than monovalent cations on a molar basis at reducing the electrostatic repulsion of suspended solids. The simplest such coagulants are salts of iron (iron chloride) and aluminum (alum). By adding a coagulant, the electrical double layer becomes compressed, and charge-charge repulsion is reduced to the point where the short-range van der Waals attractive forces can bind particles together.

Coagulation is enhanced by intense mixing applied immediately after chemical addition. Intense mixing promotes the migration of the coagulant chemical to the surfaces of the suspended particles. However, it must not be so intense as to shear the particles and make them smaller, which would defeat the overall purpose. Through the process of coagulation, aggregates of particles begin to form because the repulsive barrier has been reduced in size and intensity.

Flocculation takes the aggregation process a step farther. It is the process whereby a flocculating agent, usually a polyelectrolyte polymer, is added to promote the formation of macroscopic aggregates (flocs). The polymer binds suspended particles together by forming bridges, strands, or by forming a mesh. Once aggregated, the suspended material will migrate up or down, depending on its density relative to water. The larger the flocs and the more tightly aggregated the suspended solids, the faster the migration rate.

Gentle mixing is important for uniform distribution of the chemical. Flocs are delicate objects and too much mixing will break them apart. Flocs are typically settled in a quiescent tank for separation to occur. Filtration or flotation can also be used for separation.

Coagulation and flocculation are considered to be separate processes in large part, because they involve separate chemical treatment and separate unit operations. The processes differ in the intensity of mixing and in processing time. Although they also differ somewhat in the chemicals used, there is some overlap.

In conventional coagulation/flocculation chemical selection, dosage and treatment time are important. There are three types of chemicals used in coagulation/flocculation. The trivalent salts (iron chloride, alum) were developed first and are mostly used for coagulation. In industrial and municipal water treatment in which there is a steady water quality and flow, they can be optimized. They are effective at breaking down the electrical double layer, but are tricky to use in the field. They require a precise knowledge of the water chemistry and pH adjustment in some cases to avoid side reactions, unwanted precipitates, and to assure their effectiveness. Under optimum conditions, they form polymerlike polyhydroxide structures that reduce the electrical double layer and help bind suspended solids particles together.

The polyelectrolytes are effective for both coagulation and flocculation, but tend to be used primarily for the latter. As a class of chemicals, they include synthetic polymers, natural compounds, and derivatized natural polymers. When used as coagulating agents, they are more expensive than the simple salts, but are more compatible with other ions and are more effective over a wider pH range. They can have limitations in compatibility with the wastewater. Premixing is often effective in overcoming compatibility problems. Given the large number of products on the market, on-site bottle testing is often necessary. When a proper coagulating step is included upstream, the effectiveness of a polyelectrolyte flocculating agent can be exceptional. This reduces the cost of the polyelectrolyte significantly. Due to their wide applicability and robust performance, they are widely used.

The third class of chemicals is the prehydrolyzed alum salts. Although there are many varieties, they are generically known as PACl (polyaluminum chloride). No pH shift occurs when they are applied because they are pH stabilized. Formulated with an optimum hydroxide, sulfate, and alumina ratio to promote the formation of large cationic aluminum hydroxide polymer chains, PACls are effective as flocculating agents. They are more expensive than the simple metal salts, however, they have essentially none of the compatibility and performance problems.

Coagulation and flocculation processes are more complex than described above. Only the dominant mechanisms and the most common chemicals used have been described here. An in-depth discussion is provided by Crittenden et al. 2012.

All things considered, coagulation and flocculation are well understood and there is precedent and good reason why they should be successful in the treatment of HF flowback water. Service companies have overcome the challenges in logistics, cost, universality, and robustness. They have enabled the delivery of the technologies to remote locations and the application of them to unknown fluids with variable characteristics.

Coagulation/Flocculation: Application

An example of a successful application of coagulation/flocculation to flowback water recycling is Fountain Quail Energy Services' Rover technology (Halldorson 2013). The process flow involves prefiltration, clarification, flocculation, settling, and sludge handling. The details of the clarification and flocculation steps and the chemicals used are proprietary. The technology is being applied using a range of fluids in the Permian and Eagle Ford basins. The company has shown success in slickwater fracs.

Guar and x-linked gels are the most demanding applications, because of high organic solids loading (thousands of mg/L) and the high fouling potential of the sticky polymer. Generally, gel fracs use less water so there is less fluid to handle. On the other hand, gel fracs require higher quality water than slickwater, so treatment needs can be more intensive.

The drivers for this application are limited water availability and the operating company's desire to reduce trucking and to limit the environmental liability related to transportation and storage of salt water on the surface. The Eagle Ford play has a limited number of disposal wells. Even if the disposal well is nearby, truck unloading times can be long, resulting in high costs.

Electrocoagulation: Background

In industrial water treatment, electrocoagulation is used to remove metal ions. The mechanisms are similar to those described for coagulation and flocculation, but with minimal or no required chemical addition.

An electrical current is generated through the water by applying a voltage across two electrodes immersed in the water. The voltage is proportional to the electrode separation, conductivity of the water, and amperage applied. Many HF flowback fluids have high conductivity, which reduces the power consumption of electrocoagulation processes.

The anode is made of iron, aluminum, or an inert metal. In the case of iron or aluminum, the anode is sacrificial and dissolves in the water. At the cathode, hydrogen gas and hydroxyl ions are produced. The metal ions from the anode and the hydroxyl ions combine to produce a coagulant. The electric field, together with the introduction of metal ions into the water, changes the charge potential of the water enough to collapse the electric double layer around the suspended particles in the same way as achieved with the addition of the trivalent cations of a simple coagulant. Oxidation takes place, which also aids in the breakdown of hydrogen sulfide, organics, and bacteria. Chlorine is generated, which hydrolyzes immediately to form hypochlorite, which provides biocide functionality. The hydrogen gas bubbles generated at the cathode provide an in-situ gas flotation effect, which promotes separation of the flocs from water.

An advantage of electrocoagulation is that coagulant addition is usually not needed. Thus, chemical handling is essentially eliminated. The electric field and chemical effect of the sacrificial anode are sufficient to collapse the electrical double layer. Since chemical addition is replaced by an electric field, the amount of sludge generated is reduced.

However, the technology is not as simple as suggested. The chemistry of the sacrificial anode is similar to that of the simple (metallic salt) coagulants discussed in coagulation/flocculation. Thus, compatibility and performance problems associated with the use of simple coagulants (metallic salts) can occur. Overdosing of the metal coagulant can occur if the amperage is set too high. When this occurs, residual levels of iron or aluminum can exceed the effluent specifications.

These problems can usually be overcome. Depending on the complexity and variability of the flowback water chemistry, on-site expertise is required to make the adjustments. This may involve selecting the right anode material, adjusting the flow rate, tuning the amperage, adjusting the pH, and cleaning of the electrodes.

The suspended solids migrate to the counter-ion electrode, resulting in benefits and drawbacks. The concentrated solids that migrate to the electrode form a sludge or floc blanket. A design feature of many industrial clarification separators, the blanket promotes the capture of smaller flocs and suspended solids and improves the separation performance.

In electrocoagulation, reduction takes place at the cathode, which leads directly to fouling of the electrode. The guar-based HF flowback fluids have tremendous fouling potential, which necessitates maintaining spare electrodes so that some of the electrodes can be taken offline for cleaning. It also necessitates a larger staff count on site for the labor-intensive job of cleaning the electrodes.

Electrocoagulation: Application

An advantage of electrocoagulation is its modularity: small units that can be packaged conveniently. Individual units can be taken offline for cleaning. The technology lends itself easily to a flexible and mobile process design, providing key design advantages for delivery to remote locations.

In a process application, the electrodes are accompanied by a settling tank, filter system, and sludge dewatering unit. Sludge handling is critical to reducing manpower requirements.

However, as with most suspended solids treatment technologies, sludge thickening and handling is not easily modularized. The design of the sludge handling unit has been a drawback of the initial electrocoagulation units deployed in the field.

When electrocoagulation was first introduced as a flowback treatment technology, it was met with skepticism by the oil and gas industry. Although it was invented more than 100 years ago, it had only occupied a small niche in industrial water treatment.

It was promoted to the oil and gas industry as a treatment technology for HF fluids. Initial performance seemed to justify the skepticism. Stories circulated of equipment problems, fouling, and overall poor on-site service. This was unfortunate because electrocoagulation makes sense as a HF flowback treatment technology. The initial responses to the technology illustrate a situation that has been repeated countless times in the oil field: Technology without competent services has little value.

More recently, on-site service, reliability, and performance of electrocoagulation have improved, in part because of the oilfield service companies' involvement. For example, Halliburton partnered with WaterTechtonics to deliver electrocoagulation technology to oilfield sites. Cetco Energy Services has been in the HF flowback business since the mid-1990s and has recently added the technology to its portfolio of services.

As a result, many operating companies are re-evaluating the use of electrocoagulation. Personally, I feel that the technology is a bit tricky to apply and will require an expert on site to make it work. Overall, its inherent advantages are that it is scalable and can be modularized.

Summary and Conclusions

Coagulation/flocculation and electrocoagulation are currently being applied for the removal of suspended solids in HF flowback fluids. The chemistry and processes involved in coagulation/flocculation are simple, which helps to provide robust process flexibility and staffing flexibility. In electrocoagulation, it appears that an expert or an experienced field technician is required, thus making staff movement and scheduling more complex, but still manageable.

The separation performance of a given technology is only one of many factors that affect the overall success of a technology in the field. It is likely that application of both technologies will continue to grow. **OGF**

For Further Reading

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