DR CLAY MAUGANS AND DR ROB MCCLAIN, SELECT ENERGY SERVICES, OUTLINE APPROACHES FOR OPERATORS CONDUCTING TECHNOLOGY-BASED WATER TREATMENT AND MANAGEMENT IN THE OILFIELD.

KEEPING WATER CLEAN

This overview focuses on the treatment aspects of water management for oilfield well completions programmes and production water. Technologies and approaches to managing water are fast changing in this industry; this represents the more prominent approaches at the time of writing. It is written from the perspective of Select Energy Services, an oilfield service company that specialises in water management. Typically, the term 'flowback' applies to the water that comes off an oil and gas well during the initial production of the well and the term 'produced water' refers to water coming back from the formation a few weeks after the well is brought online. 'Produced water' will be used here to describe both fluids.

Increasingly, operators are attempting to reuse and recycle produced water for frack purposes, which may involve various degrees of treatment. This is particularly appealing in regions with high disposal costs or limited fresh water supplies for completions operations. Regardless of whether an operator fracks with fresh water, produced water, or a mixture of the two, all frack water requires some kind of conditioning

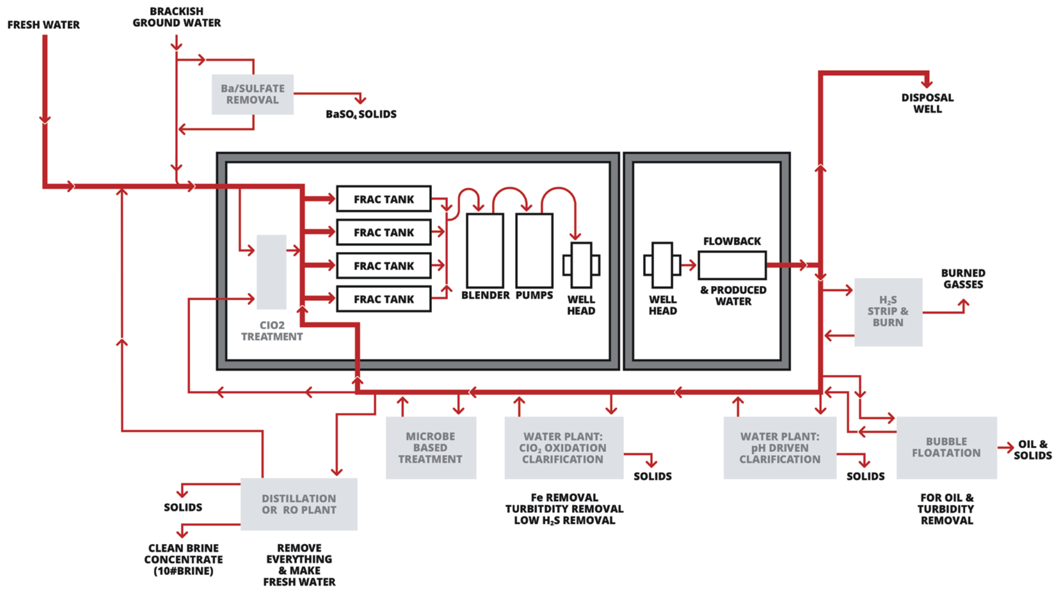

Figure 1. *Water path, indicating all the predominant potential solutions and steps (grey).*

or treatment. There are essentially three main applications of frack water treatment:

- Fresh water disinfection for completions work, usually on the frack location.
- Blending of produced water with fresh water and applying fresh water style treatment techniques, usually on the frack location.
- Water plant for recycling produced water for oil recovery and water inventory, usually away from the frack location.

Treatment of fresh water

With fresh water, inorganic (i.e. Fe, hardness, etc.) contaminants are usually minimal. The main goal is biological control (i.e. disinfection). If deleterious microbes thrive in the reservoir, production can be harmed via plugging from biomass growth, fouling, corrosion due to acid formation, and the formation of toxic gases like hydrogen sulfide (H_2S). Treatment options for managing fresh water to mitigate risks related to microbial growth include:

- Conventional biocides.
- Chlorine dioxide (ClO_2).
- Ultraviolet light (UV).

Conventional biocide

In this approach, a liquid biocide such as glutaraldehyde is added to kill microbes. The advantage of this approach is its simplicity and ability to be included within the scope of the frack chemical blender already on location. Challenges with this approach are that the biocides are not always effective, are expensive, are an environmental liability, and there is no way to monitor correct dosing. These chemicals can take up to 12 - 24 hrs for complete microbial kill, when the correct dose is used. However, performance of conventional biocides is limited by conditions downhole where elevated temperatures and pressures can degrade the biocide and formation waters dilute biocide concentration faster than it can disinfect. Standard practice is to estimate an overdose.

Chlorine dioxide

The common alternative to the above for fresh water disinfection is the addition of ClO_2. While its wide adoption is relatively recent in this industry, it has quickly become a standard oilfield practice. Chlorine dioxide is an efficient fresh water disinfectant. It is a dissolved gas and a neutrally charged molecule. This allows ClO_2 to quickly penetrate bacterial membrane walls and kill microbes from the inside out. Reaction times are extremely fast compared to conventional liquid biocides. As a result, residual ClO_2 concentration measurements downstream of addition can be used to assure high disinfection. Additionally, an in-line ClO_2 probe near the well head can be utilised to adjust the dosing rate real time, to assure correct dosing during operations. Chlorine dioxide is not a chemical that can be easily purchased in bulk or as a concentrate, so it is generated onsite by mixing stable precursor chemicals.

Two common pitfalls to avoid with ClO_2 are:

- Not continuously measuring residual concentration far enough downstream (resulting in incorrect dosing).
- Using an early generation ClO_2 generation method that produces impure forms, which creates residual chlorinated byproducts that can harm the frack chemistry and even equipment.

Ultraviolet light

Treatment with UV is another method for disinfecting fresh water, with its appeal due to its low cost and lack of chemical logistics needs. It uses high energy light rays to damage microbial cell structures. It is used in municipal drinking water plants. Treatment with UV can be effective in the oilfield, however there are some challenges. It is best used on low turbidity waters, since microbes can hide in the shadows of contaminating particles, as well as inside those particles. With high hardness waters, the UV illumination window can foul. The biggest challenge is the lack of residual effect from UV. Water treated with UV can instantly be re-inoculated the moment the water leaves the illuminated area and flows through frack tanks, which are never sterile. The water instantly becomes septic, defeating the point of treating.

Treatment of blended fresh water and produced water at the frack site

In addition to the challenges in using fresh water mentioned earlier, blending with oilfield recycle/reuse waters introduces challenges on water chemistry due to different levels of salt, hardness, H_2S, iron, biology, and turbidity. With recycled waters, biological control becomes more important. Due to the high concentration of nutrients, microbes tend to thrive in oilfield waters. So, microbe concentration (and disinfection chemical demand) is typically much higher than in fresh water as well. This is the single most important aspect of recycle/reuse management, and it is often neglected.

Depending on the fresh water/produced water blend ratio and the treatment goals, the aforementioned conventional fresh water treatment steps can work here; though with higher dosing of the respective treatment chemicals. Common treatment approaches to blended recycle/fresh water management for completions include:

- Conventional biocide.

- Chlorine dioxide (ClO_2).
- Ozone (O_3).

Conventional biocide

Disinfection is attempted by simply increasing the biocide dosing over that used for treating fresh water only. Because of the slow reaction time and lack of technology to measure effectiveness in real time, this is often ineffective and at best, inefficient for treating blended waters.

Chlorine dioxide

The higher microbial activity in production water generally requires higher dosing of ClO_2 than does fresh water. With contaminated blend water, ClO_2 will first react with oxidisable contaminants such as H_2S and iron (but not hydrocarbons) consuming the ClO_2 before the microbes do. Only after those demands are satisfied will ClO_2 disinfect the water. While this increases the chemical consumption and cost of the ClO_2, this can be beneficial, since H_2S removal and iron removal are usually a priority with frack fluids anyway. As this does not affect the feedback cycle (so long as residual ClO_2 is being measured), then the operator has assurance that H_2S, iron, and bacteria are all removed. It is for this reason that ClO_2 is an appealing choice for treating blended waters near or at the frack pad. The same deployment is used as for the fresh water disinfection, with the only changes being higher ClO_2 dosing, and that some residual solids will build up in the frack tanks, as the oxidised iron will precipitate out of solution – usually co-precipitating turbidity with it. The advantage of this approach is that local but relatively small streams of produced waters can be recycled and treated on location, with minimal logistics and storage needs.

Ozone

Ozone is a powerful oxidising gas that is highly effective at destroying bacteria cell walls. Ozone tends to be an indiscriminate oxidiser, but it is not as efficient as killing microbes as ClO_2. Ozone has a short life span, so optimising dosing to achieve a complete microbial kill in a cost-effective manner requires some skill. This process is used in the oilfield and is credible, but has not become as common as chemical biocides or ClO_2. One challenge with ozone, as with UV, is that usually the treatment is done upstream of frack tanks. Residual ozone will be consumed when as it corrodes the frack tanks. The conundrum is that if the water does not contain residual ozone, the septic frack tanks will re-inoculate the water. This can be managed by using lined frack tanks or adding additional biocide such as bleach to the water prior to feeding to the frack tanks. However, both approaches increase the cost of ozone treatment.

Treatment of produced water at recycle treatment plants

Sometimes it is desired to collect and treat produced waters at a dedicated treatment plant. These plants can be mobile or fixed, and vary in capacity from 5000 to 25 000 bpd. They are located in the region of the frack activity, but not on the frack pad. They are best suited for higher contaminated waters, with high turbidity or microbial contamination.

Conventional clarification (non-oxidation based)

There are four main forms of conventional clarification, where clarification is the act of making the water visually more clear. All four approaches can be aided by the addition of speciality chemicals.

- pH adjustment and settling.
- Electrocoagulation (EC).

Figure 2. *Pre-treated water is held in an above ground storage tank prior to hydraulic fracturing operations.*

- Air flotation.
- Oxidation.

Clarification is not a disinfection approach, but does achieve high microbial kill when there are pH changes. The settling step co-precipitates both live and dead microbe bodies as well. Microbial reduction can be on the order of at least 99% and is satisfactory, since final disinfection is often done on the frack pad. Sometimes, if a higher degree than 99% microbe removal is desired at the treatment plant, a small amount of biocide or even simple bleach is added at the end for a final disinfection. Other additions are done as needed. For example, if the recycle water contains H_2S, and the treatment technology is not one that normally removes H_2S (i.e. pH adjustment), then additives such as triazine or ClO_2 can be used to remove the residual H_2S.

pH adjustment and settling

The classic approach is pH adjustment clarification. The pH is increased to above 8.5, usually by adding sodium hydroxide. This causes dissolved iron, other metals and miscible organics to become insoluble. The iron acts as a natural coagulant, which aids in pulling out turbidity. Flocculent is added. A flocculent is usually a liquid polymer with charged functional groups that attract the suspended particles made insoluble by the pH increase. Flocculation is the agglomeration of the fine particles, into larger clumps (floc) that look like popcorn or snowflakes suspended in the water. The water and floc flow into a settling tank, where gravity pulls the floc into the bottom of the tank. The clarified water flows over the top of the settling tank and is then pH adjusted back down to the desired

Figure 3. *Fresh water pit, used by Select to draw from and blend with recycled water on the frack pad for controlled blend ratios via an automated mixing manifold with concentration sensors.*

frack pH. The wet solids from the precipitated floc are sometimes dewatered, for ease of solids disposal.

Electrocoagulation

Another clarification approach is electrocoagulation. Produced water is pumped across electrically charged iron or aluminium plates that release metal ions into the water to act as coagulants. Often this is accompanied by pH adjustment, and similar processing as described above.

Gas flotation

This approach is attractive when there is high oil content in the water or other light material content in the water. Gas bubbles (air, natural gas, or other) are induced into the fluid as it flows through a tank. As they rise, the surface of the bubbles tends to collect suspended particles, which 'stick' to the surfaces of the bubbles. As the bubble complexes grow in size, materials are then left on the surface of the water when the bubbles break at the air/water interface at the top of the tank. Light materials then remain on the surface and can be skimmed off. Additional settling and dewatering steps as described above can also be done.

Oxidation

Similar to the conventional clarification chemistry, oxidation can be done instead of using pH adjustment based chemistry. This will oxidise iron to an insoluble form, and cause precipitation via that chemistry. It also tends to be more effective at water disinfection, and these routes can achieve near 100% disinfection. Below are listed some of the more common types of oxidation chemistry in the oilfield:

Oxidation by chlorine dioxide

ClO_2 treatment is described in the prior section. When used at a 100% recycle water plant, it is typically combined with solids settling and separations equipment as described above. One particularly appealing aspect of ClO_2 is its fast reaction chemistry and effectiveness even at low concentrations – eliminating the need for high residual concentrations.

Oxidation by hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a liquid oxidiser. It can be used as an oxidation technology for disinfection, clarification, and sulfide removal. Characteristics that make H_2O_2 appealing are:

- Lower initial cost than most other oxidation chemistries.
- It is 'clean' in that its decomposition products are oxygen and water.
- Ease of deployment, since it can be purchased in totes – eliminating the need for onsite generation required for O_3 and ClO_2.

However, despite these advantages, it is not heavily used in the oilfield because these benefits are often offset by safety and process limitations including difficulties in removing by product elemental sulfur, reaction kinetics that typically require overdosing for full treatment, and the generation of oxidative byproducts that may cause undesirable residual effects

Oxidation by peracetic acid

Peracetic acid is a combination of acetic acid and hydrogen peroxide, to give a stabilised form of a liquid oxidiser. It is slightly more attractive than H_2O_2 alone for safety and stability reasons, with most of the advantages of H_2O_2. It has about the same mechanism of action and effectiveness as H_2O_2. It is not heavily used though because it is a fuming acid when concentrated, and in general not quite as effective as properly-dosed ClO_2.

Oxidation by bleach

Sodium hypochlorite (bleach), is a common and low cost oxidiser. It generally does not do a good job at water clarification, and can produce messy, odorous water. Mostly, it is used as a polish on water treated via other means, as a persistent oxidiser to help keep the relatively clean water sterile as it moves downstream.

Summary and conclusion

There are numerous approaches to treating and recycling water in the oilfield, with no one set approach always being the right answer. As of early 2015, one of the most prolific engineered approaches to recycling water appears to be ClO_2 treatment, and an even greater amount of ClO_2 is used for fresh water treatment. After that, conventional treatment technologies such as pH adjustment clarification and electrocoagulation are used in multiple regions. There are also a small number of users working with H_2O_2. Although not discussed here, there is also a small level of activity with distillation and RO treatment, but those technologies represent a small portion of industrial treatment use.