OIL FIELD WATER RECYCLING

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ABSTRACT

Flow back and produced waters in the oil field are heavily laden with contaminates including insoluble iron sulfides, poisonous hydrogen sulfide, residual gels, friction reducers, and other chemicals. In this paper we will look at chlorine dioxide (ClO_2) as one possible solution to these problems. As a powerful, yet selective oxidizer, ClO_2 has the ability to break up the residual gels and friction reducers while removing the insoluble iron sulfide and killing the hydrogen sulfide. As an additional plus, ClO_2 is an EPA approved biocide that kills the bacteria which are the root cause of many of the problems with water reuse.

INTRODUCTION

Hydraulic fracturing, or fracing for short, is a procedure where fluid is pumped down a well into subsurface rock formations under high pressure to fracture the rock. This creates an interconnected set of fissures that allow the oil and natural gas trapped in the rock to move across the formation to the well bore where it can be recovered.

Typical fracs use a mixture of water and sand to fracture the rock. The high pressure slurry cracks open the rock leaving the sand to prop open the fissures and keep the rock from collapsing back on oneself once the pressure is removed. Small amounts of chemicals, mainly friction reducers and gelling agents, are added to the water/sand mixture to improve performance. The gelling agents help the sand form into an “open” network that allows easy flow of the oil and natural gas while the friction reducers, as the name implies, reduce the pumping pressure required to move the water/sand mixture down the well bore. Once the frac is completed, oil bearing water flows back up the well bore where the oil and natural gas are recovered. This is where the issues with water recycling begin.

PRODUCED AND FLOW BACK WATERS

The water coming back out of the well has been pushed through the formation picking up all sorts of undesirable contaminates in the process. These contaminates include:

Mineral Deposits – As the water passes through the formation to the well bore it will pick up minerals along the way. Calcium, iron, chlorides, potassium, sulfur, along with trace elements such as barium are absorbed out of the rock and carried along with the water. Of these components the most troublesome to the recycling of oil field water are iron, sulfur compounds, and chlorides.

Friction Reducers & Gels – Both friction reducers and gels are water soluble. Any residual material that was not actively used in the fracing process is picked up by the water and transported back to the well bore where they can plug the perforations restricting oil and gas flow. In many cases the residual friction reducer and gel will combine with the dissolved minerals and form stable emulsions. These emulsions capture fine solid particles (such as sand and silt) and carry them along to the well bore.

Bacteria & Biomass – There are significant amounts of dormant bacteria trapped in the oil formation. As the water and oil flow through the formation the bacteria is carried along. The most troublesome of these bacteria are the class referred to as Sulfate Reducing Bacteria (SRB). These bacteria take the soluble sulfur compounds and convert them into insoluble iron sulfides (FeS), and highly poisonous hydrogen sulfides (H_2S). The iron sulfides settle out and plug the well bore restricting the flow of oil and natural gas. The hydrogen sulfide is carried along with the water and oil to the surface where it presents a significant safety hazard to everyone present at the site.

As seen from the above, recycling oil field water is a complicated affair involving both organic and inorganic chemistry; as well as some very difficult problems just to get the treatment chemicals in contact with the problems.

THE FIRST ISSUE – CONTACT

In order to treat the oil field water the first issue that must be overcome is getting to the problem. Oil field water is a mixture of both oil and water. While the oil and water separate into two distinct phases the contamination, bacteria, and other problems are distributed more or less equally across both phases. This presents a problem for many chemicals in that water based chemicals find it difficult to work on the oil side while oil based chemicals have trouble with the penetrating the aqueous phase.

Chlorine dioxide (ClO_2) is a very powerful oxidizer that is present as a gas dispersed in solution. That it is dispersed in solution rather than dissolved or absorbed in the solution is a crucial point. The ClO_2 does not react to any significant amount with the water, it is not hydrolyzed like chlorine, or chemically bound to the water like sodium hypochlorite (bleach). Since there is no strong bond with the water, the ClO_2 remains extremely mobile. This mobility, combined with the fact that the ClO_2 is equally soluble in both oil and water, allows the ClO_2 to disperse through both the oil and water phases to attack the contamination regardless of where it is located.

This ClO_2 mobility actually goes a step further. When considering scales such as insoluble iron sulfides or iron carbonates or emulsions formed around and inorganic nucleus most chemicals only react with the exposed surface of the scale or emulsion. The small size and high mobility of the ClO_2 molecule allows the ClO_2 to penetrate into the solid matrix and attack the problem from inside as well as the surface. Obviously, if you can penetrate into the scale or emulsion the treatment is going to be much more effective especially if the ClO_2 penetrates to the back side of the scale where it is attached to the surface. Once the scale breaks free the remaining pieces can be fully dissolved by the chemicals or flushed out of the system.

There is a down side to this however. In many oilfield systems scale has built up over a number of years leading to a depleted oxygen environment beneath the scale. This low O_2 situation make for extensive under-deposit corrosion. Holes, pits and weakened sections may form in the pipe and, in fact, the scale may become the pipe. Once the scale is removed there may be (extensive) leaks to repair. This is particularly true in older, less well maintained systems.

THE SECOND ISSUE – REACTION

We have seen how ClO_2 is able to move through the oil, water and scale to get to the source of the problem. However, once there the ClO_2 must have the ability to correct the problem. This is where, the oxidation power of ClO_2 becomes important. Let us consider two critical problems in the oil field. These are hydrogen sulfide (H_2S) and iron sulfide (FeS).

Hydrogen Sulfide - H_2S is highly corrosive and, if left in solution, attacks the tubulars and metal components of the pump system. While this is a problem, the larger problem is when the H_2S is brought to the surface with the oil and natural gas. H_2S, even at concentrations as low as 10 to 15-ppm, can be fatal. Release of H_2S is a major safety concern in the oil field.

ClO_2 will destroy the H_2S by converting it to low levels of hydrochloric and sulfuric acid as shown in Equation 1.

EQ.1: $5\ H_2S + 8\ ClO_2 + 4\ H_2O \rightarrow 8\ HCl + 5H_2SO_4$

This is an extremely fast reaction that, under the conditions present in oil field situations, goes to completion. Provided sufficient ClO_2 is added all the H_2S will be destroyed.

Note: The best place to handle H_2S is down in the well before it ever comes to the surface. This is done by applying ClO_2 to a well immediately prior to the frac. The ClO_2 will take care of any H_2S present in the wellbore and then be pushed out into the formation by the frac. Wells treated in this manner have much lower H_2S concentrations then surrounding wells. The effect is both noticeable and long lasting. The advantage is the H_2S never makes it to the surface where it poses a safety hazard.

Iron Sulfide – Iron sulfide is an insoluble scale that forms in the formation and near the well bore. If the situation is not corrected the FeS scale accumulates to the point where it restricts flow (production) from the well.

Once again, the ClO_2 has the ability to react with the contamination and remove the problem. Under acidic conditions the ClO_2 converts the insoluble FeS into very soluble iron chloride (Fe_2Cl_3) and equally soluble iron sulfate ($Fe_2(SO_4)_3$) as shown in Equation 2.

EQ.2: $2\ FeS + 6\ ClO_2 + 2\ H_2O \rightarrow 2Fe^{+3} + 2\ Cl^- + 4\ HCl + 2\ SO_4^{-2} + 3\ O_2$

The result is that the iron sulfide is converted from an insoluble scale into a soluble form that can pass freely through the formation.

THE THIRD ISSUE – ORGANICS

The term organics covers a whole host of compounds. While the reactions between ClO_2 and these compounds are as varied as the compounds themselves some general classifications have been developed and specific reactions have been mapped. The general rules are summarized in Tables 1 and 2 *(please see at end of summary)*.

In general compounds with double bonds, like emulsifiers, friction reducers and gelling agents can be attacked by ClO_2. The exact reaction mechanism will depend on the compounds being addressed. In general, the ClO_2 cleaves the double bond, breaking the compound into smaller fragments that are easily degraded.

Note: The reactions of ClO_2 with organics and more complex and slower than the reactions with inorganic compounds such as FeS and H_2S. Contact time and the relative concentrations of the ClO_2 to the organic compound play a much larger role in determining the extent of the reaction. For example, mixing concentrated (3000-ppm) ClO_2 directly into water containing 1 gal per thousand of friction reducer will almost completely destroy the friction reducer. On the other hand, there is no measurable effect when mixing water that has been treated with ClO_2 to a residual between 2 and 5-ppm with the same friction reducer solution.

Chlorine dioxide does not affect long chain single bonded organics, i.e. oils. This allows the ClO_2 to be used to clean unwanted gels, emulsifiers and friction reducers out of recovered water preventing them from building up and plugging the system when water is recycled.

THE FOURTH (AND FINAL) ISSUE – BACTERIA

Bacteria, particularly Sulfate Reducing Bacteria (SRB) and Acid Producing Bacteria (APB) are the root cause of many of the problems that are experienced with oil field water.

The SRBs take the sulfur compounds present in the oil and convert them to sulfides. From there the sulfides appear as either poisonous hydrogen sulfide (H_2S) or insoluble iron sulfides that plug the perforations and restrict oil and natural gas flow from the well.

The APBs, as the name implies, produce acids which lower the pH of the solution and lead to accelerated corrosion of the well casing, tubulars and pump components.

There are numerous commercial biocides available for use in the oil field. Bromides, gluteralaldehydes, Quats, sulfones and a host of other biocides are available. These biocides are all effective at the start but gradually lose effectiveness over time as the bacteria mutate or adapt to the attack mechanism. The standard procedure is to select a biocide and start a program. As the biocide effectiveness decreases a new biocide, operating by a different mechanism, is then introduced and used until it’s effectiveness drops off. At that point the original (or an even newer) biocide is introduced and the process continues.

To understand what is going on you have to understand the bacteria’s defense mechanism. When attacked by a traditional (liquid based) biocide the bacteria secretes a gel film to protect itself from the chemical attack. In most cases the biocide can breakdown the gel film and kill the bacteria provided that it can get to the bacteria and the concentration of the biocide is sufficient to penetrate the film. However, a small, but significant, portion of the bacteria survive this attack. This is the population that continues to grow and in doing so pass along their resistance to that particular biocides method of attack. Over time the bacteria colony grows and a new biocide operating by a different mechanism is needed to kill off the bacteria.

ClO_2 however is not a liquid but a highly mobile gas dispersed in solution. It has the ability to quickly disperse through the entire formation, even the tiniest crack and crevices that are sometimes covered over with scale or where liquids cannot penetrate. And once it get to the bacteria the gaseous ClO_2 can readily penetrate the gel film the bacteria is using as a defense. Once inside the cell the ClO_2 disrupts the transport of food and material throughout the cell killing the bacteria. Very much like the scale issue discussed earlier the conventional liquid based biocides have to have to migrate through the oil and water (usually one or the other), get to the bacteria and then attack only at the exposed outer surface. ClO_2 can disperse quickly through both oil and water, get to the cell and then penetrate through the defensive gel film attacking the bacteria from within. The kill rate approaches 100% and therefore the cells do not have time or the ability to adapt to this form of attack.

There is a downside. The power of ClO_2 is that it gets in, kills the bacteria, and in the process is reduced down to salt. There are no bio-persistent compounds left that can accumulate in the system causing potential problems in the future. However, since the ClO_2 is completely consumed in the process there is no residual biocide in the system. The water/oil mixture is completely sterile and any new bacteria introduced into the solution after treatment has an ideal place to grow and flourish.

SUMMARY

Oil field waters are a heterogeneous mixture of oil and water that is contaminated with a wide variety of materials ranging from insoluble iron sulfides, poisonous hydrogen sulfides, residual gels, friction reducers, emulsions, inorganic salts and bacteria. In order to reuse this water it must be cleaned in such a way that it can be re-introduced into the well without causing problems. In order to do this the bacteria must be killed, the H_2S destroyed , the iron returned to solution, the gels and friction reducers broken down to the point where they will not plug the formation and the salts removed so they don’t accumulate and cause plugging issues.

ClO_2 as a strong oxidizing gas dispersed in solution has the ability to penetrate through bot the oil and water phases and correct most of these problems. The goals of bacteria kill, H_2S destruction, FeS removal and breakdown of the residual gels and friction reducer are all accomplished. The only problem that is not addressed is the removal of inorganic salts. However, even there a first treatment with ClO_2 removes the majority of the issues and opens the door to post treatment for salt removal.

Table 1
Reactive Compounds

Aromatic Hydrocarbons	
Unsaturated Hydrocarbons	
Alcohols	**R-OH**
Aldehydes	
Carbohydrates	
Organic Sulfurs	
Mercaptans	**R-SH**
Disulfides	**R-S-S-R**
Phenols	
Amines	**$R\text{-}NH_2$**
Polymers	
Guar Gels	
Emulsifiers	

Table 2
Non-Reactive Compounds

Saturated Aliphatic Hydrocarbons
Many Aromatic Hydrocarbons
Carboxylic Acid
R-COOH
Amino Acids
Nitro Aromatics