CHLORINE DIOXIDE APPLICATIONS TO OILFIELD WATER

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ABSTRACT

Chlorine dioxide (ClO_2) has been useful in various applications in the oilfield. While the chemistry has long been understood, the adaptation to proper oilfield use has been an evolution over the past several decades. With the increased pressure on all companies to properly manage both water in and water out of the oil and gas operations, Chlorine dioxide applications are increasing because of its efficiency as well as environmentally positive profile. New methods of delivering chlorine dioxide in salt water disposal systems, water floods, water for hydraulic fracturing, and tank batteries have demonstrated the value of chlorine dioxide in the separation of entrained oil, elimination of bacteria, iron sulfides, and H_2S. Important advances in the process and methods of delivery allow for economically feasible use of chlorine dioxide where it was once cost prohibitive. We will discuss the application of chlorine dioxide on salt water disposals, water floods and water for hydraulic fracturing where we have been able to alleviate many of the issues historically faced by systems, resulting in a more efficient process with dependable and predictable results.

INTRODUCTION

Chlorine dioxide has a wide range of historical applications in several industries. The pulp and paper industry as well as the municipal water market have shaped the materials and methods over the past decades. Chlorine dioxide has been considered an effective method of providing microbial control for water in systems requiring a very tight guidelines. Oilfield applications of chlorine dioxide are relatively new. Understanding the benefits of chlorine dioxide in treating oil related water comes back to understanding the objectives of the people responsible for managing the ultimate fate of the water. Water management in every phase of the oil and gas production process is important. Hydraulic fracturing has very different requirements as compared to a water flood or an SWD.

Chlorine dioxide generated using a three precursor method delivers the maximum amount of chlorine dioxide and is generated for immediate reaction to the target water. This is important to the overall process in relation to the oilfield applications. Oilfield water throughput requires a process which drives the desired result quickly and efficiently. In most cases, the chlorine dioxide is entirely spent leaving no undesirable or unsafe bi-products through its rapid reaction rate.

Salt water disposal wells are a massive growing portion of the oil industry in Texas. It is to these sites that water refuse is delivered and processed before the safe injection down a disposal well to a suitable formation deep below the surface. The water of interest at these sites is for the most part produced water from active wells or flowback from newly drilled wells. It is in the best interest of a salt water disposal operator to remove all residual hydrocarbons as well as minimize H_2S, iron sulfide, and bacteria. This desired state allows for highly injectable water which will not foul or damage the system in the long term. Many times, SWD locations run the risk of problems with biomass, biofilm, loss of skim oil, well fouling and pumping pressure increases due to the poor quality of water coming into the system and ultimately being injected. The long term effects of not dealing with this problem is the loss of the system and need for expensive overhauls to tanks, pumps and the well(s) itself.

Water flood operations are long understood means of increasing the productivity of producing formations. It is of great concern to a water flood operation to deliver the least contaminated water to the water flood injection zone. Contaminated water can result in the development of a sour system and fouled lines.

Water for the use in hydraulic fracturing is scrutinized very closely. Bacterial contamination has to be eliminated as is any scale causing iron compounds. The pH of the water must be managed in a certain range in order to keep any corrosion characteristics to a minimum. For this reason, operators look for a dependable and immediately measurable method of managing the water characteristics before they enter into the process of blending and applying a suitable water for hydraulic fracturing.

For all of the applications, an efficient reaction with a rapid delivery time is desirable. Through the use of chlorine dioxide delivery systems, throughput and contact time for reactions can be minimized allowing for an improvement in efficiency.

Chlorine dioxide has been well documented in its application to control bacterial growth. It is used extensively in the water treatment industry. It is more desirable than free chlorine. The corrosion profile of chlorine dioxide is much less aggressive than that of competitive products commonly used in the oilfield such as acid. Chlorine dioxide has an added advantage in oilfield applications of being an oxidizing biocide which will not only manage microbial growth, but scavenge sulfides from the system while destabilizing solids which tend to collect in oilfield water binding hydrocarbons and fouling systems.

MATERIALS AND METHODS

ClO_2 is generated in accordance with the technical grade preparation of ClO_2.

ClO_2 is produced from the oxidation of sodium chlorite ($NaClO_2$) by hypochlorous acid (HOCl). Hypochlorous acid is prepared by combining solutions of sodium hypochlorite (NaOCl) and hydrochloric acid (HCl):

$$\mathbf{NaOCl + 2HCl \rightarrow Cl_2 + NaCl + H_2O}$$

$$\mathbf{2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl}$$

ClO_2 generation is accomplished in accordance with the above reaction profile using the protocols outlined by Aegis Chemical Solutions. The chlorine dioxide generator is encased in a mobile trailer which is equipped to handle travel and plumbed to traffic source water through the generator, delivering chlorine dioxide to the source water and subsequent delivery into system of choice (SWD, water flood, frac tank, pit, etc.). The safe handling of all products in the process is strictly adhered to in accordance with the Aegis Chemical Solutions ACHLOR Training, Certification and Operations Manual.

In order to manage the appropriate dosage of ClO_2, we use the following demand calculations as defined by Aegis Chemical Solutions.

DETERMINING CLO_2 DEMAND

Chlorine dioxide demand is normally measured in advance of a project to determine how much ClO_2 will be required to perform treatment so that a cost estimate can be developed and required precursor volumes can be calculated. Demand is expressed in terms of mg/L, or ppm, of ClO_2 that must be added to the system before a very slight ClO_2 residual appears.

The ClO_2 demand test method utilized by Aegis involves the use of potentially hazardous chemical reagents. As such, care must be taken to protect the health and safety of all employees involved in the testing process.

The Aegis CHP and MSDSs for each reagent being used should be reviewed before an employee participates in sample collection and analysis. Each employee involved in testing should also wear appropriate PPE (such as safety glasses with side shields and either latex or nitrile gloves) during both sample collection and analysis.

The following 14-step procedure should be used to test for ClO_2 demand when evaluating water in a pit, tank, etc. that is to be treated:

Assemble the required equipment and reagents, including clean 160 ml prescription bottle, clear 250 ml plastic beaker, 10 ml syringe, oxidation reduction potential (ORP) meter, pH meter, electric or magnetic stir plate and stir bar, and stock ClO_2 solution generated using the stock solution preparation method.

Collect a 100 ml sample of the water to be tested in a prescription bottle. Pour the entire 100 ml water sample into the clear 250 ml plastic beaker. Stir the beaker using magnetic stir plate and stir bar. Turn on calibrated ORP and pH meters and place probes in the beaker. Allow meter readings to stabilize for at least 1 minute before recording initial ORP and pH values of sample. Fill syringe with stock ClO_2 solution. Add stock ClO_2 solution to the beaker at a rate of 1 ml or less per minute, while watching the ORP meter reading. Slow the rate of addition of stock ClO_2 solution to the beaker to ½ ml or less per minute when the ORP reading is above 500 millivolts (mV). Stop adding stock ClO_2 solution to the beaker when the ORP reading stabilizes around 702 mV. Record final ORP and pH readings of the treated sample. Record as "V1" the total volume of stock ClO_2 solution required to stabilize the sample at an ORP reading of 702 mV. Calculate the total amount of ClO_2 added to the water sample (i.e. demand) in micrograms (ug) using the following equation:

Total ug ClO_2 added = V1 x C1
Where:
V1 = Volume in ml of stock ClO_2 solution used
C1 = Concentration of ClO_2 stock solution in ppm
Convert the ClO_2 water sample demand value from µg to ppm using the following equation:
ClO_2 demand of sample in ppm = ClO_2 demand in ug /100 ml.

At salt water disposal sites, the average demand of the water is taken over a course of a day and re-tested at intervals throughout the year. Chlorine dioxide is generated upon sensing flow and delivered to the incoming water at the disposal site. In the case of water floods, chlorine dioxide is generated and delivered to the water for injection when the system senses flow. Finally, in the case of water for hydraulic fracturing, the chlorine dioxide is generated and delivered to the frac tanks. The water is constantly measured using ORP and pH both pre and post at each tank to ensure an agreed upon residual of chlorine dioxide is present. This will ensure top quality water for the process about to take place.

RESULTS

We report the results of the study on three different examples of SWD installations at different sites, taking various types of water. In each case the benefits of chlorine dioxide are reported.

Case 1)

Before the installation of continuous chlorine dioxide, the issues the customer faced were as follows. There was a pad issue and sludge on the open pit where water was taken in before being pumped into the SWD system. The skim oil quality from the system was low, resulting in discounted sales and less revenue for the customer. An iron scale issue was cropping up in the system resulting in pressure problems and fouled lines to the SWD. High well head pressure had become an issue due to the issues with the water getting downhole and limiting the porosity of the formation. Pump health issues had become persistent as a result of poor water quality and pressure issues at the well. ClO_2 application was decided on based on data taken at multiple points and recurring tests throughout the application. Demand study revealed initial demand at pit to be in excess of 150. Demand study of water at injection point determined to be 80. Average incoming water demand over the course of a full day determined to be 40. Initial dose of ClO_2 was 250lbs per day. (Surge) Dosed back to 80 lbs./day after 1 week. The results were evident almost immediately. The initial surge of ClO_2 into the pit resulted in a visual change in the water at the site of injection in less than 30 seconds. The water turned color from black to green to brown and the pad that had accumulated began to break up quickly. Over the course of the next 4 hours, the water in the pit was transformed. The persistent odor from the pit that had been a concern of the owner and the neighbors had gone away. Over the course of the next three weeks, the system was able to take more water and the quality of the water being injected to the well was of much cleaner. This resulted in small drops in pressure at the well head over that time period before the well stabilized after a 350 lb. drop. The customer reported an increase in the amount of skim oil they were able to recover to be an average of 22% higher which could be attributed to the quality of the treatment of the water resulting in better separation as well as the ability of the system to take on more water. In addition, the customer was able to sell the oil at a much less discounted price.

Case 2)

In this closed system SWD, the customer faced several issues before continuous ClO_2 was introduced. Iron scale and high bacteria were the observed challenge in what was mostly produced water taken in. Very little flowback was taken (10%) at this site. The system was reporting H_2S measurements varied from 10 to 60ppm and growing. Biofilm was observed in serviced lines causing flow and pressure issues. Skim oil quality and quantity had decreased over the past months with a high amount of oil entrained in a pad at the gun barrel as well as oil carryover in water delivered downhole at the SWD. ClO_2 application levels were determined through the following data sets. Demand study at gun barrel determined to be 80. Demand study at final settling tank determined to be 30. Average incoming water demand over the course of a full day determined to be 35. Introduced ClO_2 into gun barrel at a rate of 80. Dosed back ClO_2 concentration to 40 after 1 week. After three weeks, the iron scale had dramatically decreased with health restored to pump and lines serviced. The pad in the gun barrel had dissipated with the help of a small dose of 382b (Aegis) breaker to dissipated residual paraffin. Reported skim oil quantity had increased by 15%.

Case 3)

Prior to ClO_2 treatment the H_2S was borderline at 40 ppm measured in headspace of tanks. There was a pad of oil heavy Iron and bacteria pad in pit where water was unloaded from trucks before being pumped into system. High bacteria and biofilm was observed in lines and water from lines serviced at site. Pressure issues at the well had grown to levels near the allowable limit.

ClO_2 application was determined based on the following. Demand study at well head determined to be 50. Demand study of water in gun barrel determined to be 90. Demand study of water in pit determined to be 150. In this case, the customer agreed to flowback the well and follow with downhole ClO_2 application (100barrels of ClO_2). Introduced ClO_2 to pit before lift pump to gun barrel (Continuous). Introduced ClO2 to gun barrel (Continuous). Continuous ClO_2 introduced at 200lbs per day and throttled back to 35 after 2 weeks. In this case, the pad on the pit was easily dissipated, and the gun barrel health was restored. The H_2S readings were diminished to trace. The downhole application of ClO_2 was done with 100 barrels of ClO_2 generated at 2500ppm and delivered to fresh water before delivery downhole and left to sit for 1 hour. The results of the treatment was a drop in well pressure of 350 lbs. Over the course of the next month, there was an enhanced ability for the site to take more water and an increased number of loads of flowback. This resulted in a 29% increase in the quantity of skim oil to be collected and sold by the SWD.

In the case of water for hydraulic fracturing, the simple application of chlorine dioxide to the water offers a dependable method of ensuring the cleanliness of the water in preparation for the addition of components and delivery downhole. In this case, a mobile unit capable of delivering up to 6000 lbs. per day of ClO_2 is used. An adapted header and manifold allows for the diversion of a stream of water from the incoming lines to add a dose of ClO_2 to the frac tanks lined up on site. The ORP and pH of the water is measured at each tank pre and post treatment. These residual readings are captured and recorded and a desired residual of ClO_2 is reported at 2ppm. Serial dilution Bottles are taken and documented over the next 90 days for bacterial regrowth. All results are shared with the customer. In this application, chlorine dioxide has been successfully implemented on both vertical and horizontal hydraulic fracturing sites. (See Table 1)

Water flood application results have been two fold. The most obvious improvement made has been around the removal of biofilm and iron scale from injection wells and the decrease in bacterial contamination that could sour the well. Chlorine dioxide was also found to diminish existing H_2S issues throughout a field. In one case, the addition of chlorine dioxide to the injected water at a water flood demonstrated the ability to manage bacteria and reduce H_2S readings that were documented weekly over a time period of 6 months. Slowly the H_2S levels at each producing well have diminished which is believed to be the effect of ClO_2 being pushed through the water flood, removing bacterial contamination and the resulting H_2S becoming less and less of an issue at the producing wells. (See Table 2)

Another small water flood application was at an old producing well which had experienced an increasing issue with the amount of water that the operator was able to inject (30-50 bbl. /day). It was decided that a small introduction of chlorine dioxide to the water injection sites would be investigated. In addition, a continuous delivery of chlorine dioxide to the produced water would help with hydrocarbon separation and overall yield from the system. To the great surprise and delight of the operator the well health was restored to be able to take over 200 bbl. /day and the oil yield doubled.

CONCLUSIONS

Chlorine dioxide is a very useful compound for oilfield applications. When managed and delivered properly, chlorine dioxide will rapidly improve the separation of hydrocarbons from produced water and flowback, drastically reduce bacterial populations, oxidize iron sulfide and scavenge H_2S. All of these things can be accomplished with added benefit of chlorine dioxide having a positive environmental footprint.

Salt water disposal wells potentially benefit from the use of chlorine dioxide in several ways. Primary to the operators of SWD's is the potential for increased skim yield which drives economics. However, the replacement of several traditional chemicals in favor of one that has a positive environmental footprint may become more attractive. Chlorine dioxide was demonstrated to alleviate issues with iron compounds which damaged components and tend to lead to pressure issues. Overall, when chlorine dioxide is introduced to the incoming water at an SWD, the rapid reaction yields faster separation, reaction with undesirable iron sulfide, scavenges H_2S, and manages microbial populations resulting in a saltwater disposal process that is more robust and predictable than prior to treatment.

The delivery of chlorine dioxide down the well can be a compliment to enhance acidizing of a well. Where microbial population and biofilm have been present with high iron issues in the water, chlorine dioxide was shown to help with the eradication of issues and help restore the pressure health of the well. It is important to note in this case that chlorine dioxide will not be of assistance in the case of calcium scale as well as in the case of a well that is plugged with sand or gels that have been pumped down an SWD.

Water for hydraulic fracturing can be treated with chlorine dioxide as a means to manage microbial control in rapid fashion. This is because of the rapid rate at which chlorine dioxide acts to disrupt the cell membrane of microbes. The measurable change on ORP along with a residual amount of chlorine dioxide gives a strong indication of the desired nature of the water about to be used in the process downstream. An added benefit of using chlorine dioxide is that the process does crowd existing apparatus on site and can be placed at some distance which alleviates spatial concerns that are often the case at a well site.

Water flood operations also benefit from continuous as well as spot treatments of chlorine dioxide. In the case of floods with diminished capacity to take water due to pressure issues, chlorine dioxide can be investigated as a possible solution to remove film which can build up over time in the injection well. Restoring the injection wells ability to deliver water can enhance production. In the cases studied, this was a common theme among aged wells that have had a slow and continued drop in the amount of water an injection well can take. It is important to understand the nature of the water before the decision is made to use chlorine dioxide. Additionally, chlorine dioxide has shown to be effective in helping to manage H_2S levels in a flood that had sporadic spikes in H_2S. Over time, with continued delivery of chlorine dioxide into the water for flood, the H_2S levels became managed. When added, chlorine dioxide not only managed the microbial population of the incoming water, but delivered a method of managing populations in the flood and ultimately at the producing wells. The results suggest that a contaminated water flood may benefit from the use of chlorine dioxide over a long period of time.

Overall, the investigation suggests that chlorine dioxide can enhance the treatment of oilfield water at several venues. Chlorine dioxide may become an increasingly complimentary additive to processes that have been in use for many years. Chlorine dioxide also offers solutions with an environmentally positive profile.

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Table 1

Frac Water Data

	Pre ORP	Pre PH	Demand				Post ORP	Post PH	Residual	
	81	7.3	4							
Stage 1	Post Orp	Post PH	Residual				Stage 2	Post Orp	Post PH	Residual
	731	6.6	2	Total Barrels Treated:				694	6.9	2
						223170				
Stage 3	Post Orp	Post PH			Clean Bbl	Pump down	Stage 4	Post Orp	Post PH	
	726	7.3	1	Stage 1	4177			710	7.6	5
				Stage 2	11098	290				
Stage 5	Post Orp	Post PH		Stage 3	10804	533	Stage 6	Post Orp	Post PH	
	709	7.4	1	Stage 4	10045	299		751	7.3	2
				Stage 5	10959	269				
Stage 7	Post Orp	Post PH		Stage 6	10317	333	Stage 8	Post Orp	Post PH	
	749	7.5	2	Stage 7	10222	559		746	7.5	2
				Stage 8	10555	271				
Stage 9	Post Orp	Post PH		Stage 9	9902	273	Stage 10	Post Orp	Post PH	
	725	7.6	1.3	Stage 10	9895	296		727	7.2	1
				Stage 11	10214	246				
				Stage 12	10476	186				
				Stage 13	9666	134				

Table 2

Water Flood H2S Readings

	9/11/2013	2/12/2014	ClO_2
PW 10	**1200**	**400**	**Yes**
PW8	**2000**	**0**	**Yes**
PW 11	**1.5**	**1**	**Yes**
PW 5	**1100**	**0**	**Yes**
PW 6	**125**	**800**	**No**
PW 4	**0**	**900**	**No**
PW 3	**250**	**0**	**Yes**
PW2	**4**	**0**	**No**
PW 1	**1**	**0**	**No**