

GENERATION AND APPLICATION OPTIONS FOR CHLORINE DIOXIDE AND ITS VARIOUS APPLICATIONS IN OILFIELD OPERATIONS

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ABSTRACT

Chlorine dioxide has a wide variety of applications in the oilfield, including fracturing, water flood, salt water disposal wells and producing well stimulation. It is uniquely suited to deal with the core problems of microbiological fouling, H₂S, iron sulfide and oil/water emulsions. The unique attributes of this oxidizing chemical mean that it will not react with hydrocarbons and most amines (unlike other oxidizers), and thus is effectively targeted on the problems most commonly encountered.

There are multiple ways to generate chlorine dioxide, both from the standpoint of the precursor chemicals used, and the equipment used for the generation. This paper will address these methods of generation and application of chlorine dioxide, along with the advantages and disadvantages of each for specific types of application.

WHY CHLORINE DIOXIDE?

Virtually all oilfield systems contain and/or utilize water. This may be in the form of fresh water used for fracturing operations or produced water used for anything from fracturing to water flood or disposal. Any aqueous oilfield environment inevitably results in several ubiquitous problems.

- Bacteria will be present, both aerobic and anaerobic varieties. These bacteria result in:
 - Formation of biomass that will
 - Form rag layers in gathering tanks,
 - Foul piping, well bores and formations
 - Cause differential cell corrosion on metal surfaces
 - Form emulsions with hydrocarbons
 - Anaerobic sulfate reducing species will produce H₂S, which is both
 - Highly toxic, and
 - Corrosive
- H₂S corrosion of piping systems and formation iron results in large amounts of iron sulfide (FeS) in both the water and hydrocarbon phase
- FeS stabilizes oil/water emulsions, producing additional fouling

The total effect of bacterial growth on oilfield systems is generally substantially underestimated by producers. However, if it is controlled and the downstream effects (H₂S and FeS formation) prevented, most production limiting issues can be largely eliminated. While efforts have been made to address individual issues in recent years (various nonoxidizing biocides for bacterial control; H₂S scavengers, etc.), none have been completely successful.

Over the last five to seven years, however, chlorine dioxide (ClO₂) chemistry has proven to be extremely effective at targeting all these issues. As an oxidizing chemistry, it will rapidly provide 100% bacterial kill (unlike nonoxidizing biocides) when fed to obtain a small residual. It also destroys H₂S, which vastly

improves personnel safety and resolves most corrosion issues. In addition, by eliminating FeS, it rapidly resolves most emulsions, which are typically stabilized by the presence of the FeS. Finally, being a relatively weak oxidizer, it will not react with hydrocarbons – resulting in much lower dosages than other oxidizing chemistries and none of the objectionable reaction byproducts those others form with hydrocarbons.

Chlorine dioxide is, thus, an almost perfectly targeted chemistry for resolving a great many vexing oilfield problems.

USES AND APPLICATION METHODS OF CHLORINE DIOXIDE IN THE OILFIELD

As previously mentioned, probably most long term operational problems in oilfield operation result from bacterial growth. Not only do the bacteria form biomass (bacteria within slimy exopolymers) that directly foul tanks, form rag layers, plug formations downhole, etc., but they result in the formation of H₂S and FeS due to H₂S corrosion of iron/steel in the systems.

So, most applications center around accomplishing the following goals:

- Killing bacteria
- Eliminating H₂S
- Eliminating FeS
- Destroying biomass and emulsions that result from bacteria and FeS

The next question that arises is – “By what process does ClO₂ accomplish these goals?” So, a brief discussion of how the chemistry works is in order.

Bacterial kill/Biomass

Chlorine dioxide has several advantages over other biocides under these conditions. A summary of its advantages is presented here, but for a more thorough discussion two books by Dr. Greg Simpson are highly recommended: Practical Chlorine Dioxide Volume 1 – Foundations, and Practical Chlorine Dioxide Volume 2 – Applications.

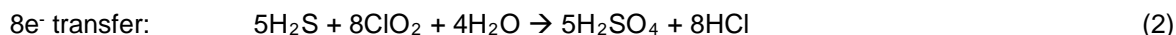
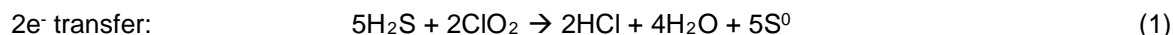
- ClO₂ rapidly kills all microorganisms at lower dosages than other biocides and maintains a residual for downstream disinfection and biofilm mitigation.
- It is rated as a “green” chemistry, ultimately decaying to salt.
- Does not react with hydrocarbons in the water, thus offering much lower dosage requirements than other oxidizing chemistries
- A neutral charge molecule that easily penetrates biomass to kill
- A “recycle” feature – when ClO₂ reacts with the bacteria/biomass the majority reverts to chlorite ion. Acid from acid producing anaerobic bacteria species reacts with the chlorite and forms additional ClO₂. Thus, a high level of ClO₂ is regenerated inside the biomass and results in a rapid and complete kill and dissolution of the biomass. See Figure 6.

One crucial factor favoring chlorine dioxide over nonoxidizing biocides is that you can directly measure a residual concentration. Given the way it works (physical oxidation/destruction of key cellular components) all bacteria will be killed when there is a measurable unconsumed residual amount of ClO₂ present. This is not true of nonoxidizing biocides. The relative effectiveness of ClO₂ compared to nonoxidizing biocides is illustrated in Figure 7.

H₂S/Sulfide Reactions

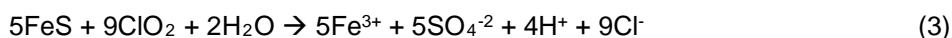
Chlorine dioxide oxidizes sulfide to sulfate in most cases, but there is some potential for formation of elemental sulfur. Multiple reaction pathways are possible, and are highly dependent on pH and concentration. In any case, researchers have shown that, depending on conditions, it takes between 2.5 ppm and 4.5 ppm of ClO₂ per ppm of sulfide present. Two of the possible reaction pathways are shown below. It should be noted that many alternative H₂S scavengers are amine compounds, and with those

products the H₂S is adsorbed rather than converted to a different, harmless, molecule. These scavengers may release the H₂S again if pH or temperature change significantly. Thus, they do not permanently eliminate the H₂S hazard. With ClO₂, H₂S is rapidly oxidized and eliminated.



Iron Sulfide (FeS)

Iron sulfide serves to stabilize oil/water emulsions in many oilfield systems, particularly in tanks and pits handling produced water. It is also present in the biomass found in pipelines, well bores, etc. It may be dissolved with ClO₂, with the general reaction equation shown below.



The ferric ion formed reacts with water above a pH of 4.0 to produce ferric hydroxide Fe(OH)₃ an insoluble floc. It can be easily removed by filtration. Common sock filters work well for this.

Now that we've shown how ClO₂ resolves three of the core problems associated with oilfield production systems, the next step is to apply it to the various types of applications. The differences between the uses outlined below is simply which of the specific problems exist and where they are located. That is, how do we get the chlorine dioxide where it needs to be in the most efficient manner?

Hydraulic Fracturing

The primary goal of frac water treatment is to sterilize the fluids going downhole. Any live bacteria that are in the fluids will serve to inoculate the wellbore and formation. Over time, these bacteria colonies grow to plug formations, produce H₂S (sour the wells) and FeS - ultimately producing all the problems discussed above. Therefore, if we can prevent bacterial colonization to start with, then the field will produce at higher rates, longer, with fewer problems.

Whether using fresh water, produced water, or a combination of both, the basic process is simple. Chlorine dioxide is injected into the water at some point in the water transfer lines upstream of the working frac tanks. The reaction with bacteria and other contaminants present is rapid, and a residual may be tested in the frac tanks to insure sterility. A ClO₂ residual of 3 – 5 ppm is typically maintained in the frac tanks. See the attached case history for a typical system layout.

Produced Water

Produced water typically has significantly higher microbial populations than fresh water, and frequently has high H₂S and FeS levels present. As would be expected, more ClO₂ is required to treat these waters, as they contain more contaminants than fresh water. The key point, however, is that they can be, and are, successfully treated.

The order of reaction with the contaminants is H₂S, then FeS, and finally, bacteria. Thus, it's relatively easy to tell how the treatment is progressing by watching ORP (oxidation/reduction potential) and ClO₂ residual. The presence of H₂S produces a reducing environment, thus ORP is highly negative, being as low as -300mV in some cases. When ClO₂ is added to the water, the ORP increases and H₂S is rapidly destroyed. Longer reaction time is required to fully destroy FeS, which is then followed by bacterial disinfection. By the time a stable chlorine dioxide residual is attained, all contaminants have been eliminated.

Produced water is used for numerous applications, from water flood injection, to frac water or simply

disposal via injection well. In most cases handling it involves collection in a gathering tank system or pits initially. These tanks/pits have their own unique problems, which are discussed below. It is becoming common to treat the produced water and then put it into a pit for use as frac water, which also causes specific issues addressed below.

Gathering Tanks/Pits

Gathering tank systems and pits tend to have common issues. They serve to provide long residence time and allow oil to accumulate. This is an ideal environment for bacteria, allowing large amounts of biomass to grow and form a “rag” layer. This, in turn, provides an excellent medium for the growth of anaerobic, sulfate reducing bacteria and the resulting H_2S . This, of course, further results in FeS formation due to corrosion. The combination of these factors forms a “rag”, or emulsion, that is extremely difficult to break.

The iron sulfide (FeS) acts to stabilize oil/water emulsions. When done in combination with the already existing biomass, most operators ultimately resort to draining and mechanically cleaning the tank/pit. This, of course, results in paying to dispose of hazardous waste. Thus, ClO_2 is an extremely attractive alternative, since it will destroy the H_2S , dissolve FeS and kill the biomass. The result is that the rag/emulsion layer in the pit or tank is resolved with much reduced need for solids disposal. In addition, the remaining solids can typically be disposed of as non-hazardous, for much lower cost. Routine low-level treatment (continuous or intermittent) of the system with ClO_2 going forward prevents recurrence. Long term benefits of maintaining clean pits/tanks are clear – good quality water for injection or fracturing operations. And the treated water will not inoculate formations with bacteria to start the cycle again downhole.

Methods of treating tank systems vary. If individual tanks can be isolated, a good approach is to circulate a tank while maintain a 25 ppm to 50 ppm residual of ClO_2 in the water. This will provide for rapid breakup and elimination of the rag layer, typically requiring less than one day. Alternatively, ClO_2 may be fed upstream of the tanks and maintained at a low level (5 to 10 ppm) and gradually clean up the entire system. This method may require from a week to a month, depending on the amount of contaminants present.

Pits are treated similarly for cleaning. The difference is one of scale. They typically require a large pump (i.e. a 6” or larger diesel trash pump) to circulate the pit, and chlorine dioxide is injected into the stream being recirculated. Special attention needs to be paid to insuring the sludge layer normally found on the bottom of pits is adequately treated. Best practice would be to put the circulating water discharge into or near the sludge layer and split the discharge line into multiple smaller ones.

Injection Wells (Water Flood or Salt Water Disposal)

In most respects, injection wells have issues very similar to tanks and pits. There is a continuously water wet environment with hydrocarbon present. Thus, you end up with the same problems with biomass, H_2S , FeS and emulsions. Consequently, similar treatment approaches are effective. ClO_2 will resolve them, with a few differences in approach. Either a stimulation, or “shock” treatment, or continuous treatment approach may be used.

Stimulation Treatment - Due to temperature and solubility issues, there may also be scale formation in the well bore and near wellbore formation. While conventional acidizing treatment won't be effective on biomass downhole, it is useful for scale removal prior to ClO_2 treatment, allowing the ClO_2 to more efficiently contact and react with FeS and biomass. So, an acidizing treatment is normally combined with use of a ClO_2 slug (normally 100 to 200 barrels) for wellbore treatment. Results are rapid and dramatic, lasting from 6 months to several years between treatment.

Continuous Treatment – For a more gradual cleanup and maintenance approach, ClO_2 may be applied to the injection water to maintain a 3-5 ppm residual. This maintains a clean system at all times.

Producing Well Stimulation

Producing wells, again, have similar issues to injection wells. Once contaminated with bacteria, usually during drilling and completion, biomass begins to grow and eventually produces the same cycle of H_2S , FeS and formation pluggage. A stimulation treatment with acid and ClO_2 will typically produce a major increase in well production, which is maintained for a long period of time. Production increases are frequently 3x to 5x the rate before treatment, often near or equal to original well production rates.

Polymer Floods

Polymer floods are relatively few in number, but they have unique issues. A polymer/water emulsion is injected into the field to sweep low API gravity oil from the formation to the producing wells. The produced fluid, therefore, is an emulsion of water, oil, and polymer. The challenge is to break the produced fluid and recover the oil from it. ClO_2 in conjunction with a new nanofluid surfactant technology has proven extremely effective in breaking this emulsion. Commercial application is still developmental, but it shows great promise.

APPLICATION AWARENESS

Safety

There are two primary aspects for safe chlorine dioxide application:

1. Storage and handling of precursors
2. Safe concentration limits of chlorine dioxide in water

As with virtually all chemicals, there are hazards, and well-established procedures exist for handling and storage. Chlorine dioxide is most commonly produced (as discussed in the next section) with sodium chlorite, sodium hypochlorite (bleach), and hydrochloric acid. Bleach and acid are already commonly used in oilfield operations, and operators already have procedures in place for handling them. The additional precursor involved here, sodium chlorite, has generally similar handling and storage requirements as sodium hypochlorite. However, it has one additional characteristic that must be addressed. If it is spilled and allowed to dry, it is a strong oxidizer and will typically cause a fire if it contacts organic materials (paper, wood, leather, hydrocarbons, etc.). Common safe handling practices include:

- Provide proper containment, as with all chemicals
- It is innocuous as a liquid, so do not allow it to dry.
 - It is also easily neutralized with sodium sulfite.
- Contain oxidizers (chlorite and bleach) separately from acid.

Chlorine dioxide is a gas dissolved in water. As such, if there is a spill, it will evolve out of solution. A ClO_2 concentration of 10% or more in air is flammable. Thus, properly designed ClO_2 generation equipment will have a design that inherently limits product concentrations to levels that preclude the possibility of producing dangerous concentrations in the event of a spill. This is generally accepted in the industry to limit concentrations to 3,000 to 3,500 ppm exiting the generator.

Corrosion

A few companies have raised concerns about the potential impact of ClO_2 on the frac equipment. Several recent studies have addressed this concern.

In one study, N80 carbon steel coupons exposed to 15% Inhibited HCL for 5 min and subsequently to 50,000 ppm Sodium Chloride Brine with 1-5 ppm ClO_2 for 1.5 hr, simulating a frac stage duration, showed no significant difference in corrosion rate from control samples without ClO_2 present. Corrosion was dominated by presence of inhibited HCl and brine.¹

In another study, the corrosion rate of N80 steel coupons exposed to 7.5% HCl made from either deionized water or produced water each containing ~5 to 40 ppm ClO_2 residual and 2.5 gpt corrosion

inhibitor did not show statistically significant difference in corrosion rate from baseline comparison with no ClO₂ present. Inhibited tests did show statistically significant difference from baseline uninhibited test. ClO₂ was shown to regenerate from residual chlorite ion in produced water used in making 7.5% HCl by dilution of more concentrated acid. However even these higher concentrations did not impact the corrosion rate of the inhibited acid.²

In a third instrumented pilot scale study, which simulated actual conditions used in a slick water frac stage (velocity, temperature, duration, fluid additives, proppants, in fresh and in produced water, with and without ClO₂ present) a variety of carbon and stainless-steel alloys used in high pressure fracturing showed no statistically significant detrimental impact of maintaining 1 to 5 ppm ClO₂ residual in the fluids. However, the study showed the general corrosive, erosive nature of the frac operations. Corrosion rates were extremely high during the inhibited acid phase of each stage. Corrosion performance of carbon steel in fresh water started out poor.³ Adding ClO₂ had minimal impact. The presence of brine increased the corrosion rate by more than 30 – 40 %. Corrosion increased with pH 5.8 or below and was reduced above pH 6. While it is known that O₂ levels have significant impact on corrosion rate, the presence of ClO₂ did not increase O₂ levels. Corrosion rate of stainless steel alloys was consistently good even with ClO₂ present. Pitting was not detected over the course of this study.⁴

From these studies acidic solutions are the biggest contributor to corrosion in frac systems followed by salt from produced water. Frac iron systems just like salt water systems experience wet dry cycles that allow concentration of salts that significantly increase general corrosion and pitting.⁵ Proper use of inhibitors can minimize corrosion but not eliminate it.⁶ ClO₂ when used at typical 1- 5 ppm residual concentrations for disinfection of frac water has minimal impact on the corrosive erosive nature of fracturing operations. See Figure 8.

METHODS OF GENERATING CHLORINE DIOXIDE (PROS/CONS)

There are multiple reaction chemistries used to generate chlorine dioxide on the scale required for oilfield use. In general, they either oxidize sodium chlorite or reduce sodium chlorate. These methods have specific characteristics (safety, efficiency, cost) that strongly influence their suitability for our purposes. Below are brief descriptions of the most common processes along with their pros and cons. In all cases the primary precursor (chlorite/chlorate) is in aqueous form, as are sodium hypochlorite (bleach) and acid (sulfuric/hydrochloric).

While it is not in the scope of this paper to address all the various ClO₂ generators available on the market, there are two basic methods of feeding the chemicals into the generation process – pumps or vacuum eduction. It is the authors belief that the vacuum eduction process is much to be preferred for two reasons.

- Motive water flow through an eductor is used to create a vacuum that in turn pulls the precursor chemicals into the system to form ClO₂. If motive water flow is lost, chemical flow stops and the reaction shuts down. Thus, it is inherently much safer than pump fed systems.
- Since chemicals are fed under vacuum, any leaks will draw air into the system rather than result in a pressurized leak of chemical to the outside environment.

Sodium Chlorite/Cl₂ Gas (2-Part)

In this method, gaseous chlorine is educted into a water stream as shown by the first reaction equation below.



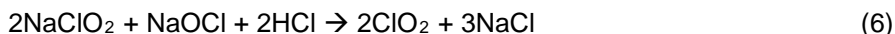
The hydrolyzed chlorine solution is then used to activate the chlorite ion as shown in the following equation.



This process is the most economical method to produce ClO_2 from sodium chlorite, as well as being very simple. There is, however, one major drawback to this process that prevents its use. It requires the use of 1-ton chlorine cylinders to transport the Cl_2 gas precursor. Any leaking chlorine cylinder can potentially expose many square miles of country to lethal concentrations of chlorine. This is the same reason that most industrial facilities have discontinued the use of chlorine gas.

Sodium Chlorite/Bleach/Acid (3-Part)

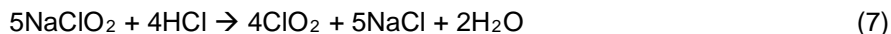
This reaction chemistry is similar to that shown above, except that the hydrochloric acid and bleach are fed as separate liquid precursors.



This is the most efficient, safest, and economical reaction chemistry available for use in all oilfield applications. With properly designed equipment, reaction efficiency is typically 98+% and precursors are readily available from numerous sources.

Sodium Chlorite/Acid (AC)

In this process, chlorite is acidified to produce chlorous acid which disproportionates to produce chlorine dioxide. While researchers state that several reaction pathways can occur in this reaction, the general equation is as follows:



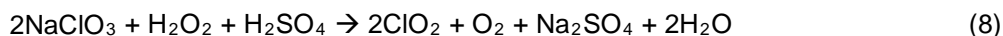
While this reaction is used relatively commonly, it does have several serious drawbacks, such as

- Poor yield, thus higher cost. Note that only 80% of the sodium chlorite is converted to ClO_2 (4 moles of ClO_2 are produced from 5 moles of NaClO_2).
- To achieve reasonable reaction efficiency and speed, acid must be overfed significantly versus stoichiometry to achieve a pH of <0.5. This typically requires an acid overfeed of 3x to 5x. This adds further cost as well as corrosion concerns.
- Precursors are reacted in concentrated form, thus resulting in ClO_2 concentrations of well over 100,000 ppm in the generator. Refer to safety discussion above.

Some vendors have also claimed that the cost inefficiencies are not real, since the “unconverted chlorite” is in fact still available in the water and is pumped downhole (assuming it is being used for fracturing operations) and will convert to ClO_2 in the acidic environment that exists there. This claim is patently false, for as the reaction demonstrates, any unconverted chlorite will still be subject to the reaction stoichiometry in Equation (7) if and when it is activated downhole.

Sodium Chlorate

This generation chemistry has been used for many years for large volume applications such as pulp and paper bleaching. Small scale generators were developed relatively recently that are suitable for oilfield use. Sodium chlorate is reacted with hydrogen peroxide and sulfuric acid. The ratio of chlorate to peroxide is fixed, so these two precursors are combined into one product. Thus, the three chemistries are available in the form of two precursor products. Several sources of these chemistries are now available.



Chlorate chemistry has the advantage of being economical. Sodium chlorate is produced as an interim step in the production of sodium chlorite; thus, it is less expensive as a precursor. However, the reaction chemistry causes a couple of concerns.

- The reaction requires high purity sulfuric acid of 78% concentration. If the acid is not sufficiently pure (less than approximately 50 ppm iron content), the reaction may be inefficient or the reaction

chamber suffer damage due to micro-“puffs”. The generator must then be flushed/cleaned of the contaminated acid, repaired if necessary, and a clean acid supply provided. Thus, the purity of the acid supply and its handling is of high importance.

- The sulfate present in the solution from the sulfuric acid can be problematic in many oilfield waters. If even low levels of barium or strontium are present, they will form an insoluble precipitate with the sulfate and scale equipment and downhole formations.
- Precursors are reacted in concentrated form, thus resulting in ClO_2 concentrations of well over 100,000 ppm in the generator. Refer to safety discussion above.

CONCLUSION

While no chemical is a panacea for all problems, chlorine dioxide does have a unique ability to solve several of the core problems universally encountered in the oilfield environment. H_2S , corrosion and emulsions are in most cases traceable back to microbiological growth. Chlorine dioxide, as an oxidizing chemistry, kills all forms of bacteria and eliminates H_2S . The elimination of H_2S then greatly reduces system corrosion and the resulting FeS that aids in stabilizing emulsions. Where FeS does exist, ClO_2 dissolves it, generally resolving the emulsion and any blockage that is present. At the same time, ClO_2 is weak enough that it does not react with hydrocarbons and most other organics, unlike stronger oxidants like bleach, ozone, peroxide, etc. Finally, it has an easily testable residual which allows precise dosage control.

Taken all together, chlorine dioxide provides the ability to solve several key problems with one flexible chemistry. As the discussion of ClO_2 production methods indicates, the 3-part chlorite/bleach/acid generation method is preferred to other options for oilfield operations. When combined with generation equipment that utilizes vacuum eduction for chemical feed, it optimizes cost, safety, and performance.

Bibliography

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⁴ Monroe, Stephen. “Corrosivity of Chlorine Dioxide on Typical Oilfield Iron”. Produced Water Society Seminar 2018, 13 February 2018, Marriott Sugar Land Town Center, Sugar Land, TX, Conference Presentation.

⁵ Fontana, Mars G. (1986) Corrosion Engineering. McGraw-Hill Book Co., NY, ISBN: 0-07-021463-8, Fig. 8-1 Corrosion of ordinary steel in the sea

⁶ Prues, W. et al., “Chemical mitigation of corrosion by chlorine dioxide in oilfield waterfloods,” Material Performance, Vol 24, No.5, pp 45-50 (May 1985)

⁷ International Dioxide White Paper L-0002 Rev 1 Dated 11-30-16 “Chlorine Dioxide in Fracturing Water Disinfection - Effectiveness Brings Competitive Scrutiny”

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CASE HISTORY – CENTRAL TREATMENT OF TANKS/PIT

A producer in west Texas has multiple locations where produced water is collected in a central facility with the goal of treatment and reuse for fracturing operations. Prior to the introduction of chlorine dioxide, the systems performance suffered due to emulsions formed by biomass/FeS/oil as well as H₂S with its associated corrosion and employee safety issues. A typical system is illustrated below.

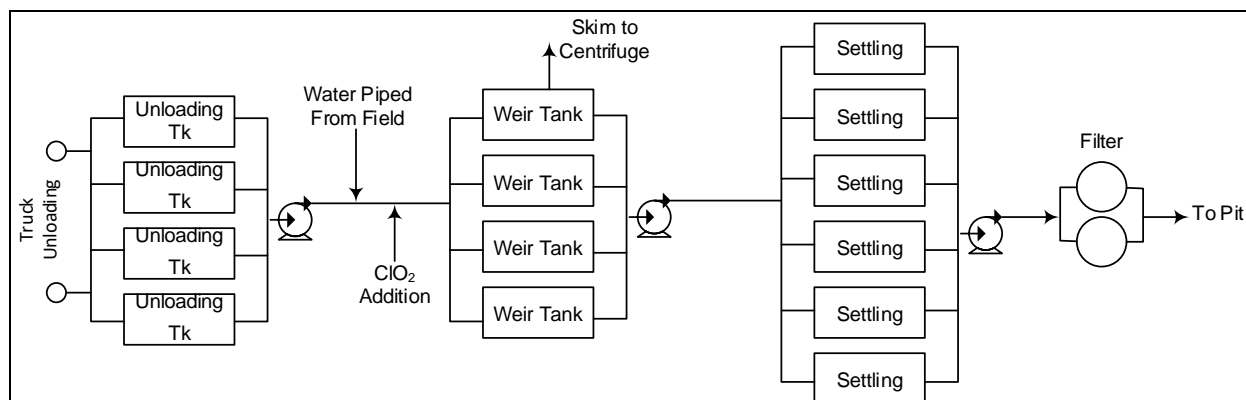


Figure 1
Typical Central Treatment

With chlorine dioxide, the treatment approach is common to all:

- Oxidation with chlorine dioxide for H₂S removal, bacterial control and elimination of emulsions
- Use of weir tanks to provide initial solids separation (oxidized iron and other incoming suspended solids)
- Weir tank solids are centrifuged prior to disposal as non-hazardous waste
- Settling tanks after the weir tanks
- Filtration
- Storage in a pit for use as needed.

The end result is

- Availability of reliably clean produced water for fracturing
- Much reduced need for tank cleaning
- The solids disposed at much reduced cost
- Reduced maintenance
- Improved employee safety

Table I. Typical treatment data is below.

Location	ClO ₂ Dose (ppm)	ClO ₂ Residual (ppm)	Iron (ppm)	Bacteria	
				ATP	~Bottles
In	30		30.5	3500	4
Weir Tanks		16.2			
To Pit		4.0			
Pit			1.5	<5	0

CASE HISTORY – H₂S DESTRUCTION IN OILFIELD PRODUCED WATER GATHERING SYSTEM

A Canadian producer had severe problems with high atmospheric H₂S levels in a produced water gathering tank facility. The problem was so severe that employees had to work with supplied air respirators. Previous efforts were made to treat with conventional H₂S scavengers (typical amine based products), but these proved unreliable. This type of product only adsorbs the amine and if pH and/or temperature change significantly the H₂S can be (and was) released again.

In contrast, ClO₂ permanently destroys the sulfides/H₂S present by converting to sulfate. Treatment with ClO₂ was initiated and an appropriate dose was applied to achieve a positive ClO₂ residual. Costs were equivalent to the previous treatment, but provided reliable results with complete elimination of H₂S in all phases. Workers were able to dispense with supplied air respirators.

Given that H₂S is the most highly reactive of all contaminants present with ClO₂, it would be possible to achieve its destruction without oxidizing other reactive species (iron, bacteria, etc.). Thus, with the single goal of this application being elimination of the safety issues resulting from H₂S, a lower dosage would work well, and significant cost saving are possible. Further work is ongoing, and initial bench testing indicates that approximately 50% cost saving are possible going forward.

Table II. H₂S levels before treatment and at Poseidon Tank after ClO₂ Treatment

Location	H ₂ S		ORP (mV)
	Water	Air	
Before Treatment	120 – 180 ppm	0.5 – 2.0%	-200 to -400
After Treatment	0	0	>625

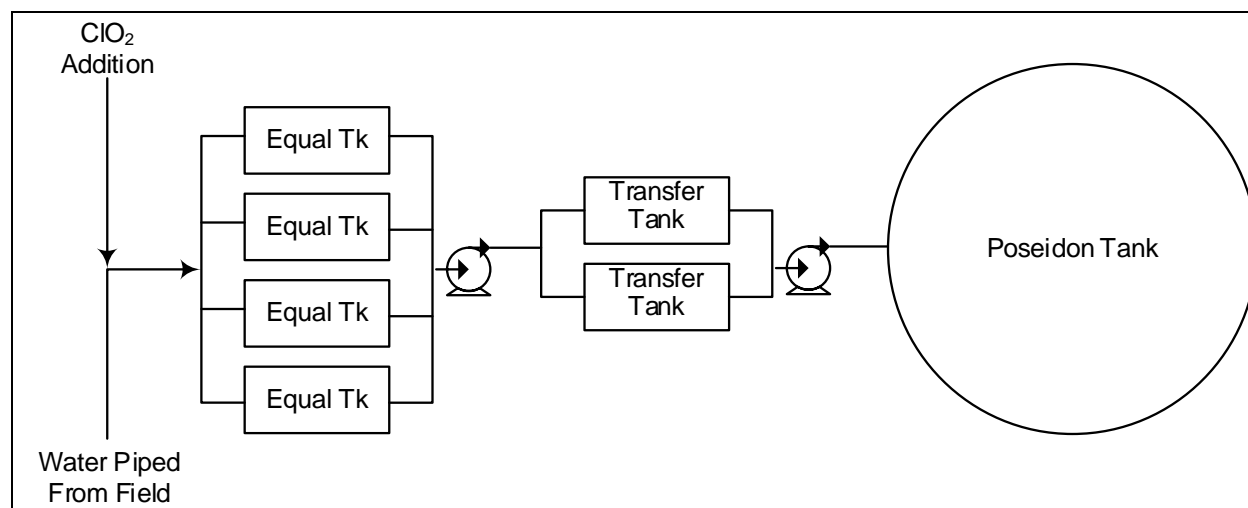


Figure 2
Produced Water Surface Treatment Process

CASE HISTORY – FRAC ON THE FLY

At present, frac-on-the-fly is the most prevalent use of chlorine dioxide in the oilfield. Complete disinfection of the water is critical to avoid inoculation of the wellbore and formation with bacteria which will later foul them, form H₂S, FeS, and all the attendant problems.

In this typical example (see drawing below) ClO₂ was applied to the incoming fresh water stream to obtain a residual of 3-5 ppm as ClO₂. The average applied dosage was 8 ppm with an average residual of 4.6 ppm as ClO₂. Samples for bacterial analysis were pulled from upstream of ClO₂ addition, and from the equalization tanks.

Table III. Bacterial Analyses of Frac Water before and after ClO₂ Treatment

Date	ClO ₂ @ Equalization Tank (ppm)		Treated ORP (mV)	Untreated Bacteria (cfu/ml)		Treated Bacteria (cfu/ml)	
	Dose	Residual		APB	SRB	APB	SRB
Apr 27	8			1,000	10	0	0
Apr 28	8	6.9	743	100	10	0	0
Apr 30	8	5.0	747	1000	10	0	0
May 1	8	5.3	753	10000	100	0	0
May 2	8	4.0	745	100	10	10	0

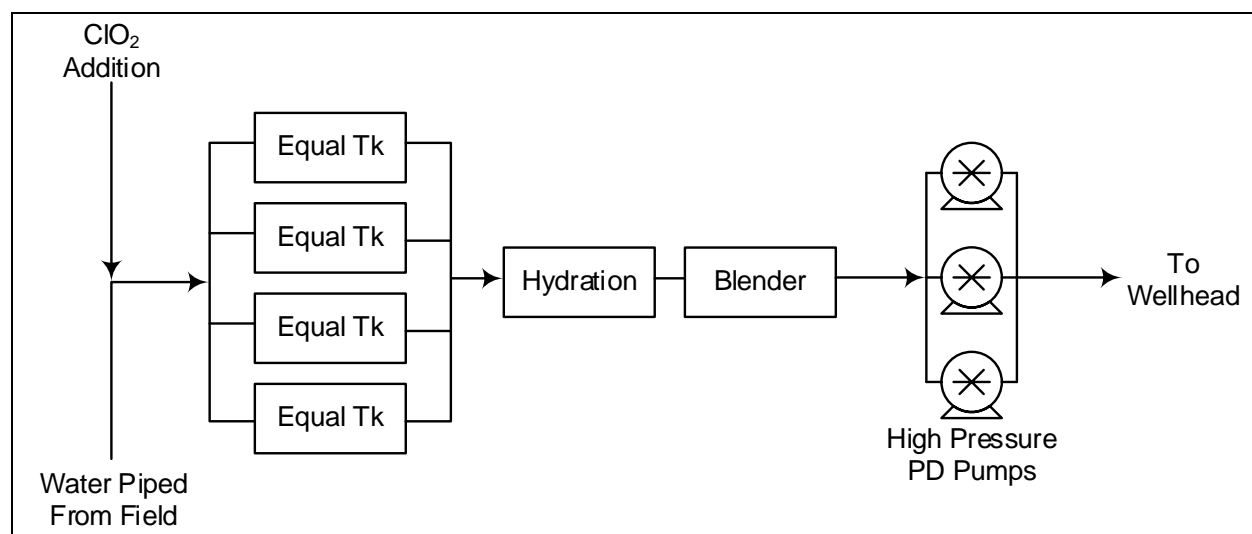


Figure 3
Frac-on-the-Fly Process

CASE HISTORY – PRODUCING OIL WELL

Work recently done on producing oil wells shows the benefits of chlorine dioxide for improving oil and gas production on wells that have experienced production declines. These declines are typically due to growth of bacteria introduced into the well during drilling and completion. As discussed earlier, the bacteria will eventually be sufficiently numerous to produce H_2S , with its subsequent corrosion byproduct of FeS . The combination of bacterial biomass and FeS will plug the formation and wellbore.

Acid stimulations will temporarily dissolve FeS (until the pH rises again), and is totally ineffective for the removal of biomass. The introduction of ClO_2 into the acid stimulation program, however, shows dramatic improvement. It kills and dissolves biomass as well as converting the sulfides in the FeS to sulfates. The addition of an organic nano-surfactant to the fluids injected downhole speed the penetration of ClO_2 dramatically, making this a very fast and effective treatment.

In this case, the result was an increase in oil production from 250 barrels per month to 700 barrels per month. Production improvement lasted for 18 months. These treatments are simple and economical, with a high return on investment.

Note the scale on the graph below is logarithmic.

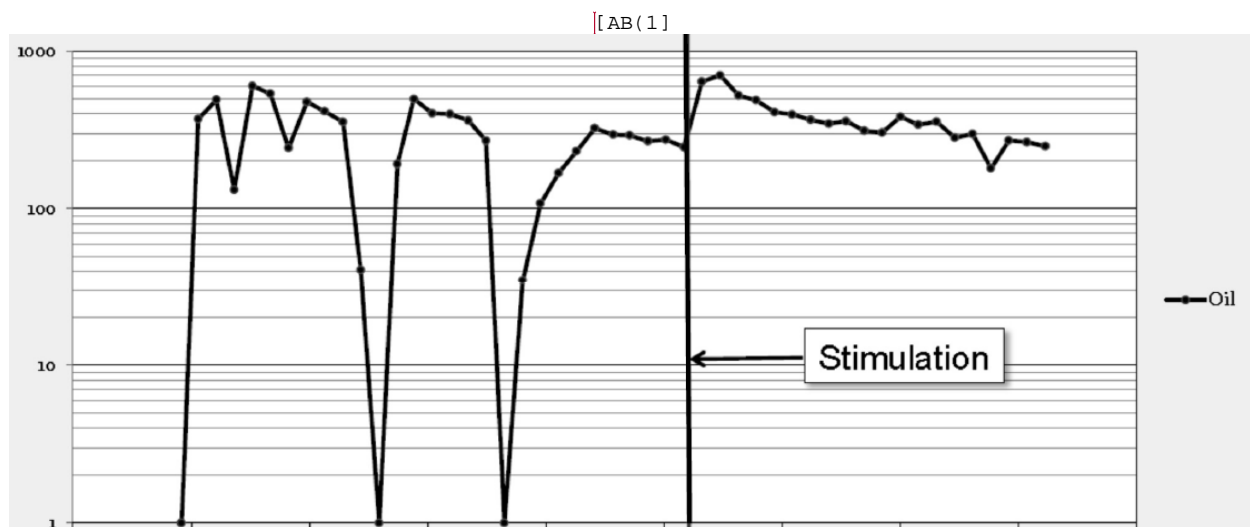


Figure 4
Remediation process works by oxidizing relative perm block mechanisms,
i.e. FeS , paraffin, asphaltenes, emulsions, etc.

CASE HISTORY – WATER INJECTOR WELL

Work recently done on water injection wells shows the benefits of chlorine dioxide for improving injection rates on wells that have experienced declines. These declines are typically due to growth of bacteria introduced into the well from the fluids being injected. As discussed earlier, the bacteria will eventually be sufficiently numerous to produce H_2S , with its subsequent corrosion byproduct of FeS . The combination of bacterial biomass and FeS will plug the formation and wellbore.

Acid stimulations will work on many scales and temporarily dissolve FeS (until the pH rises again), but is totally ineffective for the removal of biomass. The introduction of ClO_2 into the acid stimulation program, however, shows dramatic improvement. It kills and dissolves biomass as well as converting the sulfides in the FeS to sulfates. The addition of an organic nano-surfactant to the fluids injected downhole speed the penetration of ClO_2 dramatically, making this a very fast and effective treatment.

In this case a stimulation treatment consisting of Acid – Brine – ClO_2 – Brine – Acid in combination with the organic nano-surfactant showed an immediate and dramatic increase in injectivity. Before treatment injection rates were 10 bwpd. After the treatment they increased to 312 bwpd at the same pressure.

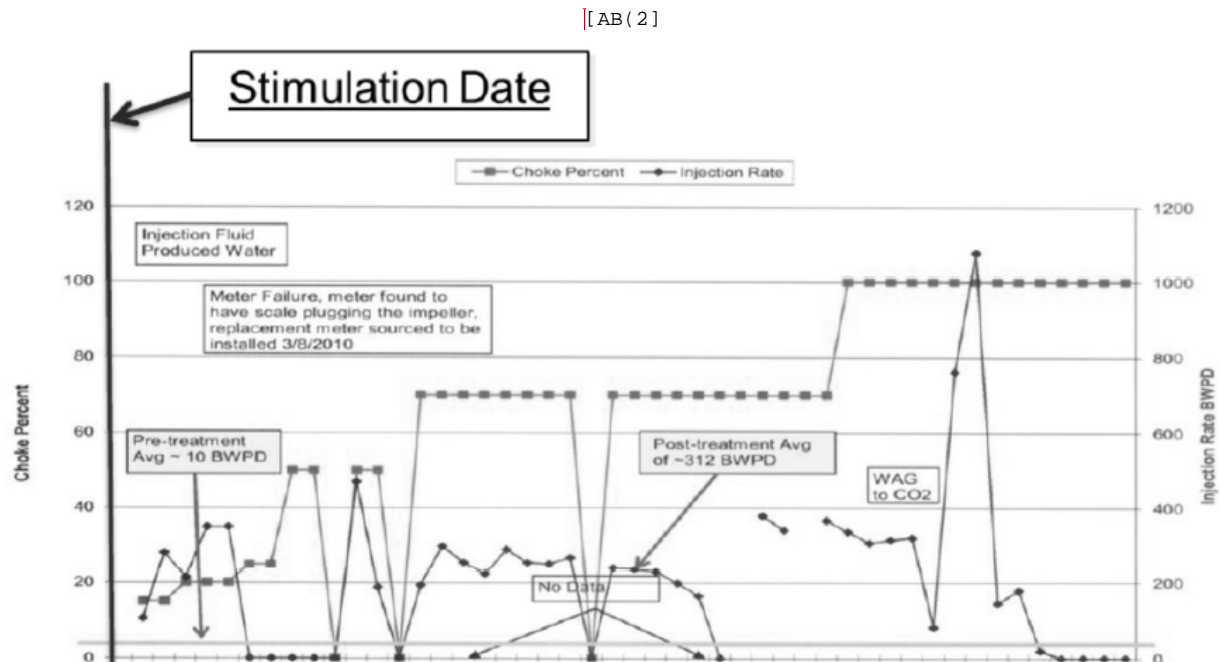


Figure 5
Improved water injection rates during acid stimulation and ClO_2 treatment.

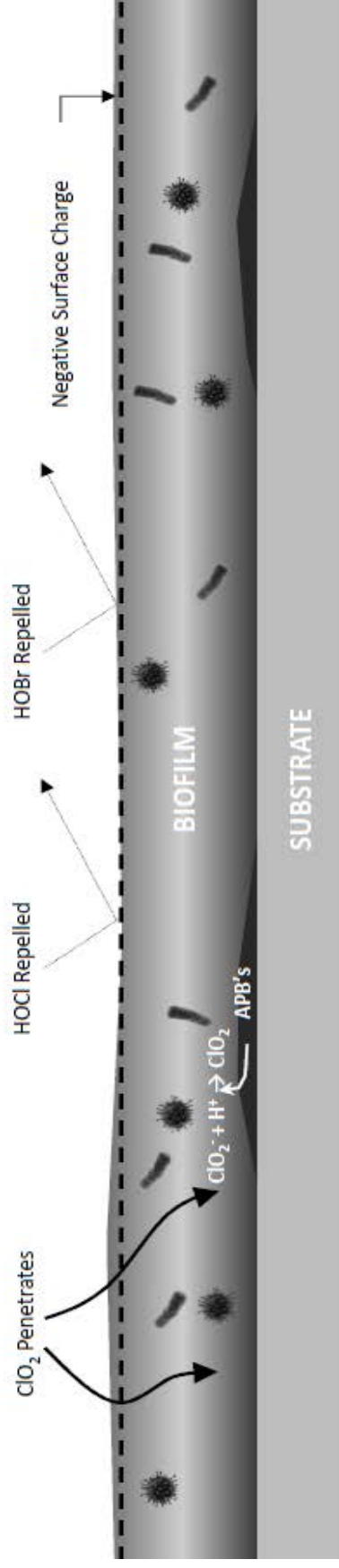
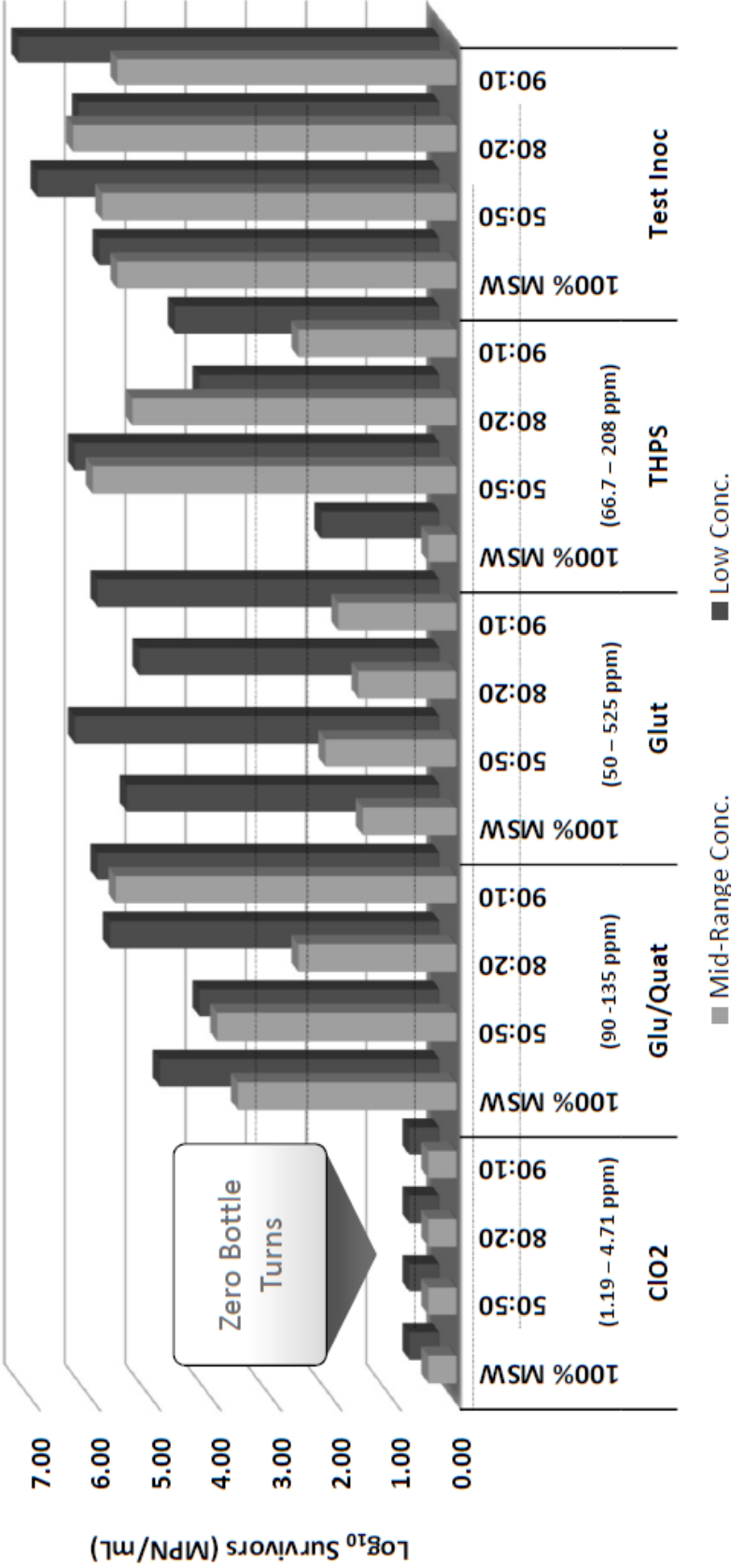


Figure 6
 ClO_2 Recycle Effect

Performance: Lab ClO₂ vs Nonoxidizing Biocides

Surviving SRBs After 30 Minute Contact Time (SPE174560)

Microbial Efficacy: Marcellus Shale Water Sulfate-Reducing Bacteria (SRB)



All ClO₂ test results were below the level of detection (i.e., <3.0 CFU/ml or 0.48 log/ml)

Figure 7
ClO₂ vs Non-Ox Biocides

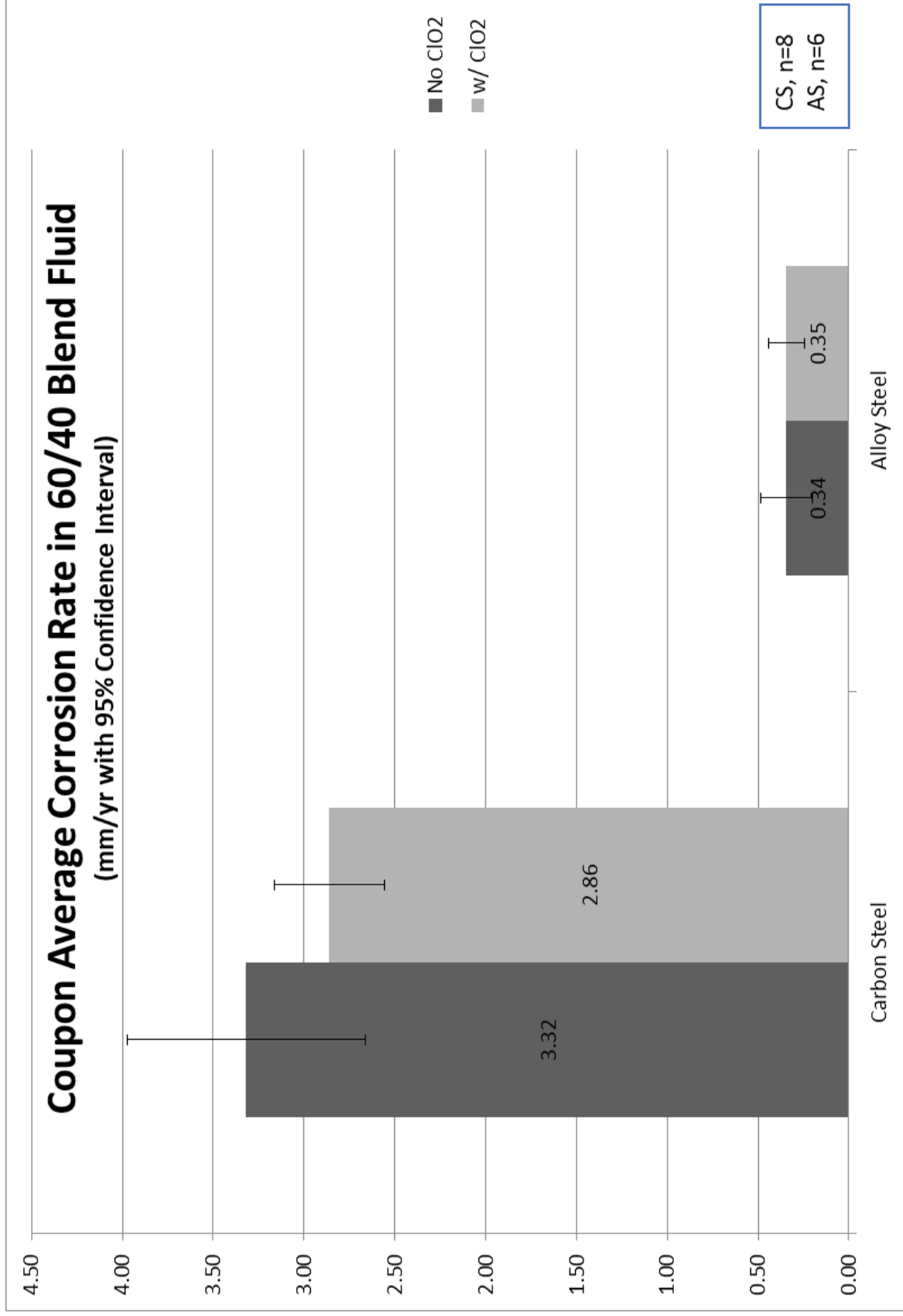


Figure 8
Corrosion W & W/o ClO₂