IMPACT OF PRODUCED WATER SALINITY ON THE CORROSION BY CHLORINE DIOXIDE AND ITS INHIBITION

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A. INTRODUCTION

A number of different metals are used in upstream operations. These vary from low carbon steel (1010, 1018, 1020) to higher grade API SPEC 5CT steel (P110, J55, K55, N80, and L80) to austenitic steel (304, 316). The selection of the right metal is typically dictated by the corrosivity of the produced water. Major contributors to corrosion include bacteria,[1] biofilms,[2] H_2S,[3] FeS,[4] elemental sulfur,[5] deposits,[6] and undoubtedly many other species. The seriousness of corrosion cannot be overestimated. Various cost estimates have been made over the years. In 1950, corrosion in the US was estimated to be on the order of \$5.5 Billion.[7] In the early 1990s, the corrosion caused by SRB alone has been estimated to be \$1 - 2 Billion in the US.[8] More recently, the estimates for corrosion world-wide was \$2.5 Trillion annually.[9]

Although many of the causes of corrosion have been independently identified, in reality it is impossible to separate the effect of each of these from the others, because of the interdependence of these factors. In addition to these factors, the addition of oxidants introduces another cause. This report discusses the historical use of chlorine dioxide (ClO_2) for controlling H_2S and bacteria in produced water. The results of the contradictory reports of corrosion are described, the reasons for this disparity is discussed, and the current results of on-going research into effective corrosion inhibition are presented.

B. HISTORICAL REPORTS

Because ClO_2 is an oxidizer, it is corrosive. However, corrosivity of ClO_2, when compared to that of other components on corrosion, such as bacteria, biofilm, H_2S, and FeS, *can* be significantly less. Consequently, ClO_2 is commonly applied to mitigate the corrosive effects of these other species, as illustrated in the historical work described below.

1981: In January 1981, a waterflood near Wilmington, California was experiencing excessive corrosion, measured by coupons, averaging about 30 mpy from coupons (corrosion varied from about 7 to over 80 mpy), with bacterial counts in excess of 10^8, and sulfides in excess of 10 ppm. Various combinations of aldehyde-type and thiocarbamate non-oxidizing biocides along with various corrosion inhibitors were employed. A year later, corrosion rates and bacterial control had not improved, although sulfides had been reduced to around 4 ppm.

In June 1982 in an effort to improve results, 2000 gallons of ClO_2 solution were applied for 4 hours every other day. This appears to be the first reported use of ClO_2 to reduce corrosion, bacteria counts, and sulfides, in a waterflood. By April, 1983, corrosion rates stabilized to 0.8 mpy, bacteria and sulfide remained at 10^4 and < 0.1 ppm, respectively.

The conclusion by the author was that bacteria and sulfide, thought to be the major sources of corrosion in the system, were controlled by ClO_2, which resulted in improved corrosion rates. The water chemistry was not discussed.[10]

1985: In 1985, the most comprehensive study of corrosion by ClO_2 and its mitigation was done.[11] One of their conclusions was that ClO_2 can be corrosive to oilfield equipment, regardless of the generation method, with the corrosion being more significant at the application point.

1987: In 1978, various mechanical and chemical approaches, including use of acrolein, were employed to solve a number of corrosion, deposition, sulfides and plugging problems in a waterflood in Inglewood, California. Despite these approaches, water quality continued to decline.[12]

While some thought the corrosion/plugging issue was primarily due to bacteria, others disagreed. This was because the role biofilm played had been neither clearly identified nor well understood at the time.[13]

In 1982, the belief that the problem was primarily microbiological in nature led to an increase in the existing acrolein feed rate. While the increased acrolein feed resulted in lower bulk water bacterial counts, it was ineffective at controlling slime and deposits.

The failure of the traditional program, which included glutaraldehyde initially and later acrolein, resulted in an evaluation of ClO_2. The success of the program led to its application field-wide.

Use of ClO2 resulted in a complete kill of bacteria and corrosion rates dropped from 20 to 5 mpy during the initial test period. During the next several months, the corrosion rates dropped to an average of 2.0 mpy. Slime and FeS were noticeably absent from surface equipment.

As a result of this, ClO_2 was evaluated in a 3-mile long pipeline. The ClO_2 was applied initially at intermittent periods with low dosages. Results from further testing showed that applying ClO_2 in shorter periods at higher concentrations was more effective. Even after the corrosive-causing species had been controlled, elevated corrosion rates continued, but this time it was attributed to CO_2, with trace amounts of O_2.

The authors noted the problems that have since become well known, not discounting the effects of carbon dioxide and oxygen:

1. Bulk water bacteria have not been the problem, generally. It has been the presence and growth of biofilm that resulted in the corrosion and plugging problems,
2. ClO_2, if applied incorrectly, has resulted in corrosion, and
3. ClO_2 at a minimum residual of 2 ppm maintained for 2 minutes has resulted in a "complete" bacterial kill.

2018: In a pilot scale lab study which simulated actual conditions of a slick-water frac, ClO_2 was applied to a variety of carbon and stainless steels.[14] Up to 5 ppm ClO_2 residual was maintained. No material increase in corrosion rates due to ClO_2 was observed. Factors having a substantive impact on corrosion rates included pH and salinity, although the water chemistry, other than pH was not described.

C. CURRENT WORK - EXPERIMENTAL PROTOCOL

Three separate groups of a dozen 5-gallon pails of produced water (PW) were collected from a site near Big Spring, Texas, at different times and sent to the Pureline lab in Houston, TX for testing.

The water was tested at salinities varying from 9.3% to 2.3%. Salinities lower than 9.3% were achieved by diluting 9.3% salinity water with DI water.

Four liters of the water to be tested were placed into a 5-L beaker, as shown in Figure 1. A number of probes, including duplicate Oxidation-Reduction Probes (ORP) probes, one pH probe, and duplicate Linear Polarization Resistance (LPR) probes were immersed in the water to be tested. Duplicate probes were employed to ensure the readings was as accurate as the equipment allowed. The data from these probes were sent to a Walchem eController which was used to condition and store the probe data. The minimum time required for LPR probes to achieve equilibration was 5 minutes, but the other probes were read in much shorter time frames. Consequently, the data was sampled at shorter times. LPR was used instead of corrosion coupons, because experiments could be run in fewer than 8 hours, and coupons required longer periods of time.

H_2S (~ 60 ppm in the produced water as measured by a drop test[15]), was not present in the original sample, but was very noticeable in the water once the sealed pails were opened. This illustrated the high bacterial activity in the water, and the fairly rapid production of H_2S by sulfate-reducing bacteria (SRB). SRB are strict anaerobic bacteria which utilize sulfate as a terminal electron acceptor and produce H_2S as a metabolic byproduct.

In an attempt to simulate as closely as possible field conditions, the H_2S was reacted with $NaClO_2$ prior to testing. After addition of the $NaClO_2$, the $NaClO_2$ was given several minutes to allow reaction with the sulfide present, with the goal being to achieve an ORP of a minimum of - 100 mV. The ORP slowly continued to rise somewhat as the chlorite ion continued to oxidize the sulfides present.

After the ORP stabilized, the Linear Polarization Probes (LPR) were inserted into the water to establish a corrosion rate baseline. Then, once the corrosion rate baseline had been established, aliquots of ClO_2 were added to the solution approximately every 10 minutes, to measure the response of the LPR corrosion probes to ClO_2.

When the ORP reached 500 - 550 mV, samples of the solution were caught and tested using the Palintest ChlordioX^{TM} Plus unit. A ClO_2 residual > 2 ppm measured 2 minutes after addition of ClO_2, was considered the endpoint. Figure 2 shows a considerable body of work that demonstrates that a residual of 2 ppm for 2 minutes is sufficient to provide bacterial inactivation as measured by serial dilution bottles.

Note that some groups have used a consistent target of 650 mV after 2 minutes to provide an indication of adequate bacterial inactivation. With the more precise testing of this work, sometimes a lower mV reading indicated adequate bacterial inactivation. Given the small amount of ClO_2 required to move the ORP from 550 to > 650 mV, it appeared that a 650 mV target was reasonable.

D. CURRENT WORK - THE CORROSIVE EFFECTS OF PRODUCED WATER

Figure 3 shows the typical, expected, experimental response of new (or in this case, reconditioned) LPR probes to produced water. This specific graph is for untreated 9.3% salinity water. Upon exposure of new LPR probe tips (or corrosion coupons) to produced water, the corrosion rate was initially high, but rapidly decreased as the probe metal (C1010) became conditioned to the water. (Note that a similar response has been observed for coupons, which is why coupons are exposed typically for 30, 60, or 90 days). Initially, the low corrosion rate was questioned, so the experiment was repeated a number of times, each of which confirmed the original data. Although C1010 metal was evaluated in this work, testing of P110 steel, commonly used in oil field piping, showed a very similar response.

After multiple tests with duplicate LPR probes, the general trend, in the high salinity produced water, was predominantly a function of that salinity, although iron and sulfide are also factors. For the 9.3% salinity produced water the corrosion rate equilibrated to a corrosion rate that was quite low. As the salinity was reduced with the addition of DI water, the baseline corrosion rate increased. Salinities of ~ ~7.0, ~ 4.6, and ~ 2.3%, were tested. When the salinity exceeded about 3%, the corrosion rates decreased, matching a plateau phenomenon noted in the literature, but surprising nonetheless. These results, shown in Figure 4, are in general agreement with those of previous researchers.[16]

E. CURRENT WORK - CORROSION DUE TO CHLORINE DIOXIDE

Corrosion increases due to the addition of ClO_2 to produced water was measured at various % salinities. A typical plot of the ORP and corrosion vs ClO_2 addition is shown in Figure 5 for 8% salinity produced water. The baseline corrosion rate corresponds within experimental error to prior test results for baseline corrosion.

For 2.3% salinity water, which is near the maximum baseline corrosion rate, the ClO_2 added increased the baseline corrosion rate by about 21 mpy, as shown in Figure 6. The ORP probe was taken out of its storage solution and inserted directly into the water to be tested, which resulted in a relatively high ORP initially, followed by the reduction in ORP to < 100 mV.

To double check this experiment, the experiment was repeated the next day on a fresh sample (Figure 7). In this sample of produced water, an aqueous solution of sodium chlorite was added dropwise to bring the ORP up to about 200 mV. In this experiment, the addition of ClO_2 resulted in an increase of about 26 mpy, which corresponded well with results from the prior day. In addition, this demonstrates that the addition of sodium chlorite to consume H_2S has relatively little effect on the corrosion rate increase resulting from addition of ClO_2.

It is interesting that small changes in ORP near the maximum from Figures 6 and 7 corresponded to a significant increase in the ClO_2 concentration. It is this lack of linearity that prevented ORP from being used as a direct read for the ClO_2 concentration.

Depending on a number of factors, the increase in corrosion rate due to the addition of ClO_2 varied substantially with ClO_2 concentration, as shown in Figure 8. In this experiment, for 9.3% salinity produced water, after the ClO2 demand was met, the ClO_2 residual of about 5 ppm was achieved and tracked over time. This residual declined slowly.

F. CURRENT WORK - PRELIMINARY CORROSION INHIBITORS SCREENING FOR UNTREATED WATER

Finding a suitable corrosion inhibitor to be used in conjunction with ClO_2 has been the subject of a number of studies.[11,17,18,19,20] The relative success of these varies significantly.

A different experimental apparatus (Figure 9) was used for potential corrosion inhibitor screening. This apparatus incorporated ten tall 1-L beakers. For each corrosion inhibitor, 125 ppm, as product, was used. One was left untreated as the control.

Carbon steel (C1010) coupons were exposed to ~ 2.3% salinity produced water for 2 weeks. Figure 10 shows the coupons, as removed. Some of the corrosion inhibitors had the opposite effect of actually increasing the corrosion rates. However, for corrosion inhibitors 3 and 4, results appeared to be quite effective. Inhibitor 3 was a single inhibitor. Inhibitor 4 was a blend of the Inhibitor 3 and another inhibitor.

The results for Inhibitor 3 warranted more detailed analysis.

G. CURRENT WORK - MORE DETAILED SCREENING OF CORROSION INHIBITOR 3

Inhibitor 3 was investigated in more detail using the method described previously. To determine whether the inhibitor would have any inhibiting effect on the corrosive effects of ClO_2, the inhibitor was added to the beaker after the LPR probe was inserted but before ClO_2 was added.

While the increase of corrosion due to ClO_2 varied from 21 to 26 mpy in 2.3% salinity water in duplicate experiments, Figure 11 shows the same response but with Inhibitor 3 added. In this experiment, ClO_2 was added too soon, without allowing the baseline to equilibrate. It does appear, however, that the corrosion was reduced.

H. CONCLUSIONS OF THE CURRENT WORK

Sampling: While this sampling approach has value, several phenomena were observed as a result of this method.

1. The original water had very little sulfide present, as the H_2S alarms at the collection site were silent while the water was being collected and no H_2S could be smelled in the water. Sealing of this bacteriologically-active water resulted in generation of a significant amount of H_2S during the time between sample collection and testing.
2. As only 1 - 4 L of any pail were used for any given test, once the pail was opened and exposed to air, even if rapidly re-sealed, the characteristics of the water changed which did impact corrosion

rates.

3. Soluble Fe complicated the results.

Baseline Testing: Note that there was a significant range of baseline corrosion rates, depending primarily on several things:

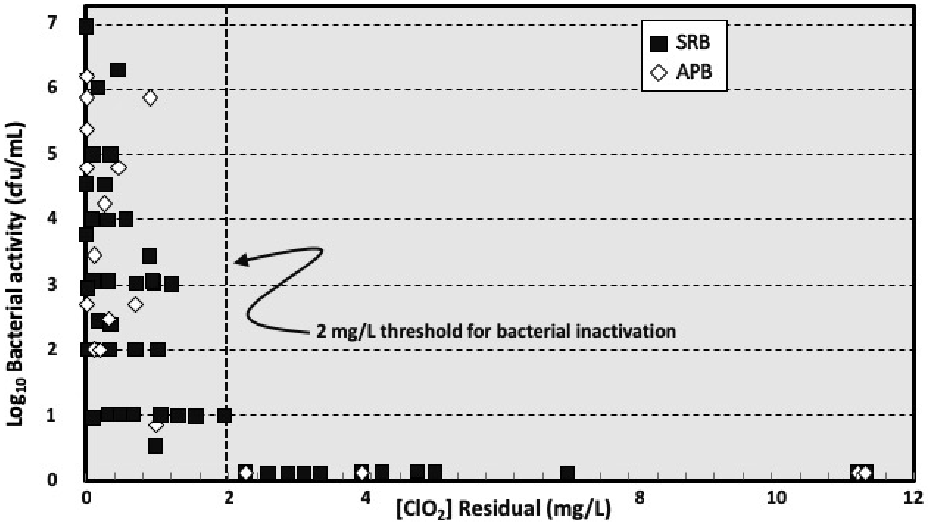
1. The nature and concentration of contaminants in the produced water.
2. The time between collection of the 5-gallon pails and the time it was received in the lab.
3. The time between opening a 5-gallon pail to remove the first sample of water to be tested and subsequent sampling from the 5-gallon pail.
4. The introduction of CO_2 and O_2 into a 5-gallon pail when the pail was opened.
5. The changes which occurred to the produced water between collections of 5-gallon pails.

General Observations:

1. The characteristics of water collected for testing were different from samples caught at different times. Sulfide and iron concentrations and bacterial activity varied considerably.
2. The natural corrosion of steel by produced water was quite low at a salinity of 8-10%. As the salinity decreased the corrosion increased to a maximum baseline corrosion rate at about 3% salinity, below which the corrosion rate declined.
3. The addition of ClO_2 resulted in an increase in corrosion rate, the magnitude of increase being a function of salinity. In general, as the salinity increased, the contribution to corrosion by ClO_2 also increased.
4. The variability of the various factors in produced water has resulted in most oil-field companies making several "simulated" produced waters for testing. This allows for better control and introduces the ability to compare various additives in an apples-to-apples way.
5. Work is on-going.

Figure 1. Experimental Apparatus

Figure 2. Minimum ClO_2 Residual [1-4]



2 mg/L threshold for bacterial inactivation

1. NL Treating Chemicals,"'Generated DiKlor Products Training Manual," 1985.
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4. Li, Z., Guiscardo, L., Lathrop, T., Sullivan, B., Croce, C., Mandagaran, N., Carrizo, C., and Aranguren, G., "ClO_2 Treatment of Oilfield Waterflood Injection Pipelines: A Field Study," Produced Water Society, Sugarland, TX, February 6-7, 2019.

Figure 3. Typical Response of LPR Probes for 9.3% Salinity Water

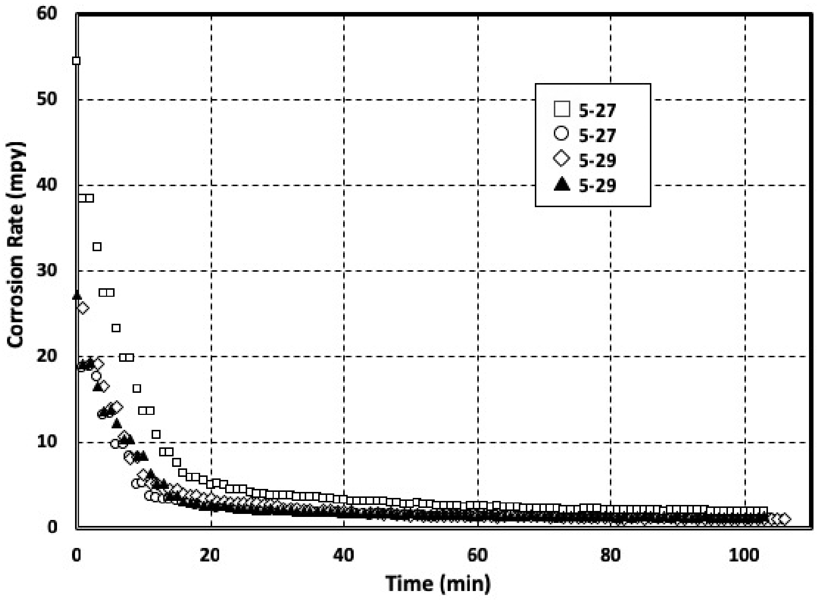
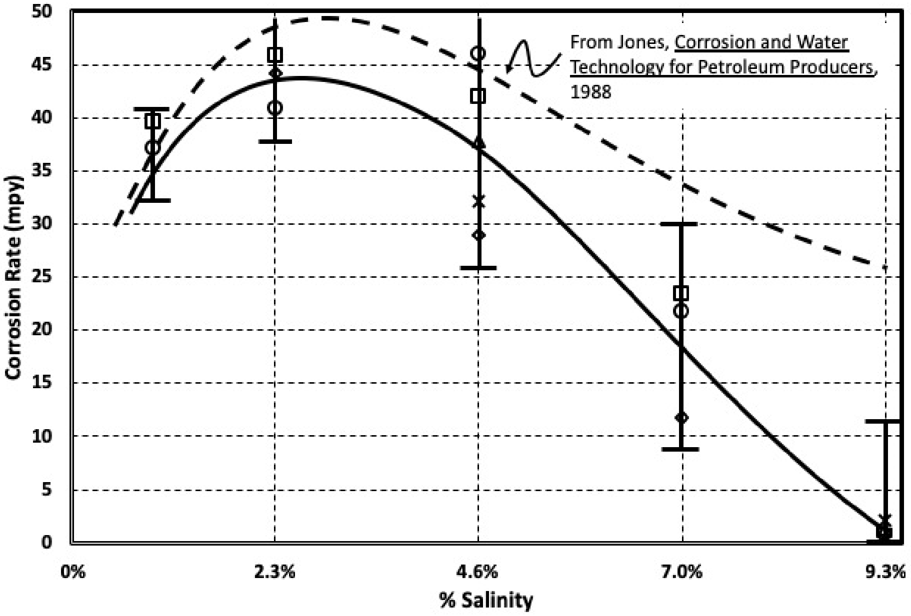


Figure 4. Baseline Corrosion vs. % Salinity



From Jones, Corrosion and Water Technology for Petroleum Producers, 1988

Figure 5. Corrosion Test with ClO_2

8.0 % Salinity - 2019-1-11

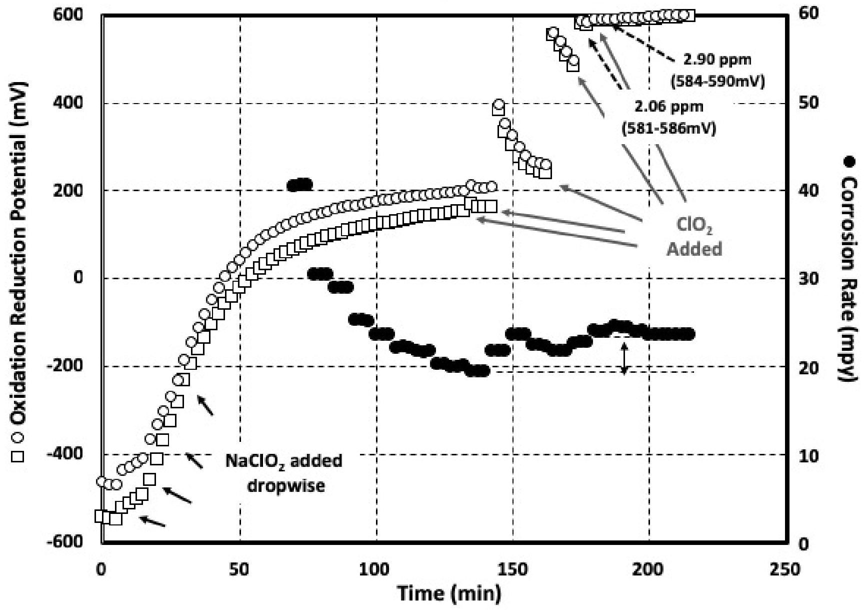


Figure 6. Corrosion Test with ClO_2

2.3 % Salinity - 2019-1-15

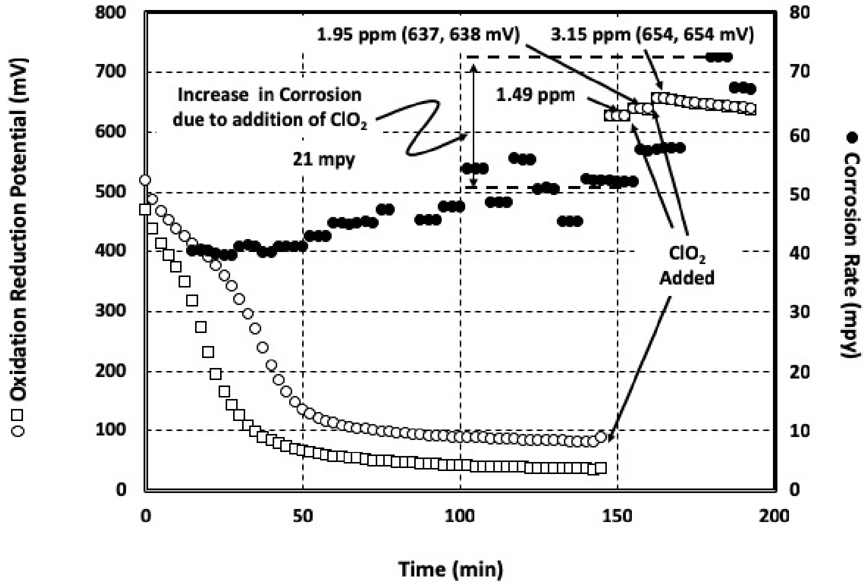


Figure 7. Corrosion Test with ClO_2

2.3 % Salinity - 2019-1-16

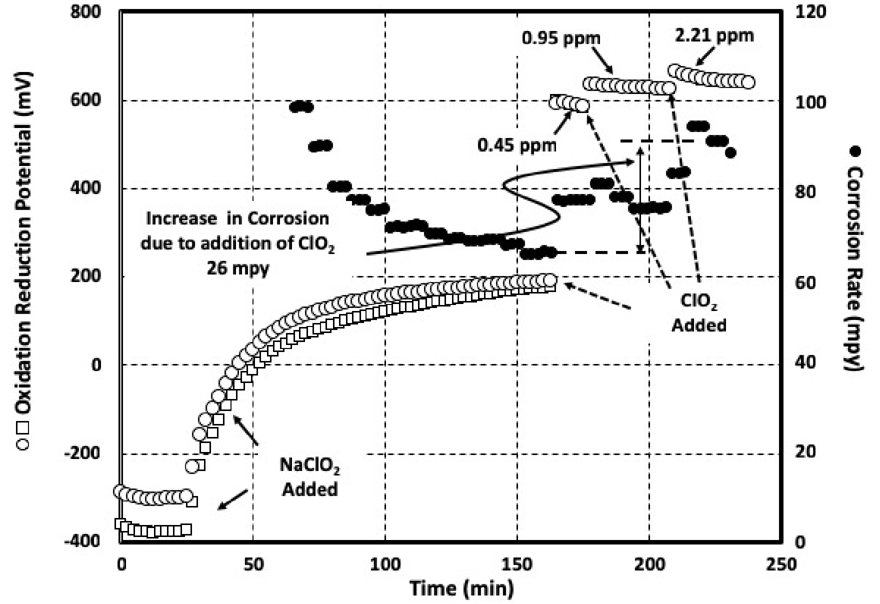


Figure 8. Corrosion Rate vs. $[ClO_2]$ Residual

9.3% Salinity – 5-29-2018

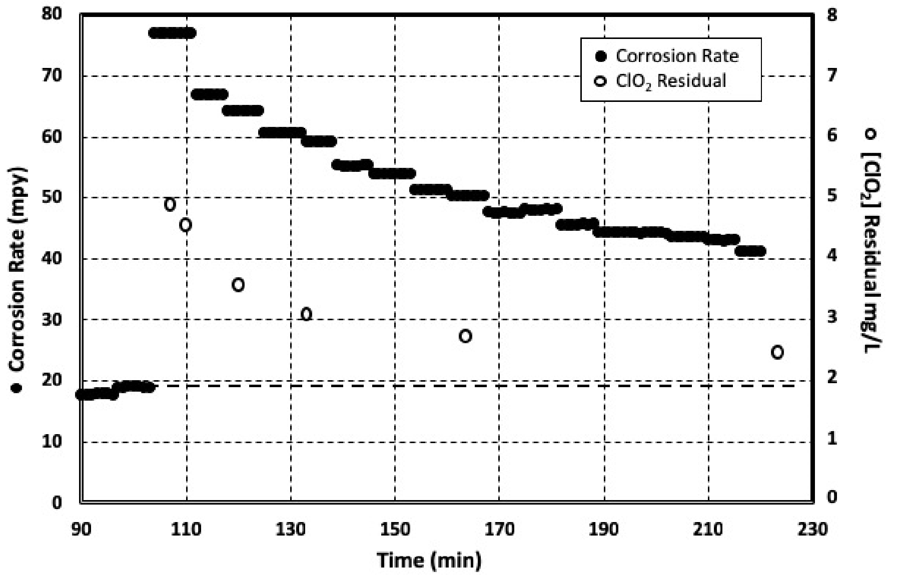
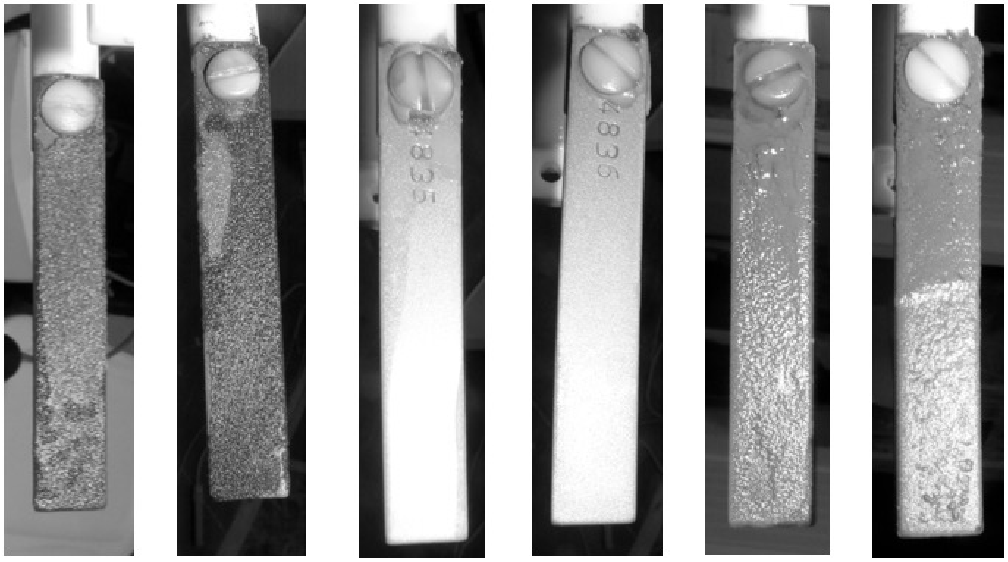


Figure 9. Experimental Apparatus for Coupon Testing

Figure 10. Coupons after Two Weeks

2018-12-7



Inhibitor 1 Inhibitor 2 Inhibitor 3 Inhibitor 4 Inhibitor 5 Untreated PW

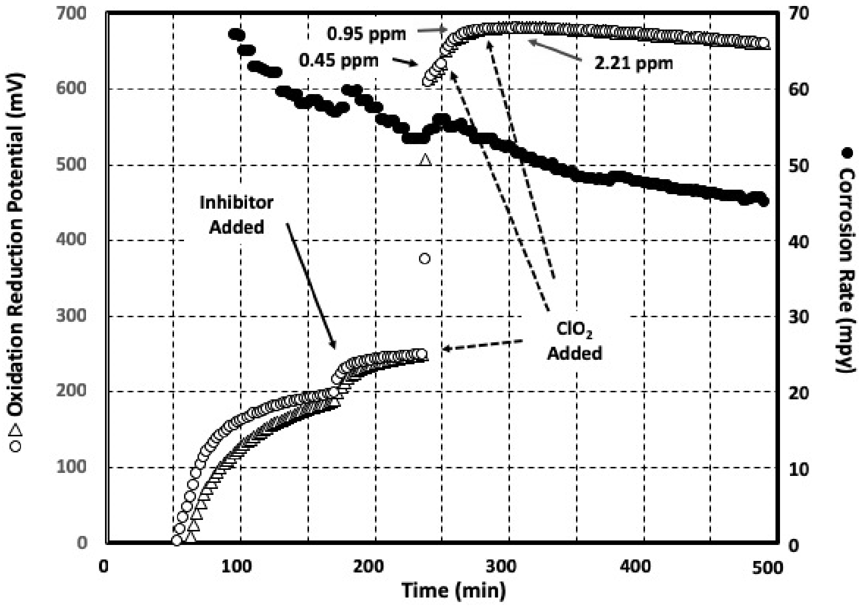


Figure 11. Corrosion Test

2.3 % Salinity - 2019-1-19 – With Corrosion Inhibitor

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