

## Development of Novel Chemical Systems to Combat Corrosion Caused by Heavy Saturated Brines

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### Abstract

Drilling in heavy brine environments, including saturated calcium chloride, calcium nitrate, calcium bromide, and various combinations, can prove to be extremely corrosive on completion equipment and production tubing. Novel chemistry approaches are required in order to effectively combat the effects of corrosion in these environments, especially in high temperature environments.

Clariant Oil Services has undertaken a range of tests to identify suitable corrosion inhibitor products for application in various completion fluids containing these corrosive elements. The initial product selection was focused on calcium nitrate heavy brines, and followed by inhibitor selections for other heavy brines such as calcium chloride, mixtures of calcium nitrate and calcium chloride.

Chemicals were screened by determining the products that showed superior solubility in these heavy brines and then several chemicals were tested using rotating cylinder electrode linear polarization resistivity testing. Next, promising candidates were further tested in high temperature/high pressure static autoclaves. The most successful chemicals exhibited a balance of heavy brine solubility and corrosion inhibition performance.

In addition to measuring general corrosion rates, surface analysis of the coupons was essential to determine the presence of localized corrosion. Static autoclave tests were conducted to determine and confirm strong performing chemicals. A high magnification enabled microscope was used to differentiate between chemical performance and identify any potential areas of local corrosive attack.

Poor performing products demonstrated metal surface morphology with high pit density and numerous deep pits, while the new chemistries with a novel approach yielded performance of either no pitting at all, or very limited pits with less than 10 microns in depth. High general corrosion rates were reduced to much less than 4 mpy even at 130°C. A review of the state of the art products show that their performance can rarely be matched especially in an oxygen rich environment. This paper details all the testing and selection criteria and

gives insight into the mechanism of corrosion attack as well as details of the synergies exhibited by the various chemical formulations.

### Introduction

A water-based solution of inorganic salts is often used as a well control fluid during the workover phase and the well completion operations. These brines are clear and should be particle free. It is important that the brines are particle free as the solids and particles can plug and damage the formation. In addition, brines can lead to clay swelling of the formation which is not desirable. Common brines used in these types of operations include calcium chloride, calcium nitrate, and a mixture of the two brines. More complex brine systems may contain calcium and zinc bromide, nitrates, chlorides, and the mixtures thereof. It is crucial that the specific gravity of the brine is in the preferred weight range to be most effective and economically feasible.

Heavy brines are used during many different stages of the oil and gas exploration in drilling and the production cycle, particularly as a component of drilling fluids, packer fluids, work-over fluids, kill fluids, and completion fluids. Packer fluids are used in the annulus of a well that surrounds the production tubing. Kill fluids are used to suspend a well either temporarily or permanently by hydrostatically over balancing with heavy brine. Completion fluids are used after a well has been drilled, but before the well has been brought online for production.

All these applications rely on one single property of the heavy brines, which is the density. The density of the brine is a key factor as the pressure of the hydrostatic head of the fluid column needs to be higher than reservoir pressure. As long as the fluid column exerts enough pressure to counter balance the reservoir pressure, blow-outs can be prevented. It is also important that the column pressure is adequate so that the brine is not lost in the formation. Heavy brines lost in the formation can harm the formation irreversibly; the heavier the brine, the higher the hydrostatic pressure. This can allow for lower volumes of fluids to balance the formation pressures. Different brines can be used to cater individual formation pressures, depth of wells,

and orientation of wells. There are various combinations of brines with various densities. The lightest being NaCl (10.02 PPG) and heaviest is ZnBr<sub>2</sub> at 22.13 PPG. The brines are usually used as single, two, or three component mixtures. Combinations of salts tend to be more corrosive than fluids comprised with a single salt.

Heavy brines tend to be very corrosive. The mechanism of corrosion with heavy brines is mostly oxygen induced corrosion. The brine corrosivity increases with the increase of temperature. The mixtures of brines tend to be more corrosive than single components. The pH of heavy brines tends to decrease with the increasing brine density. For example pH of 17 PPG ZnBr<sub>2</sub> brine is 4.92 but the pH of 18.2 ZnBr<sub>2</sub> PPG is 3.04. The lower pH brine is much more corrosive than high pH brine.

### Corrosion Inhibitor Design

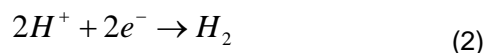
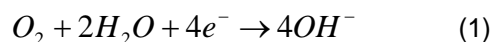
In designing corrosion inhibitors for heavy brines, one of the major challenges is solubility. It is also important that the chemical should mitigate general and pitting corrosion to an accepted level under an elevated temperature. The product should be compatible with elastomers and corrosion resistant alloys without inducing sulfide stress cracking<sup>1</sup> and elastomers.

It is very important that the corrosion inhibitor products developed for high density brines have good solubility in heavy brine. This is very challenging due to the low free water in high density brine<sup>2</sup>. The tests are performed in static conditions and the inhibitor needs to come into contact with the metal surface to inhibit corrosion. If the product is not soluble, the inhibitor can partially or completely phase separate from the brine. If the heavy brine is used as a packer fluid, low soluble product can create a much bigger problem due to the stagnant nature of the fluid.

### Corrosion Mechanisms

All heavy brines contain dissolved oxygen. All tests were conducted without removing dissolved oxygen. Oxygen scavengers are commonly added to drill-in fluids and completion fluids<sup>3</sup>. The dominant corrosion mechanism is expected to be oxygen induced. Oxygen intrusion can greatly increase the corrosion process even at very low concentrations. Most oil field corrosion inhibitors, which are developed and evaluated assuming complete absence of oxygen, do not perform well in an oxygen containing environment<sup>4</sup>. Oxygen corrosion is the most aggressive corrosion mechanism as the by-products, iron oxides, do not form a strong passivation layer. Other corrosion by-products such as iron sulfide (H<sub>2</sub>S corrosion mechanism) or iron carbonate (CO<sub>2</sub> corrosion mechanism) form highly tenacious protective films. Apart from this, the cathodic reaction with oxygen (equation 1) would reduce oxygen to water at the cathode whereas the other two systems would produce

H<sub>2</sub> (equation 2). Therefore, cathodic potential of the reaction with oxygen is larger and would produce higher a corrosion current leading to more aggressive corrosion<sup>5,6,7,8</sup>



Heavy brines such as ZnBr<sub>2</sub> brine are very acidic<sup>2</sup> and can be extremely corrosive at elevated temperatures. This corrosive nature of ZnBr<sub>2</sub> brines prove to be extremely challenging in the design and development of suitable corrosion inhibitors that can perform well in these brines at elevated temperatures. This paper describes a successful series of corrosion inhibitors developed for various brines that mitigate corrosion to an acceptable level. It is important to note, that these tests were performed without an oxygen scavenger or an intensifier and at elevated temperatures without the removal of oxygen from the brine solutions.

## Experimental

### Test Apparatus

The test apparatus used for simulating the well bore environment were 1 liter high pressure high temperature static autoclaves. Static autoclaves were used to simulate the zero shear conditions for the purpose of evaluating system corrosivity as well as inhibitor performance. Photographs of the static autoclave setup can be seen in Figure 1. General corrosion rates were calculated by weight loss measurement.



Figure 1: Static Autoclave setup

The test solution consisted of 800 mL of heavy brine. The head space (200 mL) was cleared of oxygen using

100% nitrogen gas four times before final pressurization into the autoclaves. Two weight loss corrosion coupons fixed on a PTFE cage were used in each autoclave (Figure 2).

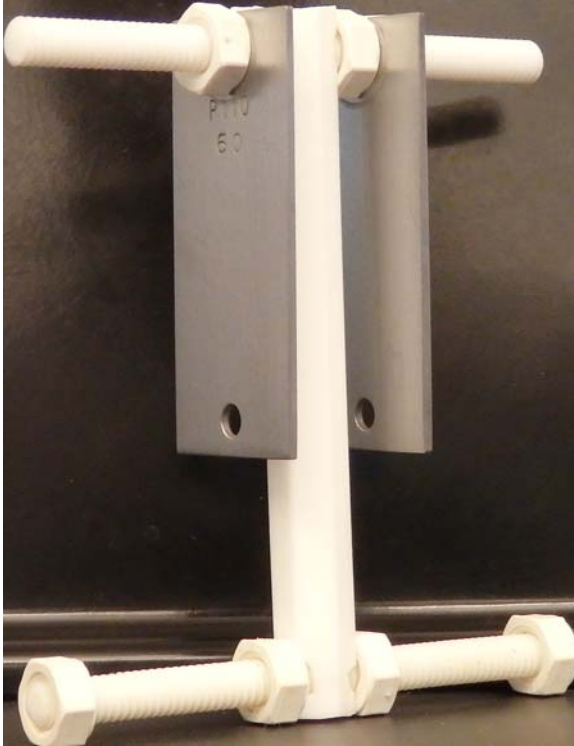


Figure 2: Autoclave Coupon PTFE Assembly

The coupon surfaces were analyzed after each test for pitting potential by using a high powered microscope (Olympus BX 51) pictured in Figure 3. The reflected light microscope is capable of analyzing samples up to 1,000X magnification. The microscope was mounted with a camera (Olympus UT-TVO 5XC-3) and includes brightfield, darkfield, and Differential Interface Controls (DIC) modes.



Figure 3: Microscope with digital camera setup

### Test Procedure

The following steps were performed in each heavy brine corrosion simulation test.

Test coupon surfaces were prepared by polishing on water lubricated wheel type polisher. Silicon carbide sand paper was used in the following order: 320 grit, 400 grit, 600 grit. Once coupons are polished, weight measurements are taken to the nearest milligram and recorded.

Coupons are attached to a PTFE cage using PTFE washers and nuts. The cage functioned as a method to suspend the coupons vertically (to simulate predominant well bore orientation of metal surface) and prevented contact with each other and the autoclave wall (eliminating the possibility of galvanic corrosion). Two coupons were used each test vessel.

800 mL of heavy brine was then measured using a 1000 mL graduated cylinder and poured into a 32 fl oz bottle with cap. The fluid was then dosed with the CI and shaken until the CI is distributed evenly into the heavy brine.

The PTFE coupon tree was inserted into the high pressure and high temperature stainless steel vessel and the dosed heavy brine was added. The coupons are completely submerged in the test fluid. The vessel was then sealed and the autoclave cuffs are tightened. It was imperative that the water loss from the fluid was allowed to precipitate back into the brine. Use of any additional container within the pressurized vessel increases the possibility water loss from the test fluid precipitating outside of the fluid which can lead to excessive brine destabilization and unwarranted precipitates. To prevent skewing of data from this phenomenon, the entire volume of the pressurized vessel was used. Any possible water loss during the test was allowed to precipitate back into the test fluid.

The sealed autoclave was pressurized to 150 PSI with 100% nitrogen gas into the top 200 mL vessel headspace. The pressure was then released through a bubbler tube to prevent oxygen back flow. This step was repeated a total of 4 times and then pressurized to 100 PSI using 100% nitrogen. The degassing and pressurization was done at ambient temperature.

The pressurized and sealed autoclave was then inserted into a heating mantle where it was heated to 265 F (129 C). The vessel remained at this temperature and resulting pressure for 7 days.

After 7 days, the autoclave was removed from the heating mantle and allowed to cool. The vessel was depressurized and the coupons were removed.

The coupons were first cleaned using a mild abrasive detergent and tap water to remove any mild scale of film present. The coupons were dried using 100% acetone and then submersed in a beaker containing 100% acetone.

The coupons were then acid cleaned using Clarke solution in a sonic bath for 30 seconds. The Clarke solution was then cleaned off the coupons using water and a mild abrasive detergent. The coupons were then dried with 100% acetone and placed in a desiccator cabinet.

The coupons weights were measured and recorded. The coupons were examined and photographed under 50X magnification. Pit frequency and pit depths were measured and recorded.

All test equipment exposed to test fluids were cleaned using mild abrasive detergent, acetone, 24 hour in 10% nitric acid solution, rinsed thoroughly with DI water, and then dried with acetone prior to using the equipment in follow-up experiments.

## Results and Discussion

### Solubility Screening

All experimental corrosion inhibitors were first screened for heavy brine solubility (Table 1). Due to the extreme salt saturations present in these fluids, many experimental corrosion inhibitors were eliminated from further testing if they did not meet a set solubility criteria. More than fifty corrosion inhibitors were screened for solubility and Table 1 illustrates an example of some selected and rejected blends.

Table 1 -Chemical Solubility in Heavy Brines

Product	Solubility in Indicated Heavy Brine at 10,000 PPM		
	CaCl <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub> CaCl <sub>2</sub>
Chemical K	S	M	M
Chemical L	S	S	M
Chemical M	S	S	S
Chemical N	S	S	M
Chemical O	M	PS	M
Chemical P	S	S	M
Chemical Q	M	S	M
Chemical R	M	PS	PS
Chemical S	M	S	S
Chemical T	M	M	S
Chemical U	PS	PS	PS
Chemical V	PS	PS	PS
Chemical W	PS	PS	PS
Chemical X	PS	PS	PS
Chemical Y	PS	PS	PS
Chemical Z	PS	PS	PS

### Corrosion Performance Screening

Those experimental corrosion inhibitors that passed solubility screening were then screened in rotating cylinder electrode (RCE) testing (Figure 4).



Figure 4: RCE setup

RCE test data showed which experimental corrosion inhibitors were likely to show promise in harsher test conditions (Figure 5).

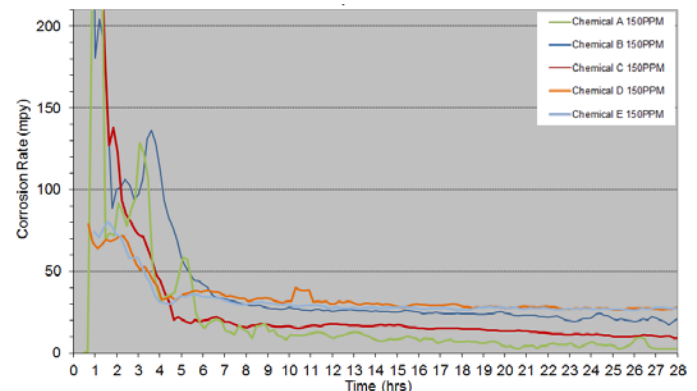


Figure 5: RCE test data

### Pressurized Corrosion Testing

Top performing experimental corrosion inhibitors from prior screenings were tested in static autoclaves (Figure 1) using P110 metal coupons attached to a PTFE cage assembly (Figure 2). The coupon surfaces were analyzed after each test for pitting potential by using a high powered microscope (Olympus BX 51) pictured in Figure 3.

Corrosion inhibitors were tested in three different heavy brines. The brines tested were CaCl<sub>2</sub> 11.6 PPG, Ca(NO<sub>3</sub>)<sub>2</sub> 12.5 PPG, and a combination brine of CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> 13.5 PPG. The results were as follows:

The corrosion inhibitor Chemical A was selected for comparison testing using static high temperature/high pressure autoclaves with 11.6 PPG brine. Coupon

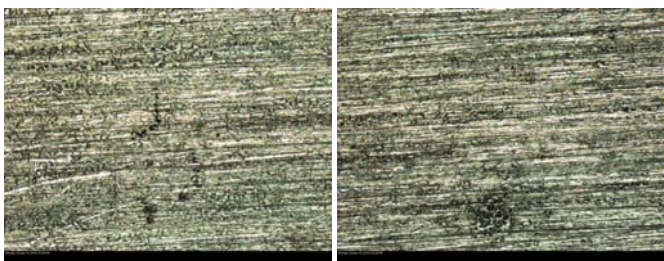
weight loss was measured and the results are given in Table 2.

Table 2: CaCl<sub>2</sub> 11.6 PPG Results

Product	Coupon Number	Weight (g)		Weight Loss (g)	Corrosion Rate (mpy)	Average CR (mpy)
		Initial	Post			
100% CaCl <sub>2</sub> 11.6 PPG Blank (P110)	21	18.9867	18.8503	0.1364	11.15	11.11
	22	18.8939	18.7585	0.1354	11.07	
100% CaCl <sub>2</sub> 11.6 PPG Chemical A 2,500PPM (P110)	33	18.5568	18.4980	0.0588	3.36	3.42
	34	18.5228	18.4621	0.0607	3.47	

The corrosion rates show that at a dose rate of 2,500 ppm, Chemical A provided excellent corrosion inhibition with a final inhibited corrosion rate of less than 4 mpy by weight loss analysis. By comparison, the untreated coupon surface experienced a general corrosion rate over 3 times as high.

The untreated coupons were then examined under the microscope at 50X magnification after cleaning and revealed abundant general corrosion and numerous pitting attacks. All of the pits observed were up to 14 microns in depth (Figure 6).

Figure 6: Microscopic photographs at 50X magnification of the two untreated P110 coupon surfaces tested in CaCl<sub>2</sub> 11.6 PPG

The coupons treated with Chemical A were then examined under the microscope at 50X magnification after cleaning and revealed very few pitting attack. Very few pits were observed and all were less than 8 microns in depth (Figure 7).

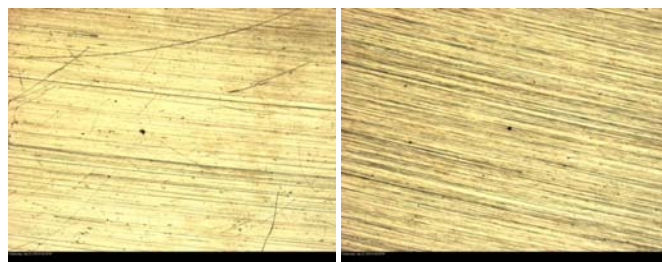
Figure 7: Microscopic photographs at 50X magnification of the two coupon surfaces treated with Chemical A at a dose rate of 2,500 ppm tested in CaCl<sub>2</sub> 11.6 PPG

The corrosion inhibitor Chemical B was selected for comparison testing using static high temperature/high pressure autoclaves with Ca(NO<sub>3</sub>)<sub>2</sub> 12.5 PPG brine. Coupon weight loss was measured and the results are given in Table 3.

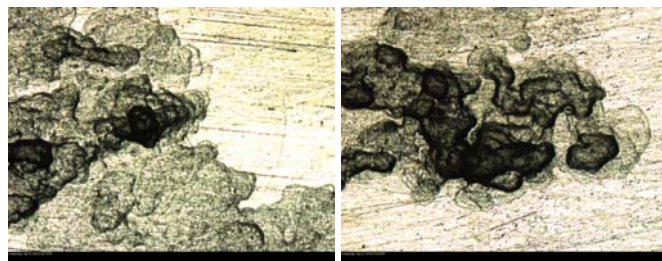
Table 3: Ca(NO<sub>3</sub>)<sub>2</sub> 12.5 PPG Results

Product	Coupon Number	Weight (g)		Weight Loss (g)	Corrosion Rate (mpy)	Average CR (mpy)
		Initial	Post			
100% Ca(NO <sub>3</sub> ) <sub>2</sub> 12.5 PPG Chemical B 5,000PPM (P110)	10	20.5010	20.5005	0.0005	0.04	0.04
	9	20.5195	20.5191	0.0004	0.03	
100% Ca(NO <sub>3</sub> ) <sub>2</sub> 12.5 PPG Blank (P110)	8	19.8726	19.8558	0.0168	1.37	1.44
	7	20.1054	20.0870	0.0183	1.50	

The corrosion rates show that at a dose rate of 5,000 ppm, Chemical B provided excellent corrosion inhibition with a final inhibited corrosion rate of less than 0.05 mpy by weight loss analysis. The coupons treated with Chemical B were then examined under the microscope at 50X magnification after cleaning and revealed very few pitting attack. Very few pits were observed were all less than 9 microns in depth (Figure 8). By comparison, untreated coupons were observed to have inclusions or flaws that were up to 10 microns in depth.

Figure 8: Microscopic photographs at 50X magnification of the two coupon surfaces treated with Chemical B at a dose rate of 5,000 ppm in Ca(NO<sub>3</sub>)<sub>2</sub> 12.5 PPG brine

The untreated coupons were then examined under the microscope at 50X magnification after cleaning and revealed heavy pitting attack. The deepest pits were observed at 67 microns in depth (Figure 9).

Figure 9: Microscopic photographs at 50X magnification of the two untreated coupon surfaces in Ca(NO<sub>3</sub>)<sub>2</sub> 12.5 PPG brine.

The corrosion inhibitors Chemical C and Chemical D were selected for comparison testing using static high temperature/high pressure autoclaves with combination  $\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$  13.5 PPG brine. Coupon weight loss was measured and the results are given in Table 4.

Table 4: Combination  $\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$  13.5 PPG Results

Product	Coupon Number	Weight (g)		Weight Loss (g)	Corrosion Rate (mpy)	Average CR (mpy)
		Initial	Post			
$\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$ 13.5PPG Blank (P110)	5	18.8611	18.5590	0.3021	24.69	25.24
	6	18.7710	18.4556	0.3154	25.78	
$\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$ 13.5PPG Chemical C 7,000PPM (P110)	23	18.8940	18.8790	0.0151	1.23	1.31
	24	18.8169	18.8000	0.0169	1.38	
$\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$ 13.5PPG Chemical C 10,000PPM (P110)	17	18.6079	18.6015	0.0064	0.52	0.58
	18	18.6557	18.6478	0.0079	0.65	
$\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$ 13.5PPG Chemical D 10,000PPM (P110)	19	18.9040	18.8962	0.0078	0.64	0.71
	20	18.7976	18.7880	0.0096	0.78	

The untreated coupons show a corrosion rate of over 25 mpy by weight loss analysis. Chemical C showed a corrosion rate of less than 2 mpy at a dose rate of 7,000PPM. Both corrosion inhibitors Chemical C and Chemical D showed less than 1 mpy corrosion rates by weight loss analysis when treated at a dose rate of 10,000PPM.

The test coupons for the blank were examined under the microscope at 50X magnification after cleaning and revealed both heavy general and localized corrosion. Countless pits were observed that were up to 230 microns in depth (Figure 10).

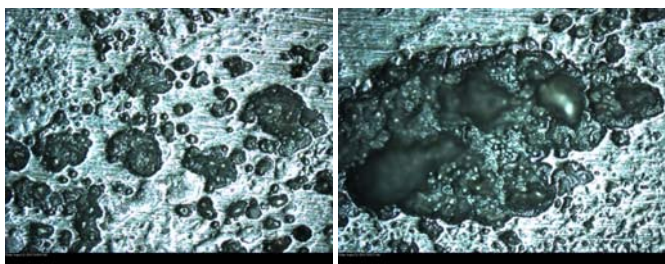


Figure 10: Microscopic photographs at 50X magnification of the two uninhibited coupon surfaces in combination  $\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$  13.5 PPG brine.

The coupons treated with 7,000PPM Chemical C were then examined under the microscope at 50X magnification after cleaning and revealed two pitting attacks. The pits that were observed were up to 37 microns in depth (Figure 11).

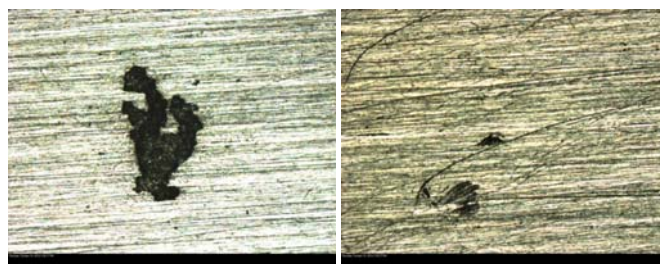


Figure 11: Microscopic photographs at 50X magnification of the two coupon surfaces treated with 7,000 PPM of Chemical C in combination  $\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$  13.5 PPG brine.

The coupons treated with 10,000PPM Chemical C were then examined under the microscope at 50X magnification after cleaning and revealed practically no pitting attacks. The few pits that were observed were all less than 5 microns in depth (Figure 12).

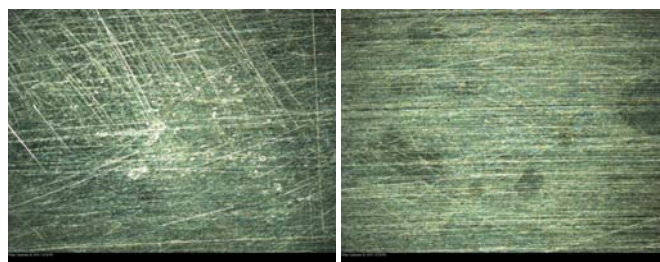


Figure 12: Microscopic photographs at 50X magnification of the two coupon surfaces treated with 10,000 PPM of Chemical C in combination  $\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$  13.5 PPG brine.

The coupons treated with Chemical D were then examined under the microscope at 50X magnification after cleaning and revealed one area of localized pitting attack. This isolated area was present on one coupon and considered to be an area affected by extraneous factors. This particular area had pitting observed to be 21 microns at the deepest. The rest of the coupon surfaces showed very few pits that were observed to be less than 7 microns in depth (Figure 13).

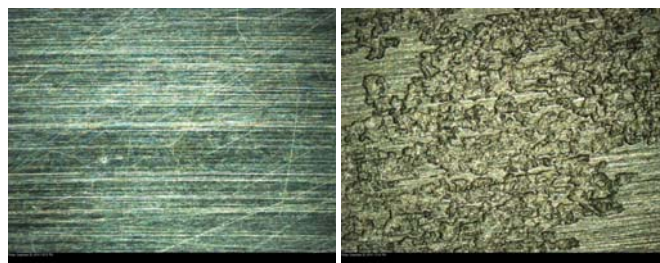


Figure 13: Microscopic photographs at 50X magnification of the two coupon surfaces treated with 10,000 PPM of Chemical D in combination  $\text{Ca}(\text{NO}_3)_2/\text{CaCl}_2$  13.5 PPG brine.

## Conclusions

- More than fifty new formulations were blended and tested for the solubility in desired brine or brine mixtures. The selected chemicals were then screened by RCE testing method. Chemicals that have achieved inhibited corrosion rates of less than 5mpy when dosed at 10 PPM were selected for further testing by HP/HT static autoclave testing.
- In static high temperature, high pressure autoclave tests, Chemical A provided the best performance and achieved inhibited corrosion rates of less than 3.4mpy in 10.8 PPG  $\text{CaCl}_2$  brine at 265°F (129°C) with minimal localized corrosion when dosed at 5000 ppm.
- In high temperature, high pressure static autoclave tests, Chemical B provided the best performance and achieved inhibited corrosion rates of less than 0.05mpy in 12.5 PPG  $\text{Ca}(\text{NO}_3)_2$  brine with minimal localized corrosion when dosed at 5000 PPM.
- Chemical A and Chemical B were both soluble in 10.8 and 12.5 PPG calcium nitrate and calcium chloride brines, respectively.
- Chemical C and Chemical D both showed significant protection in super saturated calcium nitrate / calcium chloride (13.5 PPG) brines when treated at a 10,000 PPM dose rate.
- Chemical C showed an inhibited corrosion rate of less than 0.6 mpy and pitting less than 5 microns in depth when treated at a dose rate of 10,000 PPM.

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## Nomenclature

RCE = Rotating Cylinder Electrode  
 PPG = pounds per gallon  
 PPM = parts per million

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