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# Evaluation Of Orthophosphate Based Corrosion Inhibitors In Treated Water For El Paso Region

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EVALUATION OF ORTHOPHOSPHATE BASED CORROSION INHIBITORS  
IN TREATED WATER FOR EL PASO REGION

FRANCISCO SOLIS JR

Master's Program in Environmental Engineering

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Charles Ambler, Ph.D.  
Dean of the Graduate School

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Francisco Solis Jr

2018

## **Dedication**

This paper is dedicated to my parents and all their effort they put into my education, and for encouraging me to continue my education and complete a master's degree

EVALUATION OF ORTHOPHOSPHATE BASED CORROSION INHIBITORS  
IN TREATED WATER FOR EL PASO REGION

by

FRANCISCO SOLIS JR, BSCE

THESIS

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for the Degree of

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## **Abstract**

Corrosion is an electrochemical phenomenon that involves the deterioration of a metal by the reaction of itself with its surrounding environment. One of the greatest issues for water utilities around the country is to keep the water quality safe. Corrosion can affect the quality of the water that we use on a daily basis by adding a bad taste, increasing the concentration of heavy metals, and allowing outside contaminants to enter the distribution system. The use of phosphate based corrosion inhibitors was tested in two different metals: iron and copper. The phosphate in the inhibitors react with the calcium in the water, creating a coating over the metal, theoretically preventing it from corroding.

Several tests were conducted using both metals in order to determine the effectiveness of such inhibitors. It was found that the phosphate content of the inhibitors is directly related to its effectiveness; the higher the phosphate content, the better the results for both iron and copper. Also, the inhibitors work better at higher pH, since at low pH the water is more corrosive.

The corrosion indices showed that the water used was very corrosive and aggressive towards metal, but such indices don't take into account the use of corrosion inhibitors. Therefore, further study to develop an index that considers the effect of inhibitors is recommended.

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## **Chapter 1: Introduction**

Corrosion in metallic pipelines is a result of electrochemical reactions between materials and substances in the environment. In this case, the metal pipe is the material and water is the substance. This corrosion process chemically oxidizes pipe metals.

One of the greatest responsibilities of all water utilities around the world is to provide good quality and safe water to the users. For this reason, corrosion of pipeline systems is an issue that needs to be addressed because of the consequences it can have. The two most important are health problems to the people exposed to that water, and economic losses by having to replace the pipes.

The damage to public health is the one with the most significant repercussions; corrosion can affect the quality of the water we drink by increasing the concentration of heavy metals in it. Likewise, the economic impact of corrosion is to be considered too, since an accumulation of corrosion can produce leaks in the pipeline which at the same time creates failures in the system, such as flow losses. According to The American Water Works Association (AWWA), the cost to water utilities in the U.S. in order to upgrade the water distribution systems is expected to be \$325 billion over the next 20 years (Edwards, 2004).

One solution to this problem is adding corrosion inhibitors to the water that goes into the pipeline system. Corrosion inhibitors help to create precipitates that form thin layers over the pipelines and in this way, act as a protective layer blocking the interaction of the water with the metallic pipeline itself. In this study, the inhibitors tested were all ortho-phosphate based inhibitors and, therefore, a protective layer formed by calcium phosphate was expected to occur.

The goal of this study was to evaluate the effect of concentration of inhibitor on its effectiveness in two different metals using well water from the El Paso region.

## Chapter 2: Literature Review

### 2.1 CORROSION AND ITS PROBLEMS

Water and wastewater distribution systems are part of the foundation of human civilization. The first people to realize the importance of water distribution were the Romans and Babylonians, who developed one of the greatest engineering and scientific contributions in history: why go to the water if we can make the water come to us (Edwards, 2004).

Pure metals and alloys react electrochemically in a corrosive environment to form a stable compound, a process wherein it is very common to see metal loss. The stable compound formed is called corrosion. Iron oxidation in water happens as the following reaction:  $Fe_{(s)} + H_2O_{(l)} \rightarrow 2FeO_{(s)} + H_{2(g)}$  while copper oxidation follows the next reaction:  $Cu_{(s)} + H_2O_{(l)} \rightarrow CuO_{(s)} + H_{2(g)}$  “Corrosion inhibitors reduce the corrosion rate by increasing or decreasing the anodic and/or cathodic reaction, decreasing the diffusion rate for reactants to the surface of the metal, and decreasing the electrical resistance of the metal surface” (Bothi Raja, 2008).

It is known that when using phosphate inhibitors, calcium phosphate will precipitate with free calcium in water as follows:  $3Ca_{(s)} + 2(PO_4)_{(l)} \rightarrow Ca_3(PO_4)_{2(s)}$  and if it is used in iron pipelines, iron phosphate will precipitate in the following way:  $Fe_{(s)} + (PO_4)_{(l)} \rightarrow Fe(PO_4)_{(s)}$ . In copper pipelines, copper phosphate will form:  $3Cu_{(s)} + 2(PO_4)_{(l)} \rightarrow Cu_3(PO_4)_{2(s)}$

According to the Federal Highway Administration, the direct cost of corrosion in the U.S. was estimated to be \$276 billion per year, and out of the \$276 billion, \$36 billion is the direct cost for drinking water and wastewater distribution systems (Edwards, 2004).

Water distribution systems’ pipelines are usually underground where the soil may be contaminated with several pathogens and/or viruses. Therefore, a small crack in the pipelines due to corrosion can represent not only a loss in water, but also contamination of the water to be delivered to the customers.

## 2.2 CORROSION INDICES

In order to calculate the corrosiveness of water, people developed corrosion indices. Some of the most common ones are the following: Langlier Saturation Index, Ryznar Stability Index, Aggressiveness Index, and Larson-Skold Index. The Langlier Saturation Index (LSI) was developed by Dr. Langlier in 1936 as assessment of the likelihood of water to precipitate calcium carbonate. Next, John Ryznar established the Ryznar Stability Index in 1944. This index is a modification of the LSI that takes into account the hardness of the water. Third, the Aggressiveness Index was created for asbestos-cement pipes. This index is dependent on three parameters: pH, calcium concentration, and alkalinity. Finally, the Larson-Skold index defines the corrosivity of water towards mild steel, and since many pipelines are made of steel, this index is useful in this study. A major limitation of all those indices is that none of them consider the use of corrosion inhibitors.

One important step in this study was to calculate the corrosiveness of the water to be tested. The corrosiveness was determined using the previously mentioned indices: Langlier Saturation Index (LSI), Ryznar Stability Index (RSI), Aggressive Index (AI), and Larson-Skold Index. LSI, RSI, and AI are indices that estimate the corrosiveness of water by estimating the saturation levels of calcium carbonate, while the Larson-Skold index is not pH dependent and measures the interference of chloride and sulfate ions on the solubility of calcium carbonate.

### **Langlier Saturation Index**

The LSI index describes the potential of water to precipitate calcium carbonate. LSI is dependent on five variables: pH, Temperature, Calcium Hardness, Alkalinity, and TDS. Using Equation 1 and Table 3.2, the LSI was calculated.

$$LSI = pH + (Temperature\ Factor) + (Calcium\ Hardness\ Factor) + (Alkalinity\ Factor) - (TDS\ Factor) \quad \text{Eq. 1}$$

**Table 2.1: LSI Factors (“Understanding LSI”, 2017)**

Temperature (°F)	Temperature factor	Calcium Hardness (PPM)	Calcium Hardness Factor	Alkalinity (PPM)	Alkalinity Factor	Total Dissolved Solids	TDS Factor
32	0	5	0.3	5	0.7	< 1000 ppm	12.1
37	0.1	25	1.0	25	1.4	1000 ppm	12.19
46	0.2	50	1.3	50	1.7	2000 ppm	12.29
53	0.3	75	1.5	75	1.9	3000 ppm	12.35
60	0.4	100	1.6	100	2	4000 ppm	12.41
66	0.5	150	1.8	150	2.2		
76	0.6	200	1.9	200	2.3		
84	0.7	300	2.1	300	2.5		
94	0.8	400	2.2	400	2.6		
105	0.9	800	2.5	800	2.9		

If the LSI is positive, it means the water is corrosive. On the other hand, if the LSI is negative, the water is scale-forming.

### **Ryznar Stability Index**

The Ryznar Index can be calculated using equation 2 as follows:

$$RSI = 2pH_s - pH \quad \text{Eq. 2}$$

Where pH is the measured pH and pH<sub>s</sub> is the pH at saturation in calcite or calcium carbonate.

If the RSI is less than 6.2, the water is scale-forming. If it is between 6.2 and 6.8, the water is in equilibrium, and for any value of RSI above 6.8, the water is corrosive.



## Aggressive Index

Aggressive index (AI) can be calculated following equation 3 and using Table 3.3 shown below.

$$AI = pH_{actual} + C + D \quad \text{Eq. 3}$$

Where the factor C is the log base 10 of the calcium hardness expressed as mg/L of Calcium Carbonate ( $\text{CaCO}_3$ ), and factor D is the log base 10 of the total alkalinity expressed in mg/L as  $\text{CaCO}_3$ .

If the aggressiveness index is greater or equal to 12, the water is to be considered as scale forming. If AI is less than 12 but greater than 10, the water is in apparent equilibrium, and if AI is less than 10, the water is corrosive.

**Table 2.2: C and D Factors for aggressiveness Index**

Calcium hardness or Total Alkalinity in mg/L as $\text{CaCO}_3$	C or D
10	1.00
20	1.30
30	1.48
40	1.60
50	1.70
60	1.78
70	1.85
80	1.90
90	1.95
100	2.00
200	2.30
300	2.48
400	2.60
500	2.70
600	2.78
700	2.85
800	2.90
900	2.95
1000	3.00

## Larson-Skold Index

The Larson-Skold index was calculated using equation 4, where all concentrations used are in meq/L. Also, if the Larson-Skold index is less than 0.8, the chloride and sulfate don't interfere with calcium carbonate solubility. If the Larson-Skold index is greater than 1.2, chloride and sulfate will increase the solubility, meaning higher corrosion will occur. For any value between 0.8 and 1.2 the water is at equilibrium.

$$Larson - Skold = \frac{[Cl^-] + [SO_4^{2-}]}{[HCO_3^-] + [CO_3^{2-}]} \quad \text{Eq. 4}$$

## Chapter 3: Methodology

### 3.1 WATER SAMPLES

For this study, two different sources of water were used, regular deionized water (DI) and well water from the El Paso region (Well water). Select water parameters of the well water used for conducting these tests is shown in Table 3.1 below.

**Table 3.1: Well water chemistry** (<http://www.epwu.org/water/pdf/chemanalysis.pdf>)

Parameter	Value*
TDS	454
Phenol Alkalinity as CaCO <sub>3</sub>	<1
Total Alkalinity as CaCO <sub>3</sub>	24.5
Total Hardness as CaCO <sub>3</sub>	63
Chlorides as Cl	182
Sulfates as SO <sub>4</sub>	14
Fluorides as F	NA
Silica as SiO <sub>2</sub>	NA
Nitrates as NO <sub>3</sub>	NA
Nitrites as NO <sub>2</sub>	NA
Phosphates as PO <sub>4</sub>	0.51
Calcium as Ca	14
Magnesium as Mg	3.9
Sodium as Na	109
Potassium as K	4.5
Iron as Fe	<.03
Manganese as Mn	NA
pH	7.5

\*In mg/L, except pH

### **3.2 TESTING PROTOCOL**

Two different metals: iron and copper were tested using both water sources. Likewise, both metals were tested with four different inhibitors (Inhibitor A, B, C, and D) at different concentrations while keeping the same conditions for both specimens.

#### **Testing Phosphate in Corrosion Inhibitors**

The first step in testing the inhibitors was to calculate the concentration of phosphate content. To do so, the following procedure was followed for each single phosphate-based inhibitor.

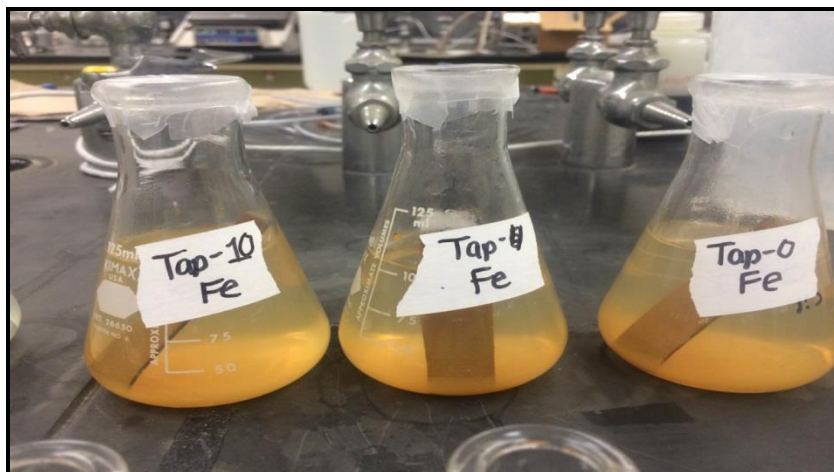
Four beakers were each filled with 500 milliliters (mL) of DI water, and then each sample was spiked with a different concentration of inhibitor (e.g., 0-100 mg/L). Next, samples were mixed for ten minutes to finally measure the phosphate concentration in the water by using HACH method 8048 (HACH Phosphorus, 2017).

#### **Testing of Iron**

Three different tests were conducted using 1" by 2" by 1/8" thick iron specimens. The first test was to determine the effects of concentration in reducing corrosion and to compare the effectiveness of the four inhibitors. The second test was conducted to study the behavior of one specific inhibitor (A) under different conditions such as different concentrations. Finally, the third experiment was performed to substantiate the results obtained in the second test.

##### ***Test number 1 using iron***

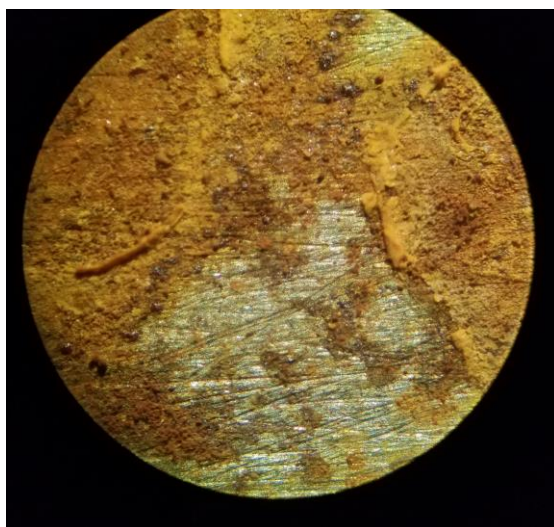
First, six specimens were each submerged in 200 mL of well water treated with six inhibitor concentrations (0, 5, 10, 25, 50, and 100 ppm) inside six Erlenmeyer flasks. Then the pH of the water was adjusted to 7 using 0.5 N sulfuric acid and 1 N sodium hydroxide. The specimens were left submerged for 24 hours. After 24 hours, a new water sample with the same concentration was used, always keeping the same iron specimen. After the first, second, third, fourth, and tenth day, the iron concentration in the water was measured following HACH method 8008 (HACH Iron, 2014) and a HACH spectrophotometer DR 5000. Illustration 3.1 below shows 3 of the specimens at the end of the first tests after ten days of testing.



**Illustration 3.1: Iron samples after ten days of testing**

***Test number 2 using iron***

According to the results in section 4.2, inhibitors A and D showed the best performance in preventing iron from leaching. For this reason, a further study on the behavior of inhibitor A was conducted. For this experiment, test number 1 was reproduced using only inhibitor A at 4 different concentrations (0, 10, 25, and 50 ppm), and using a beaker instead of an Erlenmeyer flask. Pictures of the corrosion forming over the specimens were taken using a microscope. Illustration 3.2 shows a picture of the corrosion on the specimen treated with 10 ppm of inhibitor A after one week of testing



**Illustration 3.2: Corrosion in sample treated with 10 ppm of inhibitor after one week**

### ***Test number 3 using iron***

Five specimens were submerged in 250 mL of well water in separate Erlenmeyer flasks. Each flask was spiked with a different concentration of inhibitor (0, 1, 2, 3, 4, and 5 ppm) then the pH of the water was once again fixed at 7 using 0.5 N hydrochloric acid and 1 N sulfuric acid. After that, specimens were left underwater for 24 hours. The phosphate concentration in the water was measured at time 0 (initial concentration) and time 24 (final concentration after 24 hours) using HACH method 8048 (HACH Phosphorus, 2017).

For a better understanding of the chemistry and the reactions happening in the water, the software Visual MINTEQ (Visual MINTEQ, 2013) was used. In order to corroborate the findings from Visual MINTEQ, test number 3 was performed. Five iron specimens were placed in five separate beakers, one specimen per beaker, with 250 mL of a saturated solution of calcium chloride and sodium phosphate. The specimens were submerged for 24 hours for 7 days, with a new solution prepared every day. The specimens were inspected daily to track any formation of calcium phosphate. Illustration 3.3 below shows the growth of the calcium phosphate on three specimens after being treated for 7 days.



**Illustration 3.3: Iron specimens after the formation of calcium phosphate (Day 7)**

After the calcium phosphate layer was formed, the specimens were submerged in five different beakers containing 250 mL of treated well water with five different corrosion inhibitor

concentrations (0, 1, 2, 3, and 4 ppm) and were left mixing overnight on an orbital shaker. The water solution was replaced approximately every 24 hours, and the iron and phosphate concentration in the water was measured immediately before the water was replaced following the HACH methods 8008, and 8048, respectively, and a HACH spectrophotometer DR 5000.

### **Copper testing**

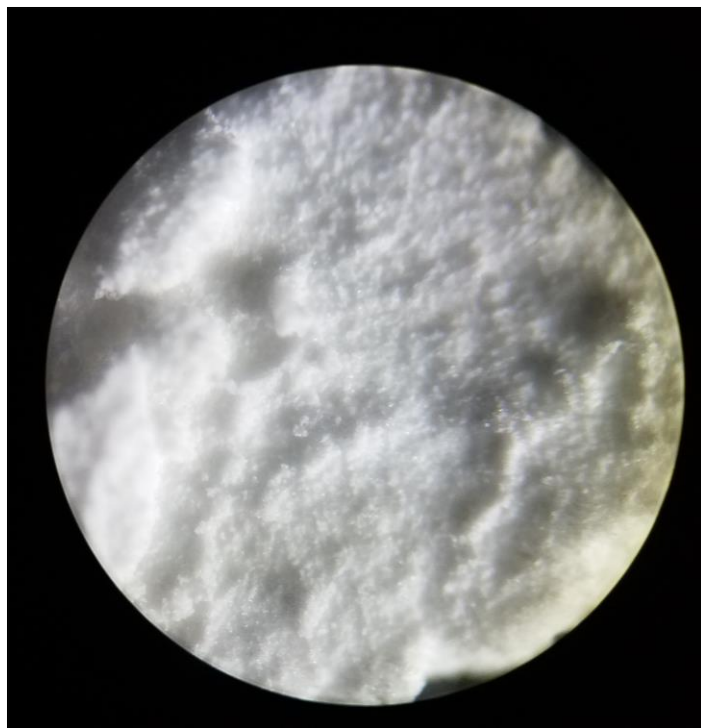
Copper testing was also carried out using 1" by 2" by 1/8" specimens. Two tests were performed in order to determine the effectiveness of the inhibitor A on copper and a third one using inhibitor D. The first test was performed to determine a relationship between pH in the water and effectiveness of the inhibitor. The second test was done to compare the difference in effectiveness of inhibitor A on copper and iron specimens. Lastly, the third test was conducted to corroborate that the more inhibitor added, the less copper is leached into the water.

#### ***Test number 1 using copper***

For the first test, two solutions were used: pure DI water and DI water spiked with 50 ppm of inhibitor A. The specimens were submerged in five different 250 mL solutions and then, using sodium hydroxide and sulfuric acid, the pH of the solutions was adjusted to 2.3, 4.0, 6.0, 8.0, and 10.0. Next, after adjusting the pH of the solutions, the specimens were left underwater for approximately 24 hours, after which time the copper concentration in the water was measured following HACH method 8506 and using a HACH spectrophotometer DR 5000.

#### ***Test number 2 using copper***

For copper test number 2, "Test number 3 using iron" was duplicated to form a layer of calcium phosphate on the copper specimens. The total copper concentration was measured at the end of each day. This test was conducted for 20 days, 4 days per week. On the non-testing days, the specimens were left in a vacuum to prevent corrosion from exposure to air. Copper specimens were inspected using a microscope to track the growth of calcium phosphate. Such growth can be observed in illustration 3.4 Also, illustration 3.5 shows the setup and some of the equipment used for this test.



**Illustration 3.4: Calcium phosphate formation in the copper specimens**



**Illustration 3.5: Test number 2 in copper setup**



### ***Test number 3 using copper***

For this test, two untreated copper specimens were submerged in a solution of DI water with calcium chloride and sodium carbonate. The solution was made to have an alkalinity of 250 mg/L as  $\text{CaCO}_3$ . The solution was then spiked with 250 ppm of inhibitor D, and the copper and phosphate concentration in the solution was measured daily for about 40 days. After 40 days, one of the specimens was removed from the solution and was then placed in 250 mL of tap water while at the same time another untreated specimen was submerged, also in tap water, in order to compare the difference between an untreated sample and a previously exposed sample.

## Chapter 4: Results

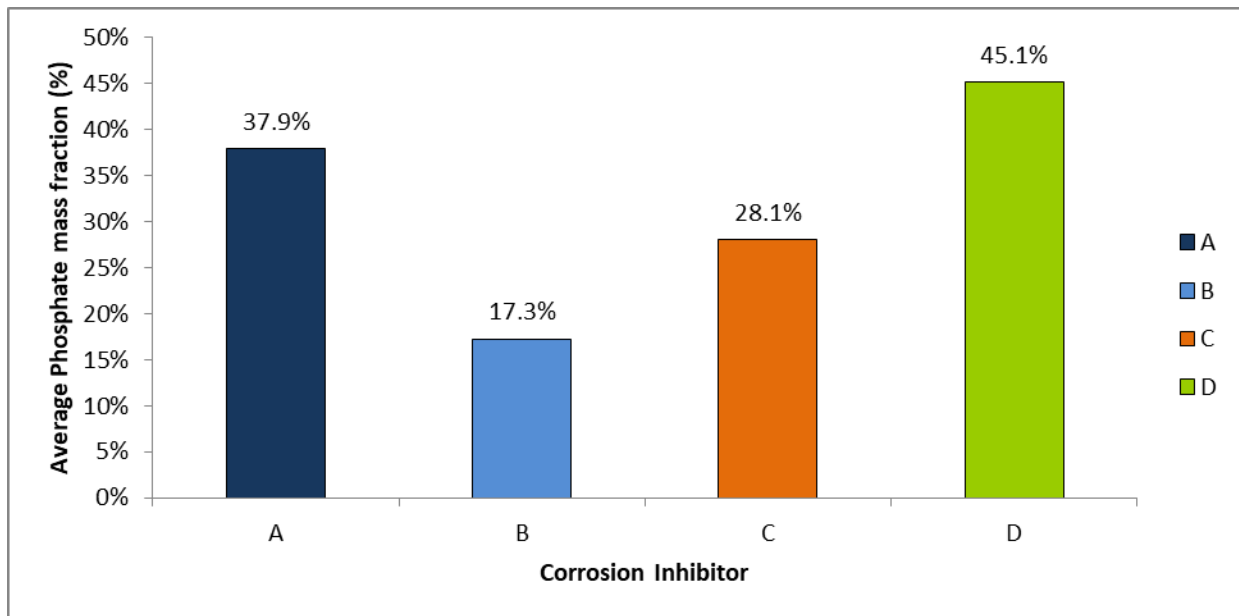
### 4.1 RESULTS FOR PHOSPHATE TESTING

All four corrosion inhibitors were tested for orthophosphate at four inhibitor concentrations: 2.5, 5, 10, and 50 ppm. Inhibitors A and D had the highest concentrations, with averages values of 37.9% and 45.1% of phosphate, respectively. Table 4.1 shows the results of the orthophosphate tests for the four inhibitors:

**Table 4.1: Mass fraction of o-phosphate concentration in the inhibitors**

	O-Phosphate Concentration (%)			
Conc ppm	W-415	TI-2901	TI-2904	TI-3054
2.5	45%	20%	33%	50%
5	38%	20%	28%	45%
10	36%	14%	31%	45%
50	33%	15%	21%	41%
Average	38%	17%	28%	45%

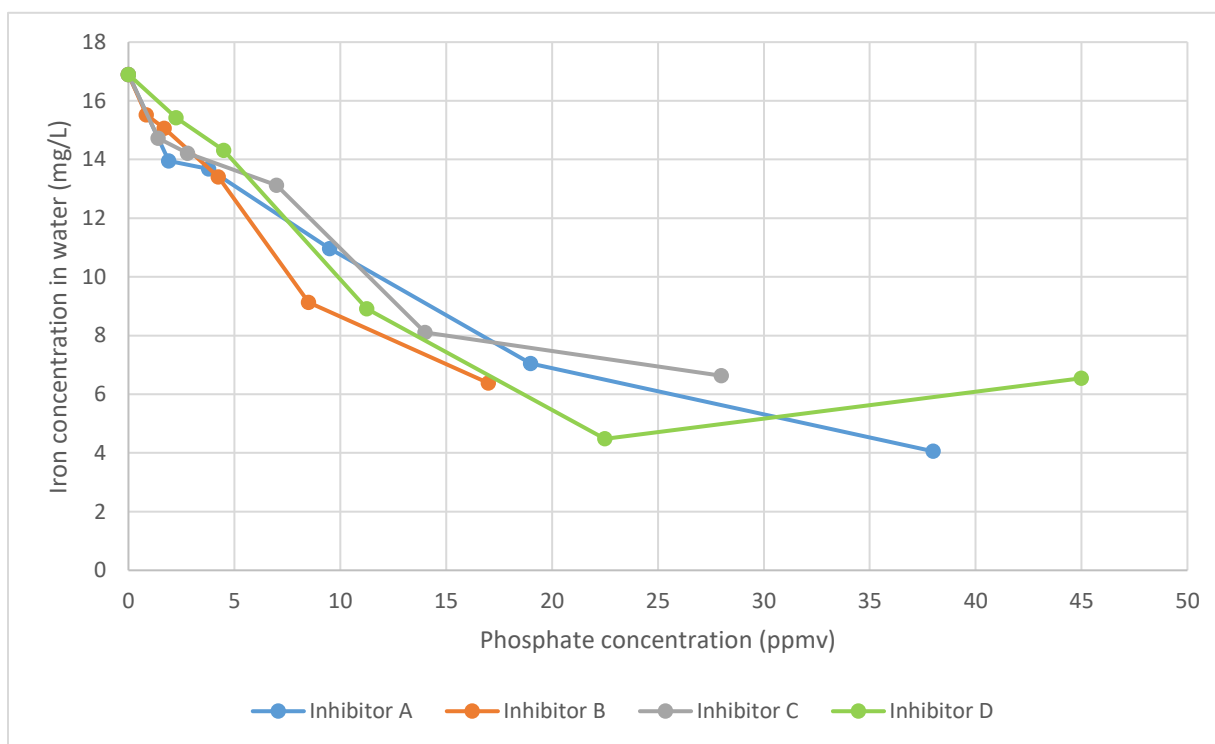
The values from Table 4.1 were plotted in Figure 4.1 to appreciate the difference in the mass fraction phosphate content between the four inhibitors.



**Figure 4.1: Mass fraction content of phosphate in the inhibitors**

## 4.2 RESULTS FOR TEST 1 USING IRON

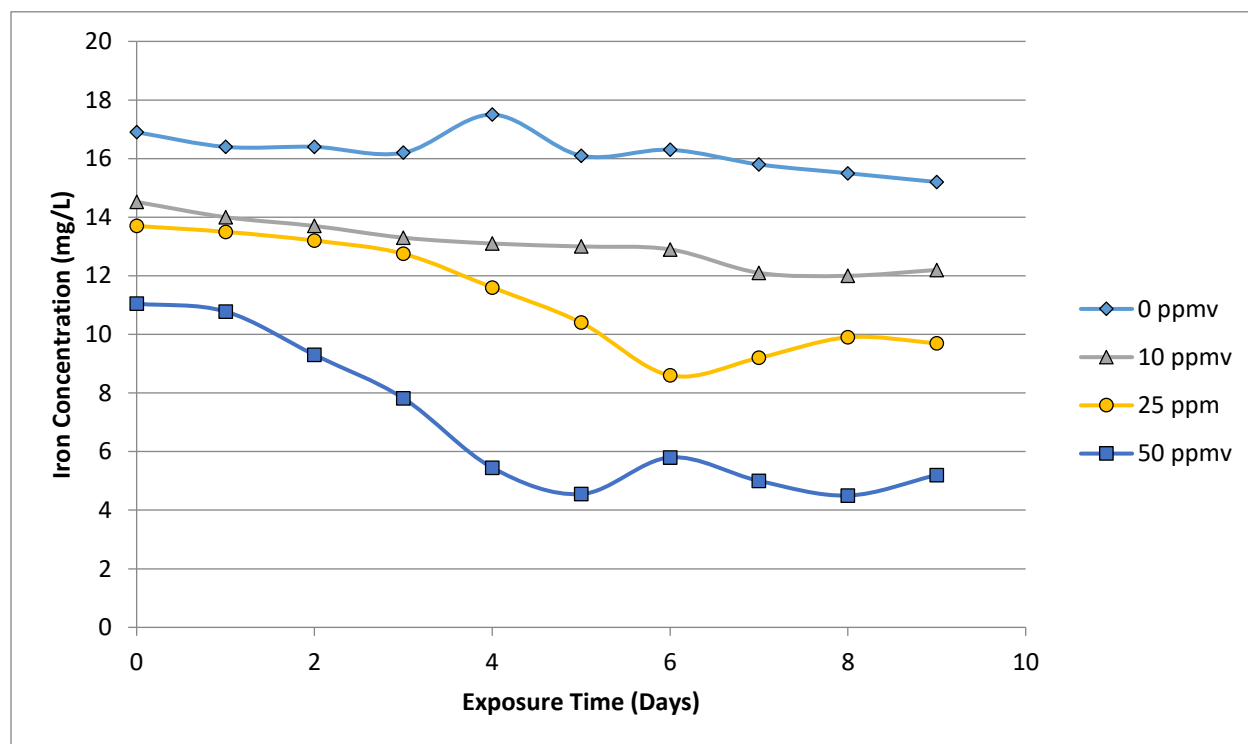
After testing the inhibitors for 10 days using the uncoated iron specimens, it was confirmed that the two inhibitors with higher phosphate concentration (i.e. A and D) acted similarly, decreasing the amount of iron in the water slightly more than the other two inhibitors (B and C) at concentrations higher than 20 ppmv. In Figure 4.2, it is observed that as the inhibitor concentration increases and, therefore, the phosphate concentration, the concentration of iron decreases. This means that the phosphate concentration of the inhibitors is related to the amount of iron leaching. Therefore, the phosphate in the inhibitors is preventing corrosion. Results for days 1, 2, 3, and 4 are similar to those shown in Figure 4.2 (see Appendix A)



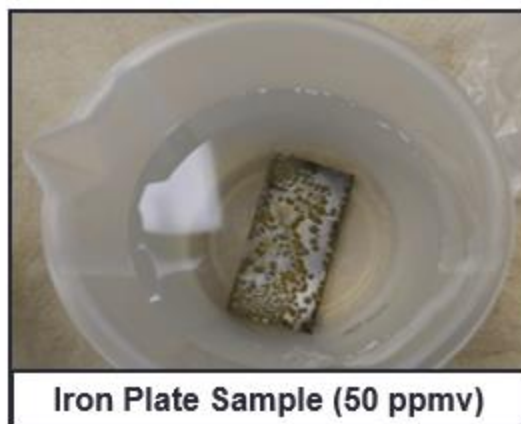
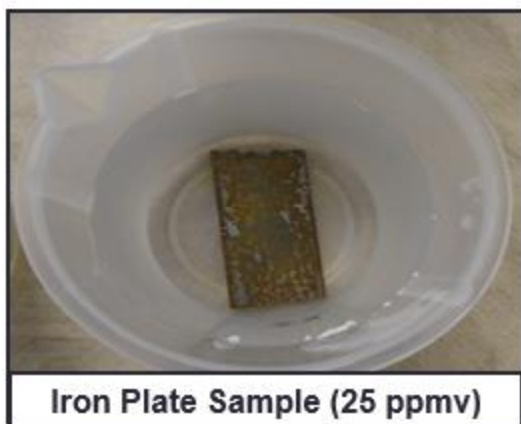
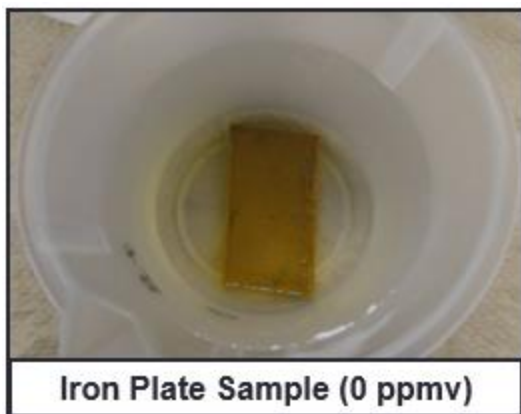
**Figure 4.2: Iron concentration in the water at pH 7 after 10 days of testing uncoated specimens at 5 different concentrations of phosphate.**

### 4.3 RESULTS FOR TEST 2 USING IRON

Out of the best two inhibitors (A and D), inhibitor A was arbitrarily selected to do further studies on the relationship between the phosphate concentration and the iron concentration. As shown in Figure 4.3, the iron concentration in the water decreases with time, meaning that the longer the specimens are exposed to the inhibitor, the better the results in preventing corrosion. In addition, it is again observed that the higher concentration of phosphate, the lower the concentration of iron leached into the water. According to these results, it seems that the phosphate concentration is precipitating or forming a scale that reduces corrosion in the iron specimens. Finally, Illustration 4.1 shows the corrosion formed on the specimens, and it is observed that the one with the higher inhibitor content is less corroded.



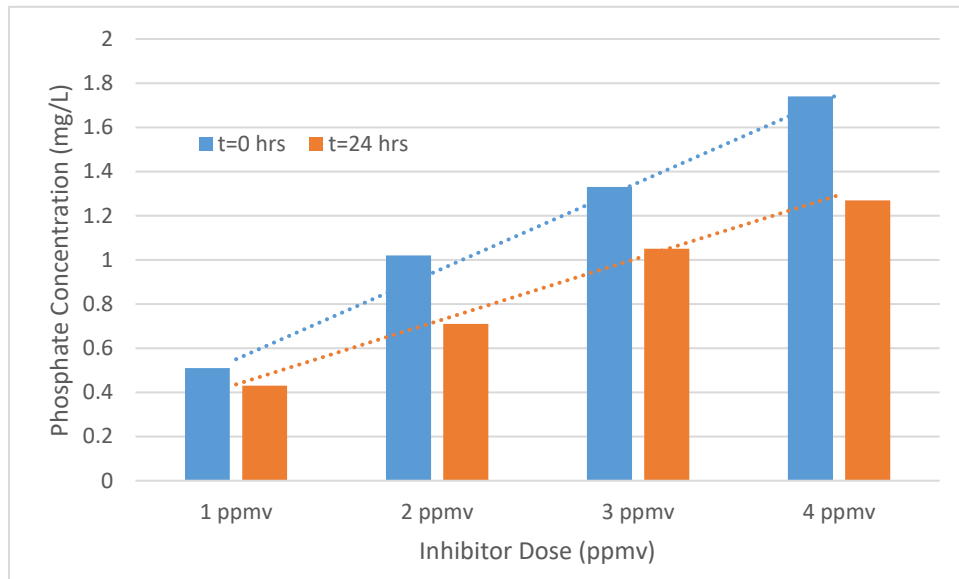
**Figure 4.3: Iron concentration over time for uncoated specimens with well water and inhibitor A**



**Illustration 4.1: Corrosion of iron specimens after 10 days of testing using inhibitor A**

#### 4.4 RESULTS FOR TEST 3 USING IRON

It was observed that the phosphate concentration in the water was lower after 24 hours in contact with the uncoated iron specimens. In Figure 4.4, the initial and final phosphate concentration in the water samples is plotted for each of the four different concentrations. By conservation of mass, the difference between initial and final concentration was assumed to have precipitated.



**Figure 4.4: Initial and final phosphate concentration in the water samples**

A chemical equilibrium analysis was performed using the software Visual MINTEQ. According to the results from the software, the missing phosphate was precipitated as calcium phosphate. A screenshot of the results is shown in illustration 4.2 below.

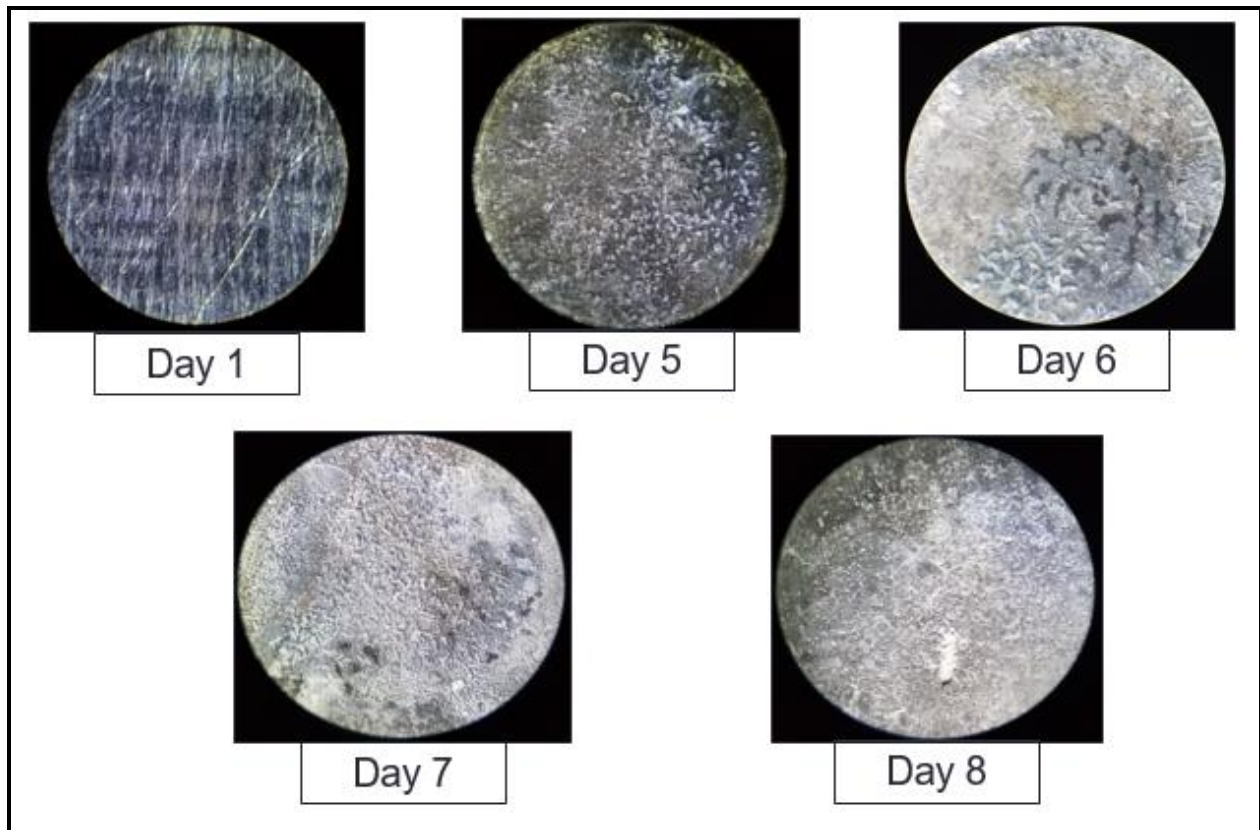
<i>Mineral</i>	<i>log IAP</i>	<i>Sat. Index</i> (=log IAP - log Ks)	<i>Stoichiometry and mineral components</i>					
Anhydrite	-6.009	-1.649	1	Ca+2	1	SO4-2		
Aragonite	-8.017	0.319	1	Ca+2	1	CO3-2		
Artinite	4.064	-5.536	-2	H+1	2	Mg+2	1	CO3-2
Brucite	12.526	-4.574	1	Mg+2	2	H2O	-2	H+1
Ca3(PO4)2 (am1)	-28.023	-2.523	3	Ca+2	2	PO4-3		
Ca3(PO4)2 (am2)	-28.023	0.227	3	Ca+2	2	PO4-3		
Ca3(PO4)2 (beta)	-28.023	0.897	3	Ca+2	2	PO4-3		
Ca4H(PO4)3·3H2O(s)	-48.519	-0.569	4	Ca+2	1	H+1	3	PO4-3
CaCO3·xH2O(s)	-8.017	-0.873	1	Ca+2	1	CO3-2	1	H2O
CaHPO4(s)	-20.497	-1.222	1	Ca+2	1	H+1	1	PO4-3
CaHPO4·2H2O(s)	-20.497	-1.502	1	Ca+2	1	H+1	1	PO4-3
Calcite	-8.017	0.463	1	Ca+2	1	CO3-2		
Dolomite (disordered)	-16.480	0.060	1	Ca+2	1	Mg+2	2	CO3-2
Dolomite (ordered)	-16.480	0.610	1	Ca+2	1	Mg+2	2	CO3-2
Epsomite	-6.454	-4.327	1	Mg+2	1	SO4-2	7	H2O
FCO3-Apatite	-92.508	21.892	9.316	Ca+2	.36	Na+1	.144	Mg+2
Fe(OH)2·7Cl.3(s)	5.715	8.755	-2.7	H+1	1	Fe+3	2.7	H2O
Fe2(SO4)3(s)	-39.166	-35.432	2	Fe+3	3	SO4-2		
Ferrihydrite	8.887	5.687	1	Fe+3	3	H2O	-3	H+1

Red text - oversaturation    Blue text - undersaturation    [Back to main output menu](#)

Green - apparent equilibrium

**Illustration 4.2: Visual MINTEQ results**

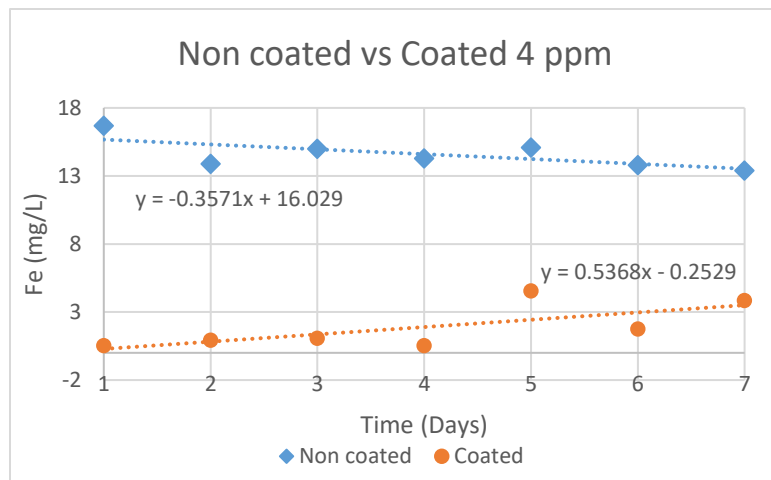
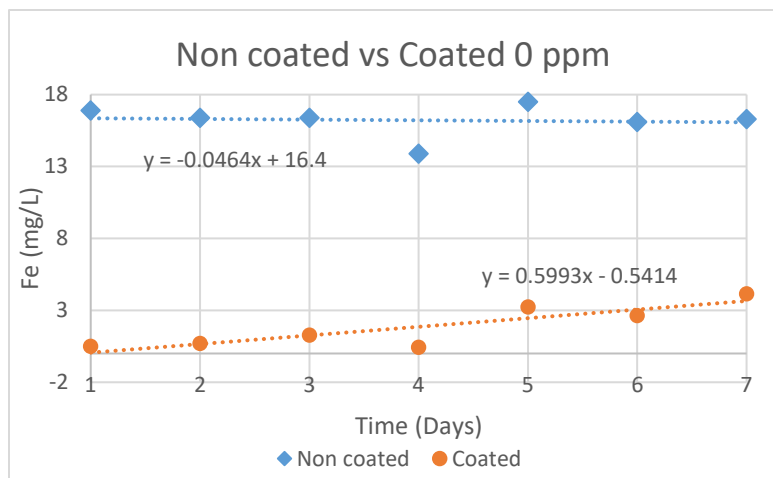
Since calcium phosphate was precipitating in the well water and inhibitor solution, new specimens were submerged in a saturated solution of calcium chloride and sodium phosphate to help the calcium phosphate precipitation happen faster. A protective layer of calcium phosphate grew over the iron specimens, reducing the surface area of iron exposed to the water. Illustration 4.3 shows the growth of this layer over time as seen from a microscope.



**Illustration 4.3: Calcium phosphate growth on the iron specimens over time**



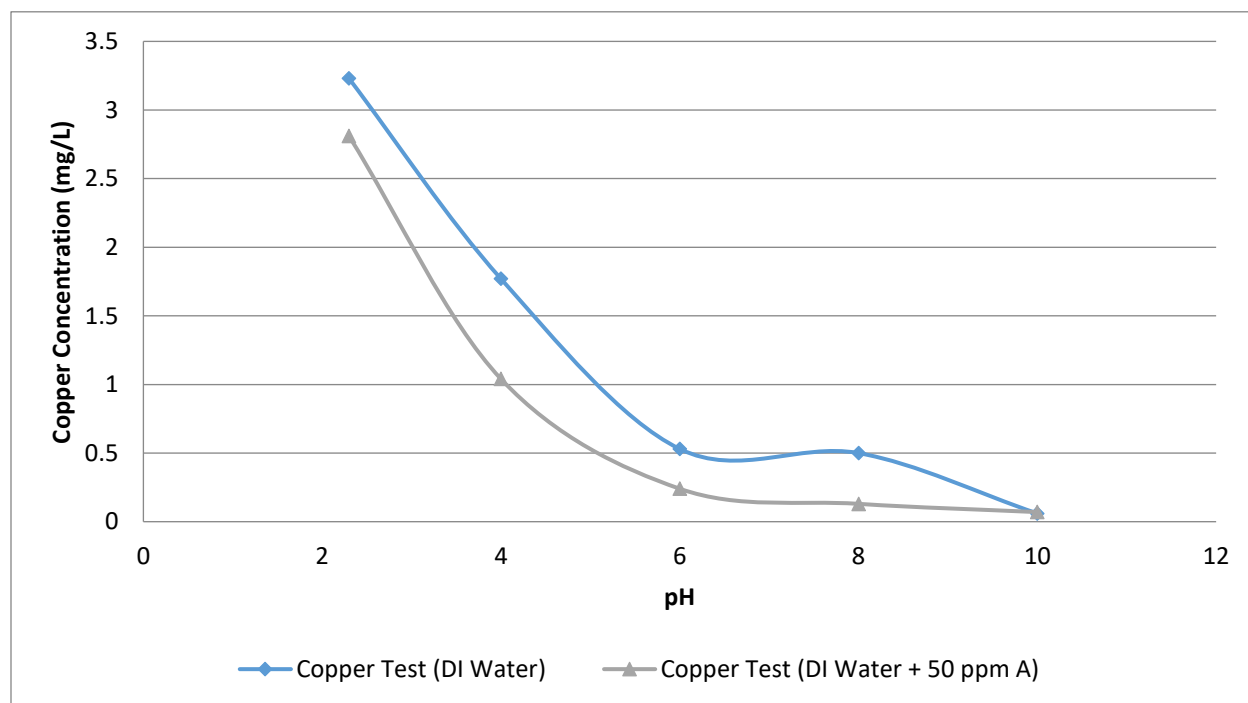
After the coated specimens were left submerged in the treated well water, the data obtained from this test was compared to the data from the uncoated specimens from the previous test. It was observed that the amount of iron measured in the water after each day was higher for the non-coated specimens, as expected. Figure 4.5 shows the iron concentration in the water over ten days for the non-coated and coated specimens at 0 ppmv and 4 ppmv of inhibitor, respectively. The iron concentration in the uncoated specimens tends to decrease over time, since the calcium phosphate layer is being formed, while on the coated specimens, the iron concentration tends to increase, since the calcium phosphate layer is being leached into the water trying to reach equilibrium.



**Figure 4.5: Iron concentration for coated and non-coated specimens at 0 ppmv and 4 ppmv of inhibitor**

#### 4.5 RESULTS FOR TEST 1 USING COPPER

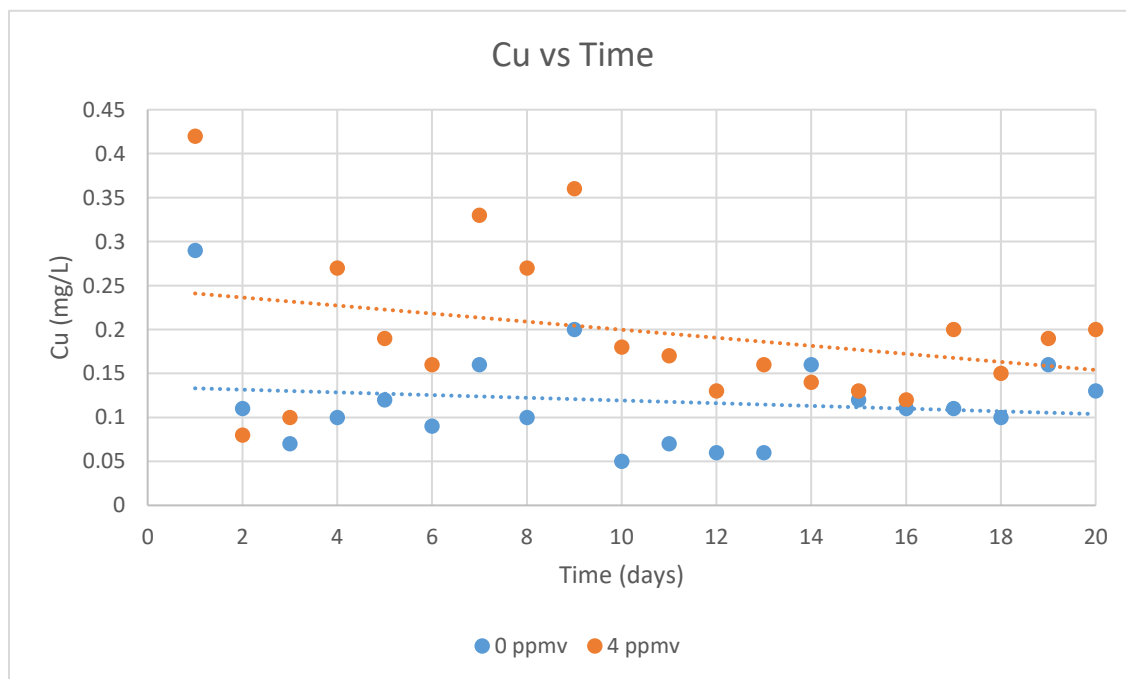
Test 1 using copper was performed using regular DI water and uncoated copper specimens. For this test, the pH of the solutions was adjusted to five different pH values using 1 N sodium hydroxide and 0.5 N sulfuric acid. After such test, it was observed that as the pH of the solution was increased, the copper concentration in the water decreased, meaning that the corrosion goes down. In Figure 4.6, it is shown that inhibitor A worked better at a pH of 6 or above.



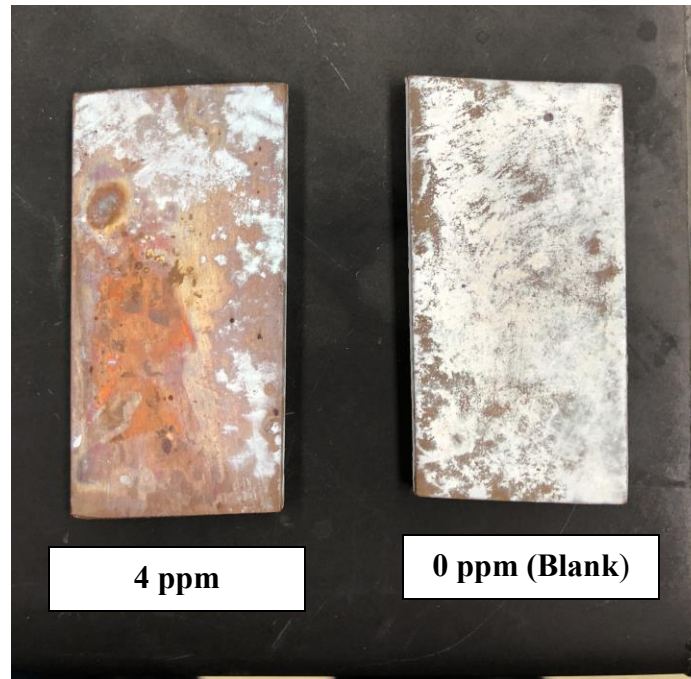
**Figure 4.6: Copper leached at different pH values with and without inhibitor**

#### 4.6 RESULTS FOR TEST 2 USING COPPER

For this test the copper specimens were treated with a solution of calcium chloride and sodium phosphate until a protective coating occurred on the specimens just like on the iron specimens. For these tests the pH of the solutions was also fixed at 7 using 0.5 N sulfuric acid and 1 N sodium hydroxide. The copper specimens behaved in a different manner than the iron specimens in that the copper concentration that leached into the water was fluctuating over time. It is believed that this was because the calcium phosphate protective layer formed on the copper specimens was not the same on all of them, and for this reason, the amount of copper leached varied slightly from day-to-day. Likewise, due to the uneven calcium phosphate coating, the copper leached by the specimens was higher in the sample being dosed with 4 ppm of inhibitor than in the sample not being dosed. In Figure 4.7, the fluctuation of the copper concentration is observed over a period of 20 days. In illustration 4.4, it is shown that the sample used as a blank is about 90% covered while the specimen used for the 4 ppm dosage has only about 10% of its area covered. This is due to the uneven coating on the plates cause by the pre-treatment by exposing the plates to the calcium phosphate solution.

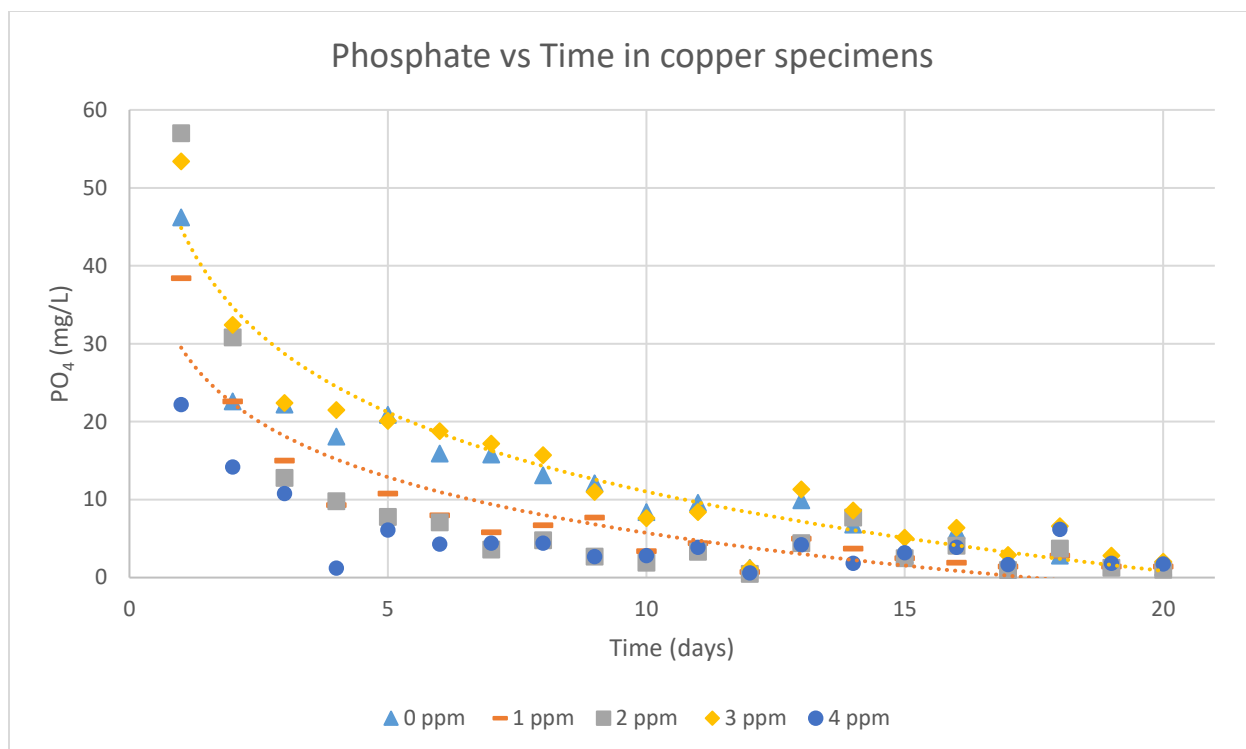


**Figure 4.7: Copper concentration over time at 0 and 4 ppmv of inhibitor**



**Illustration 4.4: Specimens used for 4 ppm and 0 ppm**

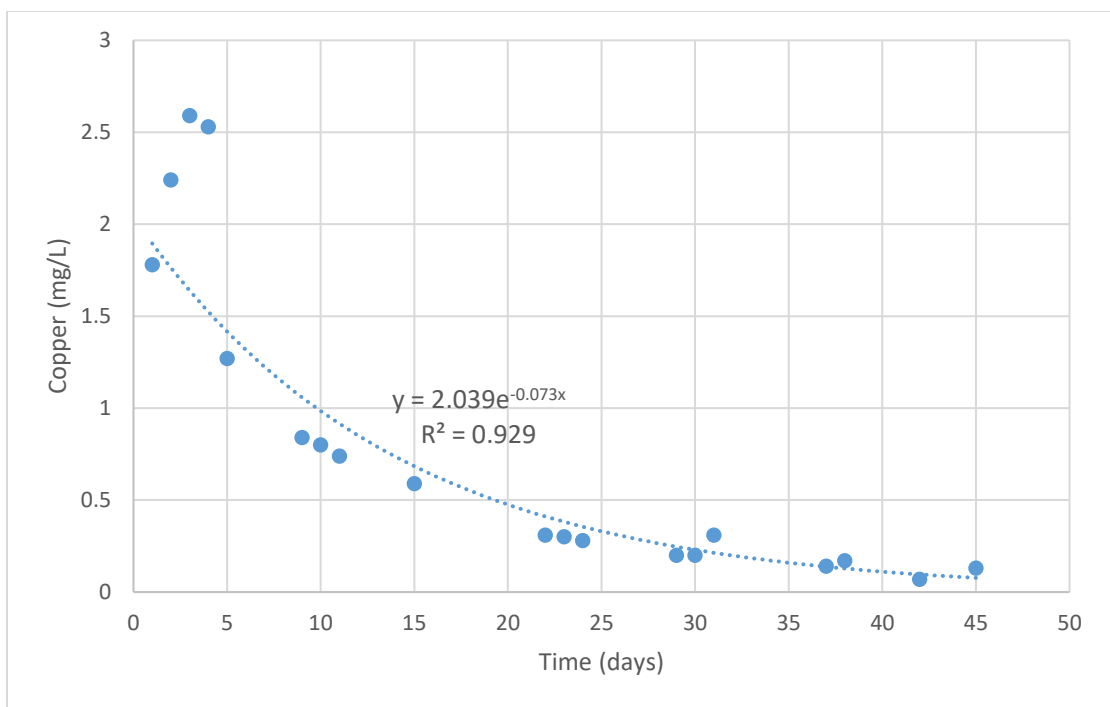
In addition, the data showed that the amount of phosphate leached from the treated specimens was decreasing rapidly with time. After 10 days of testing, the phosphate concentration was about 5 times smaller, as the leaching happened slower. Figure 4.8 shows the leaching of phosphate in all specimens over a 20 day period. Since the specimens being dosed with 0 ppmv and 3 ppmv of inhibitor were the ones with more coating after the pre-treatment they behave similarly, while the specimens with less coating then those three behave the same way.



**Figure 4.8: Phosphate leaching from specimens vs time**

#### 4.7 RESULTS FOR TEST 3 USING COPPER

After the two specimens were submerged in the DI water containing calcium chloride and sodium carbonate with an alkalinity of 250 mg/L as CaCO<sub>3</sub>, and 250 ppm of inhibitor D, it was observed that a blue precipitation started to form. This precipitation was then found to be cupric phosphate, and it started to coat the specimens. Figure 4.9 shows the decay of the copper being leached in the solution over time while the coating was being formed.



**Figure 4.9: Copper leaching from specimens versus time**

In order to prove that the cupric phosphate coating was protecting the specimens, one of the two previously exposed specimens and one with no exposure to phosphate were placed in two Erlenmeyer flasks with tap water. The concentrations of copper and phosphate in the two flasks were measured every day and it was found that the thin layer of cupric phosphate in the specimens was being leached into the water day after day.

#### 4.8 RESULTS OF CORROSION INDICES

After performing the calculations associated with the four corrosiveness indices, it was determined that all four indices indicated that the water used was corrosive and aggressive towards the media in contact with it. In Table 4.2, the results for the indices are shown.

**Table 4.2: Calculated corrosion indices values for regular well water**

Index	Value	Classification	Decision
LSI	-0.91	LSI < 0 corrosive LSI > 0 scale forming	Corrosive
Ryznar	9.32	Ryznar > 6.8 aggressive water Ryznar < 6.2 scale forming	Water is considered very aggressive
Larson-Skold	11.07	Larson- Skold < 1.2 corrosion Larson- Skold > 0.8 scale forming	High Corrosion
Aggressive Index	10.69	AI<10 corrosive 10<AI<12 moderate corrosion AI>12 scale forming	Moderately Aggressive

## **Conclusions**

The results from this investigation indicate that the well water used for this test is considered highly corrosive and aggressive and, therefore, the use of corrosion inhibitors is required to prevent or decrease corrosion. Likewise, it was observed that the inhibitors with the higher phosphate content decreased corrosion more effectively, decreasing corrosion in iron at a rate of 0.35 mg/L of iron per day when using 4 ppmv of inhibitor, meaning that the phosphate content is directly related to inhibitor performance. In addition, it was found that the performance of phosphate-based corrosion inhibitors like the ones tested herein are significantly affected by the pH of the water where they are being applied, as they will decrease corrosion by about 90% at a pH of 7.8 or higher.

Furthermore, data showed that phosphate-based inhibitors work by reacting with the calcium present in water and forming a “protecting layer” that coats the specimens, preventing the iron and copper from leaching into the water. Moreover, the corrosion indices available do not take into account the effect of phosphate presence in the water.

## **Recommendations**

Further studies of the effects of phosphate on corrosion is highly recommended in order to develop a more complete and specific index that takes into account the phosphate inhibitors.

Additionally, a better way of coating the specimens needs to be developed in order to create a more even coating through all the specimens to be tested in order to reduce the variables so that more accurate results can be obtained.

Likewise, it is recommended that the water in the distribution systems be above 7.5 to reduce significantly the corrosion, and to dose about 4 to 5 ppm of inhibitors with about 40% mass fraction content of phosphate.

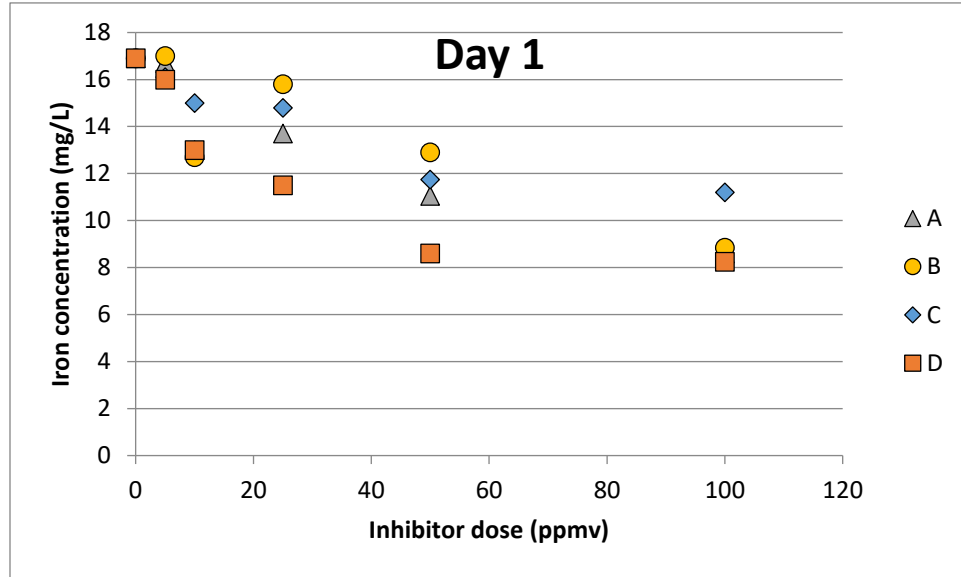


## References

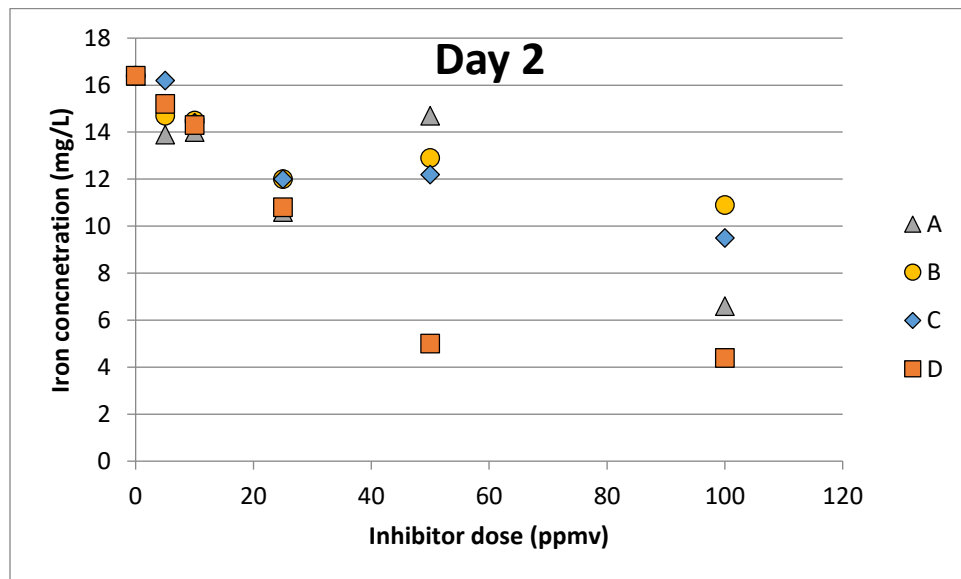
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## Appendix A

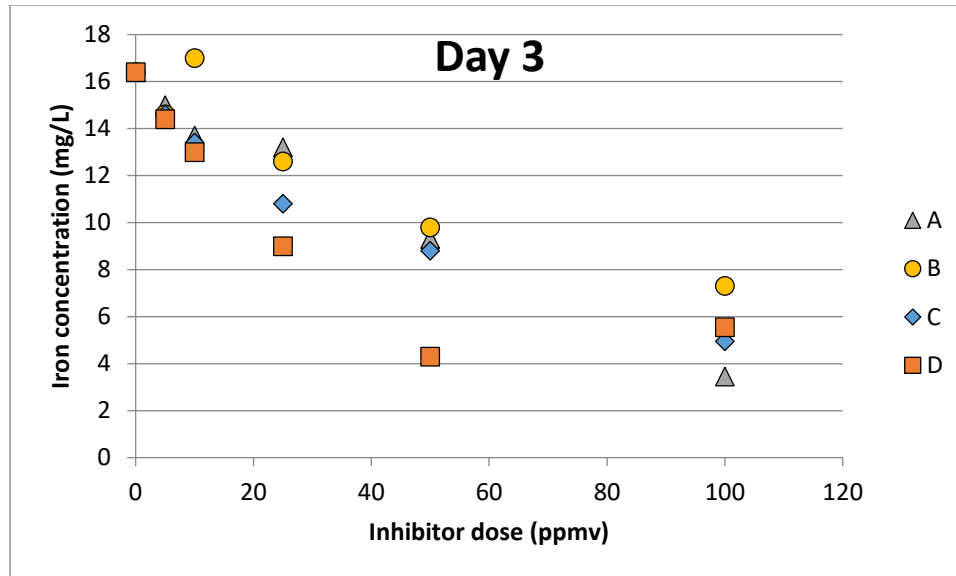
Results from test 1 using iron at days 1, 2, 3, and 4.



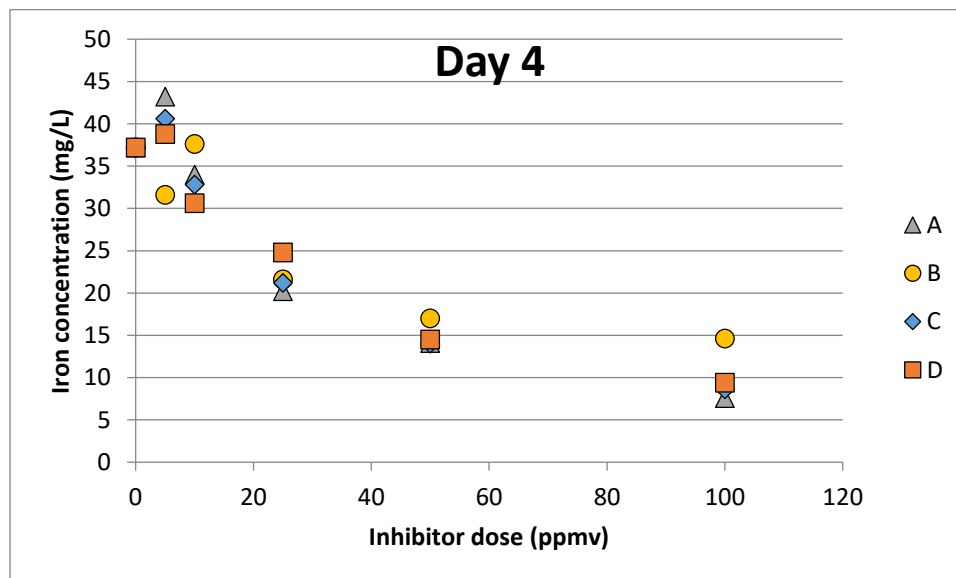
**Figure A.1: Iron concentration in the water at pH 7 after 1 day of testing uncoated specimens at 5 different concentrations of phosphate.**



**Figure A.2: Iron concentration in the water at pH 7 after 2 days of testing uncoated specimens at 5 different concentrations of phosphate.**



**Figure A.3: Iron concentration in the water at pH 7 after 3 days of testing uncoated specimens at 5 different concentrations of phosphate.**



**Figure A.4: Iron concentration in the water at pH 7 after 4 days of testing uncoated specimens at 5 different concentrations of phosphate.**

## **Vita**

Francisco Solis Jr. was born at the city of El Paso and he was raised in Ciudad Juarez, Mexico. He is a first generation college student that started collage in fall 2012 and 4 and a half years later on December 2016. He graduated from The University of Texas at El Paso getting a Bachelor's degree of Civil Engineering and right after getting his degree, he started his Master's degree on environmental engineering. During his college career he worked for 2 and a half years as a research assistant preforming research on water quality, reverse osmosis water treatment systems, organics removal in water, and waste water. After completing his master's Francisco is planning to stay in the El Paso region to get a job that allows him to apply his knowledge in water and wastewater and improve the El Paso/Juarez community.

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This thesis was typed by Francisco Solis Jr.