Metallurgical and Corrosion-Based Analysis of the USS Arizona: The Effects of pH and Crevice Corrosion Mechanisms on Corrosion Rates

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Abstract

The USS Arizona is just one of the many ships scattered all around the waters of the world which has been corroding continuously since its untimely demise. It is corroding in a salt water environment heavily populated by marine organisms and frequently disturbed by tourist and navy boats. Due to this dynamic environment the USS Arizona resides in, there is a plethora of different factors affecting the rate at which the battleship is corroding which range from chemical factors such as dissolved oxygen content, mud composition, and salinity to physical factors such as erosion corrosion from boats and ocean currents [4.] The purpose of this study is to investigate a couple of those factors and, in particular, to get a few steps closer to reaching the project-wide goal of completing a cohesive computer-based model of the corrosion of the USS Arizona.

The six samples of USS Arizona steel that my graduate advisor, Nathan Saunders, and I received from Waipio Point, HI were tested in different pH-valued mock seawater solutions to determine the relative corrosion rates of the metal specimens when in contact with different environments. Also, one of the steel samples was investigated to determine the mechanisms, extent, and effects of crevice corrosion occurring at the interfaces between rivets and steel plates. These objectives were accomplished by doing potentiodynamic cathodic and anodic polarization (PaP) tests on the metal samples, completing x-ray diffraction (XRD) investigations on oxidation samples at the rivet-plate interface, determining weight percentages of crevice corrosion-inducing minerals, and analyzing microstructures and macrostructures of the metal samples.

It was found that the metal samples corroded at similar rates at pH 4 and 7; however corrosion rates steeply increased when we tested corrosion susceptibility in pH 2 solutions. X-ray diffraction showed that there were two common minerals in the rivet-plate interfaces, goethite and magnetite, which tells us that there is at least one crevice corrosion mechanism at work in the crevices from which we took oxidation samples. The metal samples were reaffirmed as medium carbon steel based on their corrosion rate patterns and past research on carbon content of the steel sample [7], while the macroetch revealed plastic deformation around the rivet in plate A-6 based off of grain size and distribution.

1. Introduction

Steel subjected to a marine environment for a considerable length of time will corrode by numerous mechanisms ranging from biofouling to erosion corrosion by waves and sand to ordinary oxidation by rusting. This range of corrosion mechanisms can make the identification of a definite corrosion rate for any material in a marine environment difficult. As such, in 1983 collaborative research started under the Submerged Cultural Resources Unit and the National Park Service to document the state of one especially significant piece of United States history, the USS Arizona battleship, and begin working toward an evaluation of corrosion damage on the ship in order to determine when the ship will structurally fail and whether or not attempts should be made to preserve the ship [5.]

This evaluation of corrosion can be based on many different topics and the aspects we chose to analyze were the effects of differing pH levels on corrosion rates, the effects of the microstructure and macrostructure of the steel on relative corrosion rates, and the effects of crevice corrosion on the steel. There are a couple of ways to test each of these variables, but we chose to use potentiodynamic cathodic and anodic polarization (PaP) testing to determine the effects of different pH values on corrosion rates, polishing paired with microscopy and macroetching to investigate microstructure and macrostructure, and x-ray diffraction (XRD) and weight % evaluations to discover the presence and abundance of crevice corrosion products in between the rivets and plates of one of our steel specimens. In this study, each of these test methods was used to determine the relative and overall corrosion rates of the metal used to build the USS Arizona.

2. Broader Impact

The USS Arizona has been lying in solemn silence beneath the Pacific Ocean for almost 70 years. The ship serves the dual purpose of being a World War 2 memorial which represents the beginning of the United States' involvement in World War 2 in the Pacific theatre and a mass grave for the 1,102 sailors and marines whose bodies were never recovered from the ship [5.] Yet, memories are not the only thing that still resides in the hull of the USS Arizona. There are many shipwrecks around the coastal United States and southern Pacific Ocean that would be considered threats to the environment if they ever experienced a catastrophic structural failure strong enough to cause a collapse of the hull [6.] This is because many ill-fated ships, including the USS Arizona, have a large supply of oil on board left over from their operational days [6.] In particular, the USS Arizona has residual Bunker C fuel oil, a thick black viscous fuel oil [2,] remaining from its service in the Navy; it is a situation that should not be ignored.

In lieu of the memorial, cemetery, and environmental-related aspects of this project, it seems fitting that the USS Arizona receives full attention in regard to evaluating the state of the ship and preventing disaster from occurring at the memorial site in Pearl Harbor. Our research holds the potential to provide helpful information on corrosion rates relative to pH levels, steel microstructure and macrostructure, and crevice corrosion that could aid the project as a whole in progressing towards the ultimate goal of producing a full structural model of the aging ship including all aspects of corrosion. The preservation of the USS Arizona at the Pearl Harbor Memorial is vital to preserving a unique piece of United States naval history and protecting the environment of Pearl Harbor.

3. Procedure

3.1 Materials

Six samples of medium carbon steel from the USS Arizona's superstructure (everything above the main deck) at Waipio Point, HI

Lab grade sodium chloride

Deionized water

6M HCl

Methanol or ethanol

3.2 Equipment

Potentiostat/Galvanostat

Flat cell apparatus

Polishing equipment

Metal specimen mounting equipment

Optical microscope

Scanning electron microscope

X-ray diffractometer

Abrasive saw

3.3 Potentiodynamic cathodic and anodic polarization testing

     Rectangular pieces of metal less than 1in x 1in were cut from our Waipio Point metal specimens with a band saw and an abrasive saw. They were then cut to make sure they were less than 3/8in thick and polished using a 240 grit wheel followed by 400 grit and 600 grit wheels. After that the samples were put in an ethanol (or methanol)-filled beaker, which was then placed in a sonic resonator bath, and subjected to sonic surface cleaning for five to ten

minutes. Afterwards, the samples were rinsed off with ethanol and wrapped up in delicate task wipes until it was time for them to be tested.

Lastly, the samples were individually tested in a flat cell apparatus by ASTM standard G-61 and subjected to open circuit, linear polarization, and tafel testing in that order. In each of these tests, the flat cell was filled with 3.56% NaCl solution prepared with deionized water that was mixed with HCl to produce the desired pH level for each test. All mixing of solutions was done, of course, in a separate bottle before testing in the flat cell. Based off of these tests, corrosion rates were produced from a data analysis program on the computer and recorded for each metal sample with each different solution. Appendix A contains a description of the potentiodynamic polarization testing analyses.

3.4 Microscopy

Rectangular pieces identical to those described in the previous subsection were cut from the Waipio Point samples. They were then mounted in phenolic powder and polished on grinding wheels in this order: 240, 400, 600, 800, and 1200 grits followed by a 1 micron wheel, and a 0.3 micron wheel to finish. The pieces were then rinsed with ethanol or methanol to remove polishing residue and etched with a 2% Nital solution. The etching entails brushing a polished surface with the nital, waiting a few seconds for the etchant to make the surface cloudy, and then rinsing the sample off with ethanol to protect the surface from further corrosion. Following this the samples were dried using a hot air hand dryer and then observed via an optical microscope.

3.5 Macroetching

A piece of plate A-6 approximately 3in x 3in in size, which included a rivet and three layers of steel plates, was subjected to macroetching. The surface under observation was polished and then cleaned to remove any debris from the cutting process. Afterwards, it was submerged in a 3M HCl solution for an hour. Next, the sample was taken out of the HCl bath and rinsed with hot water followed by an ethanol (or methanol) rinse to preserve the specimen. Finally, the specimen was dried using a hot air hand dryer and examined on a well-lit surface for visible granular and structural properties.

3.6 Crevice corrosion analysis

Plate A-6 was cut in a fashion that split the rivets which were connecting three steel plates together in half. The crevices between plates and the rivets (Figure 1) were observed with the naked eye and a 10x zoom spy glass for areas of noticeably accelerated crevice corrosion. The rivets were then hammered loose from the plates and the oxidation from the plate-rivet interfaces was scraped off. These oxidation samples were pulverized and then analyzed using XRD to analyze the oxidations' compositions. Lastly, weight percentages of goethite and magnetite were taken to determine how prevalent the crevice corrosion mechanism was.

Figure 1: Source of Oxidation Samples

4. Results

4.1 PH Testing

The six metal samples (Figure 3) we tested from the USS Arizona were all tested in a flat

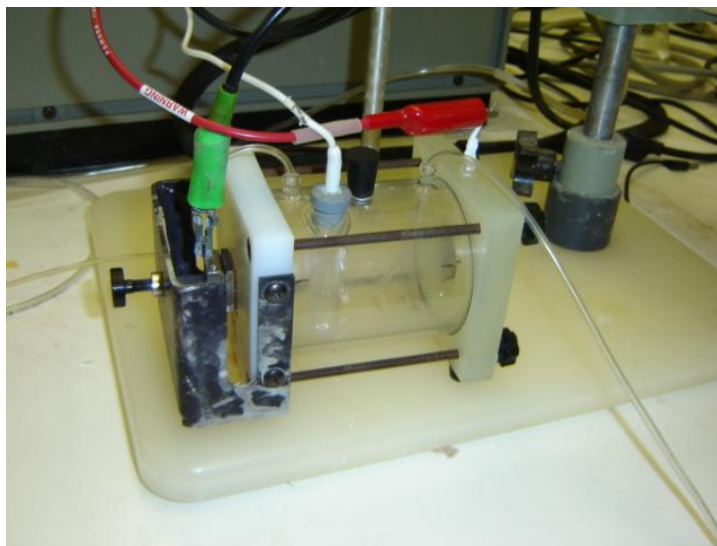cell (Figure 2) linked to a potentiostat and a computer (Figure 4) for data analysis.

Figure 2: Flat Cell

Plate A-1
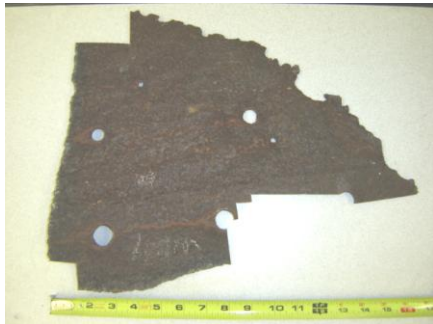

Plate A-5

Plate A-2

Plate A-6

Plate A-3

Plate A-6 with Rivet Portion Removed

Plate A-4

Figure 3: Metal Samples of the USS Arizona

Figure 4: Flat Cell, Potentiostat, and Computer Apparatus

Some of the trends we discovered during the course of our PaP testing were expected while others were quite unexpected. The main trend we found, which matched up with past research we found that dealt with medium carbon steel being tested in aerated water [3,] was that between pH 4 and 7 corrosion rates of the same metal at both pH-levels varied minimally (within ten mpy (mils per year,) with one mil equal to one thousandth of an inch) and showed few patterns in relation to corrosion rates. The pH 2 solution we tested with always gave corrosion rate results around an order of magnitude higher than those found when testing pH 4 and 7 solutions. This also goes along with the research we found [3.] When the pH of the mock-seawater solution was below pH 4, corrosion rates greatly increased. The full corrosion rate data is displayed in Table 1.

Table 1: Corrosion Rates of USS AZ Samples

Sample	Corrosion Rate (mpy) based on pH		
	pH 7	pH 4	pH 2
Plate A-1	18.76	6.77	180.4
A-2	12.28	7.92	425
A-3	11.15	16.94	290.6
A-4	17.15	5.102	44.56
A-5	9.314	10.11	248.6
A-5 rivet	18.98	10.98	93.25
A-6 top of rivet	0.564*	20.083	250.3
A-6 middle of rivet	8.019	9.824	294.1
A-6 bottom of rivet			
A-6 Plate 1	12.39	1.081	
A-6 Plate 2			
A-6 Plate 3			

* Sample was tested under less than ideal test conditions

We didn't find concrete evidence of many corrosion rate patterns between and among samples of metal. We found some evidence based off of pH 4 tests that the top of the rivet in plate A-6 may be corroding faster than the pieces of steel around it, however the results of pH 2 and 7 testing on these same pieces suggested different trends.

4.2 Microscopy

The microscopy showed us that there are a high amount of inclusions in the steel samples from the USS Arizona. This helps us characterize the steel that was used to make the ship. Seeing as the ship was built in 1915, it can be expected that inclusions would be significantly more prevalent than they are in steel today. There was little out of the ordinary in terms of observations on the microstructure of the USS AZ samples, as is shown in Figures 5-9.

They were all hypoeutectoid in carbon content with fine and/or coarse pearlite observed in the structure and proeutectoid acicular ferrite at the prior austenite grain boundaries. We observed banding in the microstructure of a plastically deformed piece of plate A-4. Banding usually prompts higher corrosion rates, but how much higher is something we don't know.
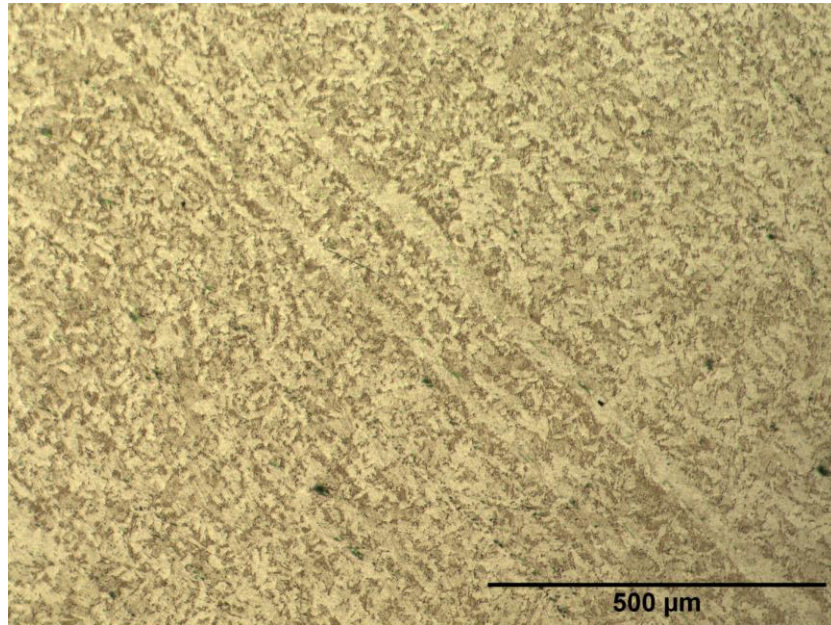

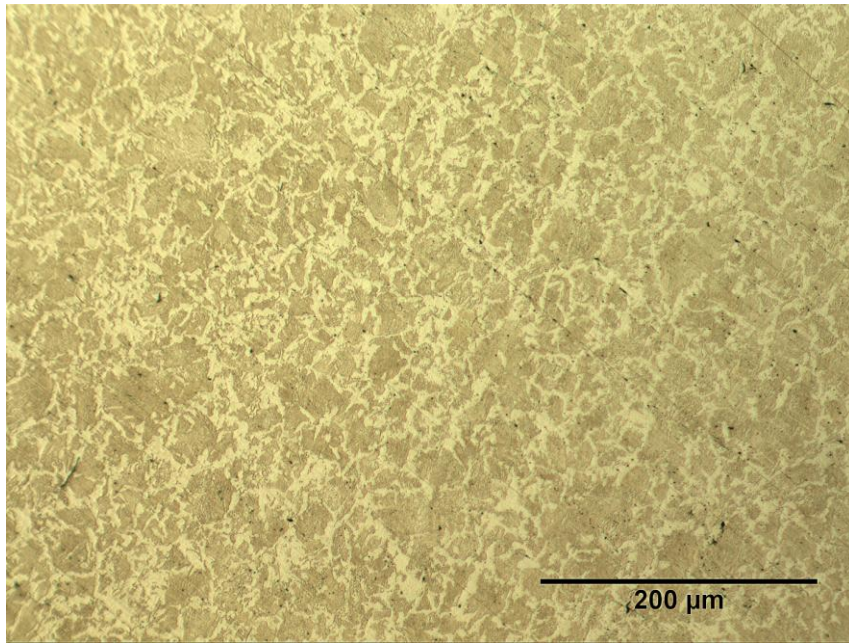**Figure 5: Micrograph of Plate A-4**
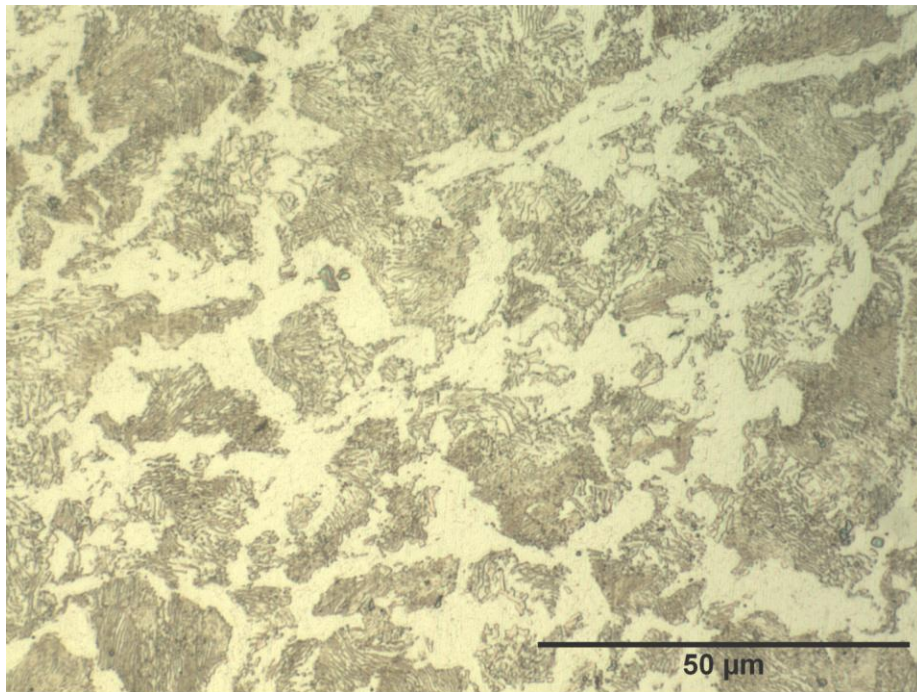
Figure 6: Micrograph of Plate A-5

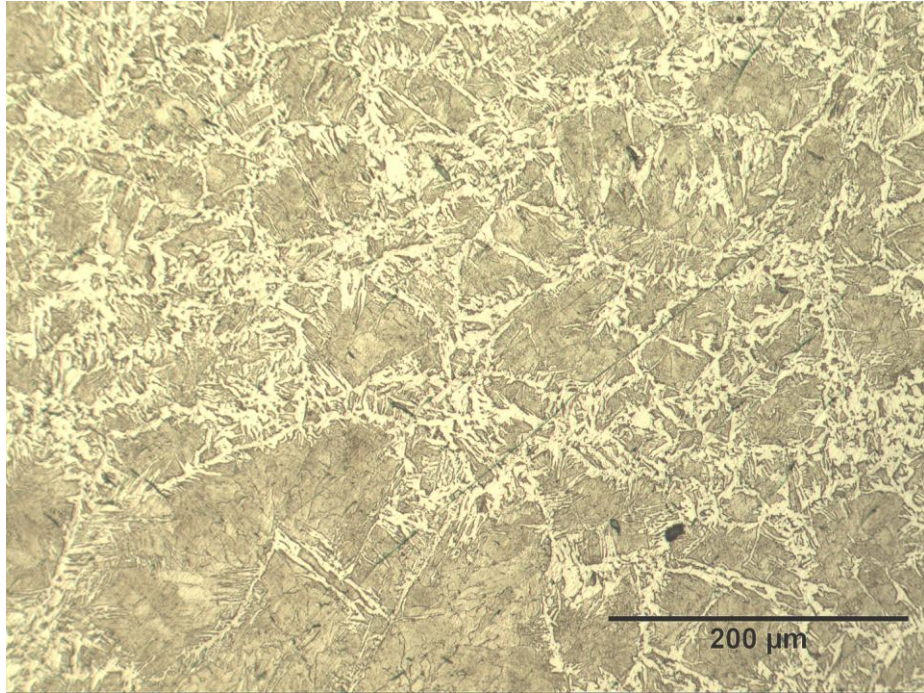**Figure 7: Close-Up Micrograph of Plate A-5**

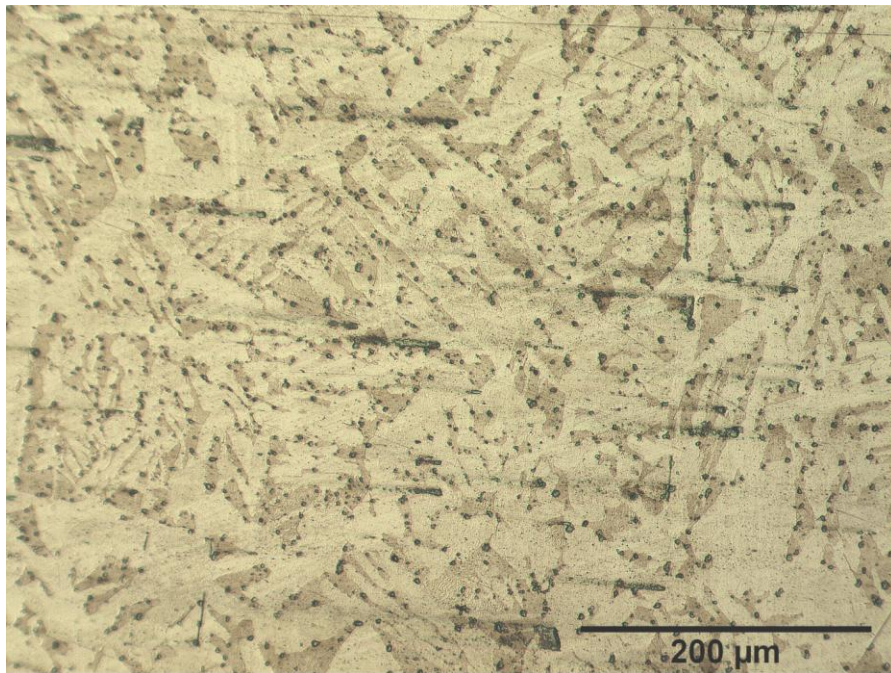**Figure 8: Micrograph of Plate A-5 Rivet**

Figure 9: Micrograph of Plate A-6 Rivet

4.3 Macroetching

  The HCl acid bath showed us the basic macrostructure of the sample from plate A-6 which consisted of three steel plates attached by one rivet. The top of the rivet seemed to be plastically deformed around the part where the shaft of the rivet meets the lip of the head. This leads us to believe that the rivets of plate A-6 have a higher propensity to corrode at a faster rate than the steel plates around them based on the plastic deformation of the rivets. However, we can't make any solid conclusions based solely off of this qualitative data. The etching seemed to reveal the grains of the shaft of the rivet were arranged in a parallel vertical fashion; while the bottom of the rivet seemed to be plastically deformed like the top, except the bottom was flayed outward from the center of the rivet instead of bent around an edge like the top of the rivet was. The middle plate showed a sign of carbon segregation as is shown by the specks in the middle of the second plate on both sides of the rivet in Figure 10.
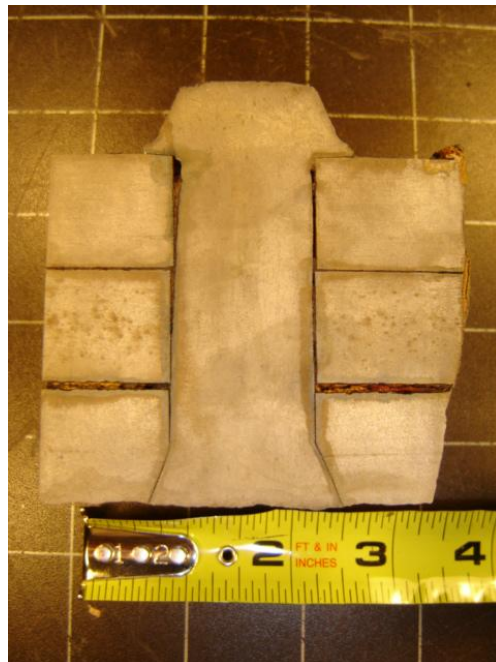

Figure 10- Macroetch of Plate A-6 Sample

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4.4 Crevice Corrosion Analysis

The results from the crevice corrosion analysis tests made us hopeful for future work. The macroetching displayed the surface characteristics of the steel, as visible by the naked eye, which were, in addition to those listed in the prior paragraph, that the interface between the top of the rivet and the top plate showed the most evidence of corrosion, possibly crevice corrosion. The XRD testing on the samples showed that both of the oxidation samples included magnetite and goethite. Below are the XRD mineral analysis results for the first and the second samples respectively.
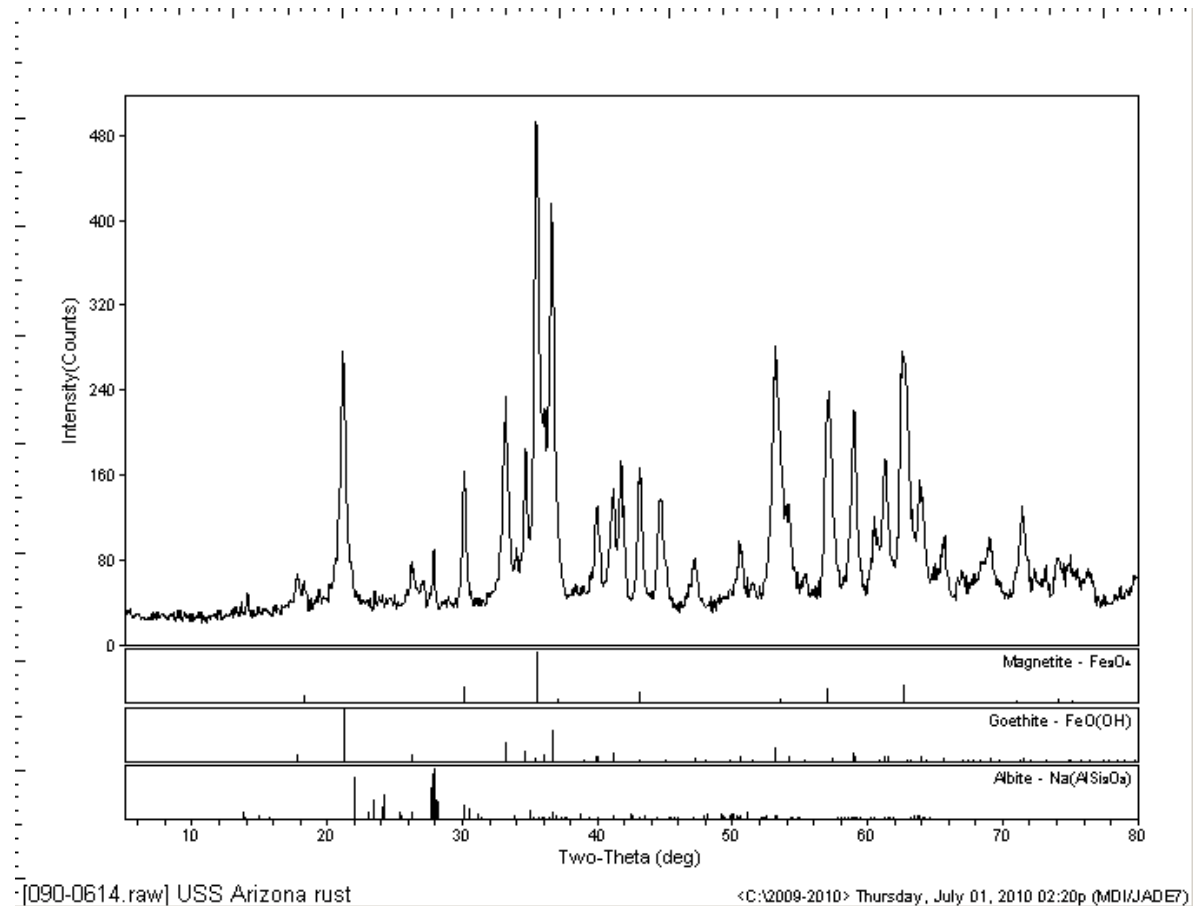

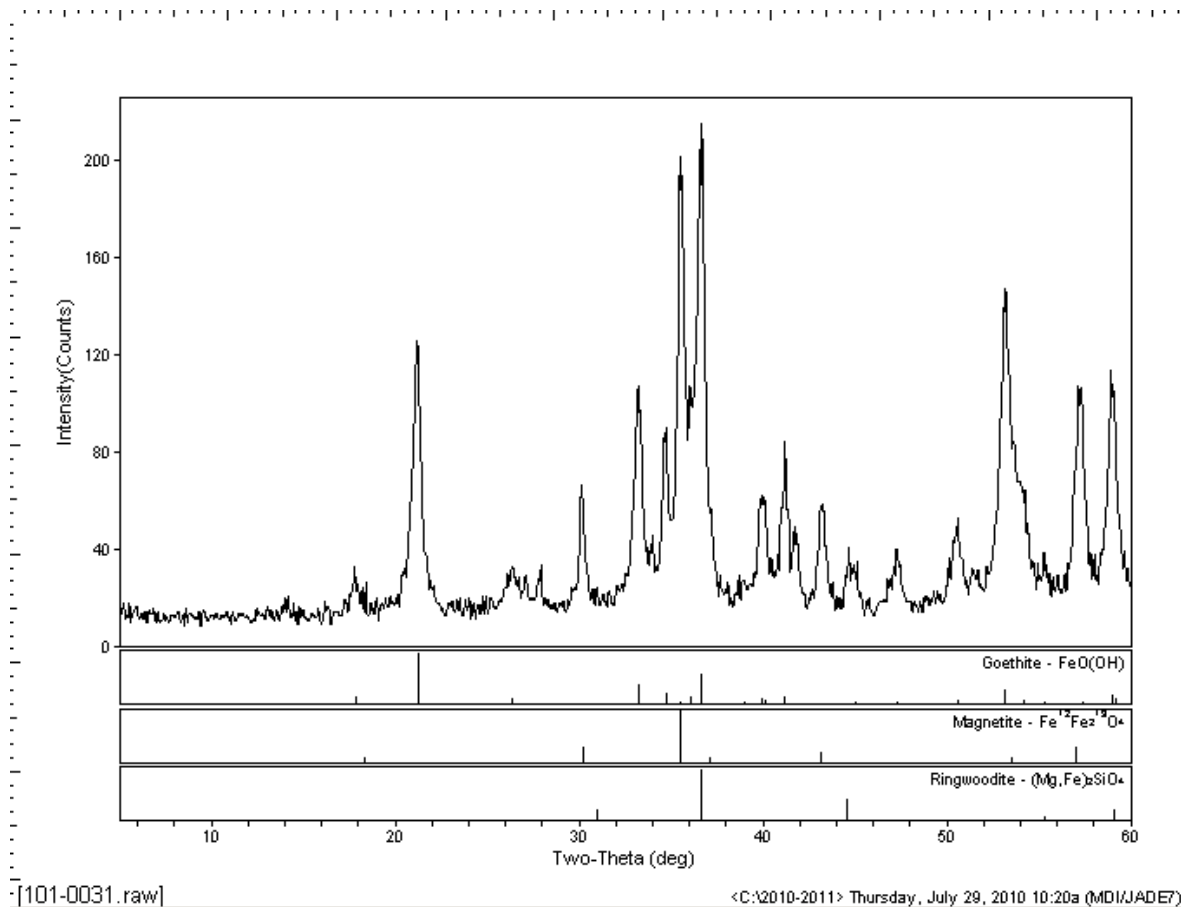**Figure 11: XRD Results from Sample 1**

Figure 12: XRD Results from Sample 2

These results show that there is or was crevice corrosion occurring because goethite, an iron oxide hydroxide, is known to be a product of a self-sustaining crevice corrosion mechanism which occurs in the presence of aerated water.

The weight percentage testing showed us that the first oxidation sample was approximately 65% goethite and 35% magnetite and the second oxidation sample was approximately 54.5% ringwoodite, 27% goethite, and 18.5% magnetite, keeping in mind that both samples' percentages are based off non-amorphous mineral percentages. This ringwoodite, an iron silicate with substituted magnesium, was an unexpected product in the

oxidation sample. The relevance of the test data, however, is that both samples showed a significant percentage of goethite. Based off of the goethite, it can be said that the rivet-plate interfaces on plate A-6 did seem to be experiencing crevice corrosion. My advisors and I have made the educated guess that the ringwoodite could have formed on the beach at Waipio Point, HI due to the contamination of plate A-6 by sand, a silicate. Therefore, the ringwoodite may or may not be affecting the corrosion of the portion of the USS Arizona still under water in Pearl Harbor.

5. Discussion

It is important to discuss the intricacies of our PaP testing procedures over the course of our research. Our procedure for testing the effects of pH on corrosion rates was initially to run the open circuit test first followed by the tafel plot with a scan rate increased from the normal 0.166 mV/s to 0.5 mV/s and ending with a linear polarization plot at normal scan rate. We used this method to retrieve most of the data on plates A-2 through A-4 with the exception of plates A-2 and A-3 in pH 7. Yet we discovered through reading more in depth in the ASTM handbook that the scan speed should not be increased more than a few percent and we found through trial and error that running the linear polarization test second followed by the tafel test resulted in more accurate and uniform-looking plots. Therefore, we started using a new testing method in which we performed the linear polarization test second and the tafel test third and we didn't alter the scan speed of the tafel plot. Figure 13 shows the possible differences between graphic results of each testing method.
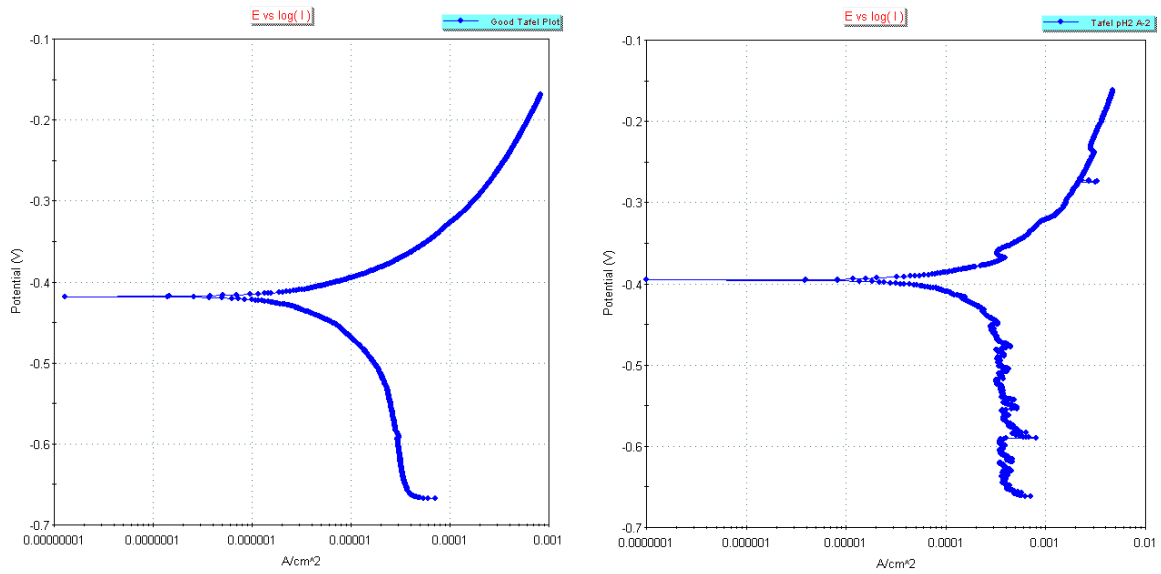
Figure 13: Tafel Plots Using the New Method (Left) and the Old Method (Right)

This means about half of our data was done using one method and half with the other. We tested some of the metal samples with the same pH solutions while using each test method and found that, while there is an appreciable difference in quantitative results (a change of 5 to 10 mpy between methods,) the patterns of relative corrosion rates remained the same. So while the earlier data we took is not valid for accurate quantitative data analysis, it is broadly accurate (the data is still close to the correctly tested results) and is still valid for qualitative analysis given we only compare tests results recorded under the same test method, which we have. In addition, the same corrosion rate patterns, in relation to the lack of influence of pH on corrosion rates between pH 4 and 7 and the severe increase in corrosion rates below pH 4, exist under both test methods.

We can attribute the lack of patterns in the PaP tests between pH 4 and 7 to a couple factors. First of all, as was stated earlier, there is research [3] showing that no significant

difference in corrosion rates exists when dealing with medium carbon steel that is exposed to a solution with a pH value between pH 4 and 7, therefore pH 4 shouldn't show higher corrosion rates overall than pH 7 and vice versa. Secondly, the inconsistencies due to human error in polishing the samples before testing, the high amount of inclusions in the USS Arizona steel samples, the minor differences in temperature and humidity on any given day, and many other nearly uncontrollable factors may have caused variations in corrosion rates that defy any type of pattern in relation to which pieces corrode faster than the others.

In the case of the USS Arizona, the water will likely never be at a pH of two, at least not all around the ship. This is because ocean water typically has a pH ranging from around 7.5 to 8.4. While some areas of the steel hull will likely be exposed to water with a pH value artificially lowered by concretion and microorganisms, it is unknown exactly how much the pH of the water can be lowered by such mechanisms. Slight changes in pH won't directly affect corrosion rates of the steel; all the same, small changes in pH can affect calcareous scale deposition on the steel, which can affect corrosion rates [4.]

The inspiration for our research dealing with crevice corrosion came from our advising professor, Dr. Medlin, who suggested the possibility that the steel plates won't be what fails when the USS Arizona finally experiences a catastrophic structural failure; the rivets holding the steel plates together might fail first due to crevice corrosion. If that were to happen, the steel plates might simply peel apart from one another, or unzip, once the rivets fail; such a situation would presumably happen before the steel plates failed if the rivets were corroding fast enough. This was Dr. Medlin's "Zipper Theory." Our research on crevice corrosion was meant

to determine if there was a significant crevice corrosion mechanism at work at the rivet-plate interfaces and to expose the relative corrosion rates of the rivets and the surrounding steel plates. Based off of our data, we can say that the effects of crevice corrosion should not be ignored by those analyzing the extent of corrosion on the USS Arizona.

6. Conclusion

6.1 Summary

In this study, steel samples from the USS AZ were tested to evaluate corrosion with respect to pH, crevice corrosion, microstructure, and macrostructure. It was found that the pH value of sea water doesn't affect the corrosion rates of the medium carbon steel from the USS Arizona, despite the high amount of inclusions found in the metal, between pH 4 and pH 7. However, corrosion rates of steel samples greatly increased when exposed to the pH 2 solution. A crevice corrosion product was found on plate A-6 samples so the presence of at least one crevice corrosion mechanism has been confirmed. The data we have on corrosion rates leads us to a preliminary conclusion that the top of the rivets might not be corroding significantly faster than the plates surrounding it, despite the presence of plastic deformation on the top of the rivet; however, this conclusion hasn't been fully proven and more testing should be done in order to confirm this theory.

6.2 Future Work

There is much room for continuation of our work in the area of potentiodynamic cathodic and anodic polarization testing on steel from the USS Arizona. For most of the samples we have, we only had time to test each sample from each plate, including rivets, with each pH solution once (or until we got a sufficient set of results from the graphs.) As any scientist worth his salt knows, one test is not enough to determine concrete results; as such, more testing should be done on these pieces of the Arizona to provide solid evidence of there corrosion rates quantitatively and in relation to each other when in a mock seawater solution.

Crevice corrosion testing has great potential for future work in relation to attaining corrosion data on the USS Arizona. Our crevice corrosion analysis went into full swing in the last few weeks of research, so there was little time to make conclusions, let alone gather data. The next step in crevice corrosion research would be to find an apparatus which can actively register the corrosion rate of the corner of a piece of metal, such as the point on a rivet where the head and the shaft meet up. This would provide the most direct method of assessing the corrosion rates of the rivet shafts in contrast to the plates the rivets are holding together.

Equally as important for future work would be a more accurate and consistent method of determining corrosion rates in general. The flat cell we used was in working order, however I believe the machine might not have been meant to distinguish between fairly small intervals of corrosion rates.

There are many factors which affect the corrosion rate of the USS Arizona that need to be tested in order for a culminating Finite Element Analysis (FEM) to be done on the USS Arizona. The FEM is a research method currently being used by the National Park Service's Submerged Cultural Resources Unit to take into account the factors affecting the stress on and shape of the USS Arizona in Pearl Harbor. This model is going to be used to predict when the USS Arizona is going to experience a structural failure [1.] In conclusion, there is a need for all relevant research to be compiled in order to accurately depict the condition of the USS Arizona and complete the Finite Element Analysis.

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Acknowledgements

Appendix A: Potentiodynamic Cathodic and Anodic Polarization Testing Data Analysis
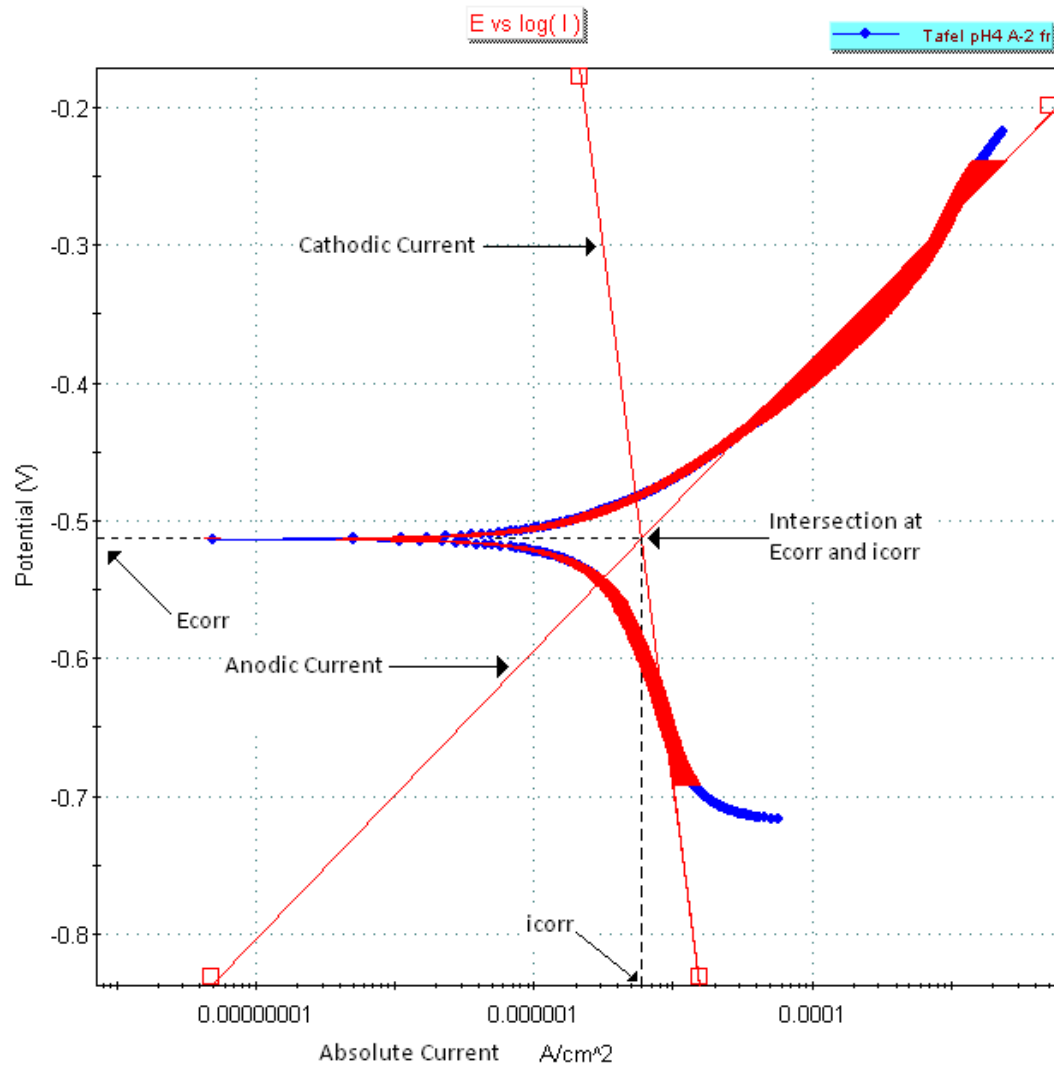

Figure 14: Instructional Tafel Plot

The corrosion rates of all the metal samples were found using the potentiodynamic

cathodic and anodic polarization testing apparatus. The reference electrode used was a

platinum wire submerged in a saturated Ag/AgCl KCl electrode solution which was in a separate

tube of sea water testing solution during all tests. The tafel plots we generated, like Figure 14

above, were used to find values for β_a and β_c (the anodic and cathodic slopes of the tafel plots)

which we used to extrapolate the corrosion rates after we had made a linear polarization plot. The tafel slopes are represented on the linear polarization plot by the straight lines.

The point of intersection of these lines gives the value for E_{corr} and i_{corr}, where E_{corr} is the value of the potential where the current density approaches zero and i_{corr} is the value of the current density where the Tafel slopes intersect. i_{corr} is used to find the corrosion rates using Equation 1:

$$r = 0.129 \times \frac{Ai_{corr}}{nD}$$

In this equation A is the atomic weight of the metal being tested, i_{corr} is the current density where the tafel slopes intersect, n is the number of equivalent exchanges of electrons in the electrochemical cell that is created for a given reaction, D is the density of the metal, and r is the corrosion rate in mils/year. The corrosion rate defines the penetration of the oxide layer in relation to the pre-testing width of the metal [7.] The flat cell, potentiostat, and computer program all work together to measure the corrosion rate of the specimen, with respect to the two hours during which the specimen is being test. It takes this corrosion rate based on a small interval of time and calculates a corrosion rate in mils/year. The procedure for conducting these potentiodynamic cathodic and anodic polarization tests is further explained by ASTM standard G-61.