Sub-surface corrosion research on rock bolt system, perforated SS sheets and steel sets for the Yucca Mountain Repository — Quarterly technical report No. 8

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Sub-surface Corrosion Research on Rock Bolt System, Perforated SS Sheets and Steel Sets for the Yucca Mountain Repository

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June 30, 2006
Statement of Work

The objective of this task is to conduct corrosion related research and predict the durability of rock-bolts and other underground metallic roof supports. In this period, we have performed tests on Split set rock bolts, and 4340 steel that may be potentially used for Bernold shields, and rock bolts or other underground support structures. The importance of these results is that we have used the Yucca Mountain water chemistry (furnished by the DOE) as an electrolyte for the corrosion experiments. During this period, we used potentiodynamic tests to obtain corrosion rates. Other tests such as oxidation tests, etc. are not complete, and will be reported in the next quarterly report.

General Statements

High-strength low-alloy (HSLA) steels are commonly used in commercial rock bolts. We have performed corrosion tests on commercial rock bolts (Split Sets – SS46), Alloy 22 baseline studies, 4340 steel that may be potentially used for rock bolts of different types, and related materials for ground support of the repository. These corrosion rates have been determined in aerated (oxygenated) and deaerated (nitrogenated) conditions at different temperatures in simulated 1X YM waters for 4340 steel. Characterization of reacted products by optical microscopy has also been performed during this quarter on other materials. Analyses and more experiments are in progress. Manuscripts for publications have been written, and one of the submitted manuscripts is being revised [Met Trans (A) Journal]. We have sent another manuscript to Electrochimica Acta based on this work.

Progress for the Period 1/1/06 to 3/1/06

Subtask 1: Selection of New High-Strength Low-Alloy Steels, Stainless Steels for Rock Bolts, Steel Sets and Perforated Roof supports. In this report we show 4340 Steel, Alloy 22 baseline material and Split Set rock bolts results.

Subtask 2: Electrochemical tests to evaluate corrosion rate and possible corrosion mechanisms

Subtask 3. Electrochemical Impedance Spectroscopy (EIS) of 4340 Steel

Subtask 6: Dry Oxidation Tests by Thermogravimetric analyses (in progress – analyses not complete)

Subtask 7: Microstructure and Phase Characterization Studies

I. Introduction

This report shows the work done for this period, in accordance to cooperative agreement of University of Nevada system for the Task 019 “Subsurface Corrosion Research on Rock Bolt System, Perforated SS Sheets and Steel Sets for the Yucca Mountain Repository”, the overall objective of which is to conduct corrosion research and predict the durability of rock-bolts and other underground metallic roof supports. We are performing oxidation tests using Thermogravimetric Analyzer (TGA), and Potentiodynamic tests to determine the corrosion rates of rock bolts, other support materials including bench mark materials.

In this quarter, we have performed:

Potentiodynamic tests were performed to determine corrosion rates (CR) of 4340 Steel, Alloy 22 and Split Sets (SS46) rock bolts. The corrosion rates of Alloy 22 were determined by potentiodynamic scans and we have compiled results of other researchers who have used other techniques to evaluate corrosion rates of this material. A manuscript, entitled “Electrochemical Evaluation of Passive Corrosion Behavior of Alloy 22 In Complex Ionic Electrolyte,” has been prepared and included as a part of the report for condensed information. This manuscript has been recently submitted to Electrochimica Acta.

III. RESULTS AND DISCUSSION

In this quarter, electrochemical studies such as potentiodynamic, EIS, corrosion rates of rock bolts or rock bolt materials and activation energies, will be presented for the Yucca Mountain underground support. We started the studies last quarter on many of these materials and have new results for rock bolts (1) Friction type Split Sets (HSLA steel), (2) Alloy 22 hydrogen permeation studies (baseline material) and (3) 4340 steel.
1.1 Corrosion Studies on AISI-SAE 4340 Steel in Simulated YM Groundwater

1.1.1 Introduction

AISI-SAE 4340 steel is currently being studied as a potential candidate material for use in rock bolts and I-beams within the Yucca Mountain Nuclear Waste Repository, northwest of Las Vegas, Nevada. As previously discussed, slotted and tapered steel tube rock bolts are currently being studied for use as underground support inside the Yucca Mountain Repository. In this study, potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) tests were carried out on 4340 steel in simulated Yucca Mountain (YM) groundwater at the normal (1X) concentration in both aerated (oxygenated) and deaerated (nitrogenated) conditions. The overall corrosion rate (CR) increased from 25°C to 90°C in the deaerated condition throughout. In the aerated condition, the corrosion rate increased to 75°C, and then decreased from 75°C to 90°C.

1.1.2 Experimental

Specimens for electrochemical tests were prepared from commercially available 4340 steel. The chemical composition of 4340 steel was analyzed by LTI and is given in Table 1.1.1. Disc-shaped test specimens approximately 0.25” were professionally cut and machined locally. The test specimen was mounted in epoxy with its ~1.2 cm² bottom surface area and electrical connection wire exposed out of it. Before the experiment, the sample was polished with 240 grit and 600 grit SiC emery papers and washed with deionized/distilled water before inserting them into the cell for electrochemical testing.

Table 1.1.1. Chemical Composition (wt%) of AISI-SAE 4340 Steel

<table>
<thead>
<tr>
<th>Element (weight percent)</th>
<th>Fe</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>97.085</td>
<td>0.43</td>
<td>0.84</td>
<td>0.77</td>
<td>0.26</td>
<td>1.86</td>
<td>0.015</td>
<td>0.02</td>
<td>0.26</td>
</tr>
</tbody>
</table>

All the electrochemical experiments were conducted in a typical 1 liter Pyrex glass flask covered with a polytetrafluoroethylene lid (please see Quarterly report No. 5 for the photos of the apparatus). The lid has many ports containing the working electrode, counter electrode (platinum), gas purge, inlet and outlet for the gas, Luggin probe connected to the silver/silver chloride (Ag/AgCl) reference electrode, and gas trap. A large (~10 cm²) platinum sheet sealed to a glass capillary was used as a counter electrode to provide good conductivity in the electrolyte. The reference electrode was a saturated silver/silver chloride (Ag/AgCl) electrode, which has a potential of 199mV more positive than the standard hydrogen potential. Continuously purged gas (nitrogen or oxygen) in the sealed cell maintained constant pressure above the solution. A fritted glass capillary was used for continuous aeration/deaeration of the solution throughout the experiment at the rate of ~100mL/min by using a flow meter. An electrically-heated water bath surrounded the test cell and maintained the temperature of the solution. The electrolyte was purged continuously with nitrogen/oxygen for deaeration/aeration for at least 30 minutes before immersing the specimen. The specimen is then inserted into the cell and is maintained at a constant distance (2-3mm) between specimen and Luggin tip to avoid any variation in corrosion current (Icorr) and corrosion potential (Ecorr). After reaching the steady-state open circuit potential, the electrochemical impedance spectroscopy (EIS) tests were carried out between 10 kHz and 10 mHz at an ac voltage of 100 mV rms. The potentiodynamic tests were carried out at a scan rate of 0.2mV/sec. Both tests were conducted using a commercially available potentiostat. The electrolyte was prepared by mixing different kinds of salts in distilled, de-ionized water. After adding the salts to the de-ionized water, the solution was stirred on a hot plate (50°C-60°C) for 2 – 3 hours, and then cooled down to room temperature. Upon cooling, the excess or undissolved salts precipitated out from the solution at the bottom of the flask. The clear water was filtered twice before using as the electrolyte. In this study we used 1X YM water and measured the pH of the solution before and after each experimental run.

The corrosion rate was calculated by following ASTM G59-97² and ASTM G102-89³ procedures. During calculations, the polarization resistance (Rp) of the solution was neglected because it was shown by Yilmaz⁴ that the electrolyte concentration was zero for 1X concentration. Tafel constants for both anodic reaction and cathodic reactions are assumed to be constant (0.12V/decade).⁵ From the polarization resistance (Rp) value, the corrosion current density was calculated.
using equation 1.1, where $K_1 = 3.27 \times 10^{-3} \text{mm-g/µA-cm·year}$, $I_{corr} = \mu A/cm^2$, $\rho = 7.87 \text{g/cm}^3$ and $EW = 27.95 \text{gm/equivalent.}$

$$CR = K_1 \frac{I_{corr}}{\rho} EW$$  \hspace{1cm} (1.1)

### 1.1.3 Results & Discussion

In this section we present the results of potentiodynamic and impedance spectroscopy studies of 4340 steel in YM 1X solution, as well as a comparison of the activation energy of 4340 steel and other materials in 1X solution.

#### 1.1.3.1A. Potentiodynamic studies - effect of temperature on the corrosion behavior (aerated & deaerated YM waters)

**Deaerated YM Waters:** Representative potentiodynamic scans, as well as their respective corrosion rates as a function of temperature, are presented in Figures 1.1.1 – 1.1.4. For 1X concentration, the observed Ecorr is -0.741V at room temperature (25°C). At 45°C, it increases to its highest potential of -0.735V, but then decreases to -0.737V at 65°C, finally dropping to -0.705V at 90°C. Figures 1.1.3 and 1.1.4 show both the corrosion rate and average corrosion rate as a function of temperature. As can be seen, the overall corrosion rate increases polynomially as the temperature increases, resulting in a 3rd-order equation. This trend is consistent with previous studies conducted by Yilmaz.4

**Potentiodynamic Scans of 4340 Steel at Different Temperatures - Deaerated at 1X Concentration**

![Potentiodynamic Scan of 4340 Steel at Different Temperatures - Deaerated at 1X Concentration](image1)

**Corrosion Rates vs. Temperature for 4340 Steel - Deaerated at 1X Concentration**

$$y = 0.0004x^3 - 0.0532x^2 + 2.7479x - 13.196$$

$$R^2 = 0.9852$$

![Corrosion Rates vs. Temperature for 4340 Steel - Deaerated at 1X Concentration](image2)

**Average Corrosion Rate vs. Temperature - Deaerated at 1X Concentration**

$$y = 0.0004x^3 - 0.0532x^2 + 2.7479x - 13.196$$

$$R^2 = 0.995$$

![Average Corrosion Rate vs. Temperature - Deaerated at 1X Concentration](image3)

**Aerated YM Waters:** Representative potentiodynamic scans, as well as their respective corrosion rates as a function of temperature, are presented in Figures 1.1.5 – 1.1.8. For 1X concentration, the observed Ecorr is -0.397V at room temperature (25°C). At 65°C and 75°C, it decreases to -0.547V, dropping to -0.571V at 85°C. However, it rebounds slightly to -0.570V at 90°C. Figures 1.1.7 and 1.1.8 show the corrosion rate and average corrosion rate as a function of temperature. As in the deaerated condition, the overall corrosion rate increases polynomially as the temperature increases, resulting in a 3rd-order equation. However, unlike the deaerated condition, the corrosion rate hits a maximum

**Potentiodynamic Scan of 4340 Steel at Different Temperatures - Aerated at 1X Concentration**

![Potentiodynamic Scan of 4340 Steel at Different Temperatures - Aerated at 1X Concentration](image4)

**Corrosion Rates vs. Temperature for 4340 Steel - Aerated at 1X Concentration**

**Average Corrosion Rate vs. Temperature - Aerated at 1X Concentration**
at 75°C, then begins to decrease to 90°C. This is not quite what Yilmaz found in his study, but its pretty close. The average corrosion rates in aerated and deaerated YM 1X solution are shown in Table 1.1.2.

**Table 1.1.2 Corrosion rates of 4340 steel at different temperatures in 1X YM water**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Environment</th>
<th>Corrosion Rate (microns/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Deaerated</td>
<td>28.7765</td>
</tr>
<tr>
<td>45</td>
<td>Deaerated</td>
<td>38.7504</td>
</tr>
<tr>
<td>65</td>
<td>Deaerated</td>
<td>53.2613</td>
</tr>
<tr>
<td>75</td>
<td>Deaerated</td>
<td>65.084</td>
</tr>
<tr>
<td>85</td>
<td>Deaerated</td>
<td>81.5452</td>
</tr>
<tr>
<td>90</td>
<td>Deaerated</td>
<td>100.6153</td>
</tr>
<tr>
<td>25</td>
<td>Aerated</td>
<td>244.1192</td>
</tr>
<tr>
<td>45</td>
<td>Aerated</td>
<td>798.6561</td>
</tr>
<tr>
<td>65</td>
<td>Aerated</td>
<td>1052.747</td>
</tr>
<tr>
<td>75</td>
<td>Aerated</td>
<td>1445.804</td>
</tr>
<tr>
<td>85</td>
<td>Aerated</td>
<td>1303.296</td>
</tr>
<tr>
<td>90</td>
<td>Aerated</td>
<td>1296.06</td>
</tr>
</tbody>
</table>

**Figure 1.1.5. Potentiodynamic scan for 4340 steel in deaerated, 1X YM water at 75°C, 85°C, and 90°C.**

**Figure 1.1.6. Potentiodynamic scan for 4340 steel at different temperatures in aerated at 1X Concentration.**

**Figure 1.1.7. Corrosion rates as a function of temperature in aerated, 1X YM water.**

**Figure 1.1.8. Averaged corrosion rates as a function of temperature in aerated, 1X YM water.**
1.1.3.1B. Impedance Spectroscopy studies - effect of temperature on the corrosion behavior (aerated & deaerated YM waters)

Representative impedance spectroscopy scans are presented for aerated and deaerated conditions in 1X YM water, in Figures 1.1.9 & 1.1.10. As can be seen from the scans, lower resistance is observed in the aerated condition, indicating a higher corrosion rate, than in the deaerated condition. This corresponds with studies done by Arjunan on Low Carbon Steel (LCS) samples. Also, in the deaerated condition, the Nyquist curves change from a semicircle at 25°C, to nearly a full Warburg tail at 85°C and 90°C. This indicates that at 45°C and higher, a diffusional process begins to take over until at higher temperatures, the process becomes nearly all diffusion-controlled.

Nyquist Plots of 4340 Steel at Different Temperatures - Deaerated at 1X Concentration

Nyquist Plots of 4340 Steel at Different Temperatures - Aerated at 1X Concentration

Figure 1.1.9. Impedance spectroscopy scans for 4340 steel in deaerated, 1X YM water. Figure 1.1.10. Impedance spectroscopy scan for 4340 steel in aerated, 1X YM water.

1.1.3.1C. Comparison of activation energies on the corrosion behavior in aerated & deaerated 1X YM waters

The activation energy required for a material to begin to corrode is dependent on the temperature and electrolyte concentration. This energy is the stored binding energy between the individual atoms - notably iron. The amount of energy stored depends on the composition of the material. High-strength low-alloy (HSLA) steels have higher hardness values than plain-carbon steels (of similar carbon content). Therefore, HSLA steels tend to have lower activation energies than plain-carbon steels, and higher corrosion rates at the equivalent temperature and solution concentration. Studies done by Yilmaz and Arjunan tend to corroborate this theory; however, this is evident only in the aerated, 1X YM environment. In the deaerated environment, this is not the case, as can be seen in Figures 1.1.11 and 1.1.12. Additionally, the calculated energies for Williams Medium Carbon Steel (MCS) do not follow the reported values exactly. In the literature, Yilmaz reports activation energies of 18 & 30 kJ/mol in deaerated and aerated environments, respectively, giving a difference of 150%. The calculated values using the reported corrosion rates show activation energies of 19.3 & 32.6 kJ/mol in deaerated and aerated environments, respectively, with a difference of 168.7%. The activation energies for 4340 steel in deaerated and aerated environments, respectively, are 16.4 and 22.4 kJ/mol, with a difference of 1.37%. These differences could be due to round-off errors, but are close to the 150% difference reported by Yilmaz. Figures 1.1.13 and 1.1.14 show the calculated activation energy (Q) values for both 4340 steel and Williams MCS.
Figure 1.1.11. CR vs. Temperature for 4340 steel, MCS$^4$, and LCS$^5$ in deaerated 1X YM water.

Figure 1.1.12. CR vs. Temperature for 4340, MCS$^4$, and LCS$^5$ in aerated 1X YM water.

Figure 1.1.13. Activation energies for 4340 steel in aerated & deaerated 1X YM water.

Figure 1.1.14. Activation energies for MCS$^4$ in aerated & deaerated 1X YM water.

References


2. Corrosion rates of Alloy 22. Using YM Simulated Waters

We use a different approach to present the next section in this report, as it is convenient to show the summary of all results in which comparison of corrosion rates of baseline material with a rock bolt are. We include the entire manuscript that was sent to Electrochimica Acta (2006) and was written in this quarter.
Electrochemical Evaluation of Passive Corrosion Behavior of Alloy 22
In Complex Ionic Electrolyte
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Keywords: Potentiodynamic Scan, Potentiostatic Scan, Corrosion Rate, Passivation, Polarization Resistance

Abstract
Alloy 22 (Ni-22Cr-13Mo-3Fe-3W) is a candidate alloy for nuclear materials storage containers in the High Level Nuclear Waste Repository as well as for other applications. In this study, we present the results of our investigation on the corrosion behavior of Alloy 22 as a function of temperature and concentration in a complex multi-ionic electrolyte. This electrolyte used in this study is a simulation of ground water which has significance the environment of the repository in which the alloys are used. Electrochemical potentiodynamic and potentiostatic tests have been used to determine the passivation behavior of Alloy 22 in simulated electrolyte. Corrosion rate was calculated by using polarization resistance method using deaerated (nitrogenated) and aerated (oxygenated) electrolyte. It was interesting to note that the corrosion rate was higher using deaerated electrolyte as compared to the aerated; suggesting aeration is conducive to formation of passive films that inhibit the corrosion process. The activation energies were calculated for the process. The corrosion rates for Alloy 22 in this study were compared to the rates reported in literature. We noted transpassive behavior in higher concentration electrolyte and at higher temperatures. Results from Potentiodynamic, Potentiostatic, Optical and Scanning Electron Microscopy (SEM) coupled with Energy Dispersive spectroscopy (EDS) are presented.

Introduction
The use of nuclear materials for production of electricity as well as for defense purposes over the past decades has produced in a large stockpile of used radioactive materials. There is an urgent need for safe storage and/or disposal of these spent nuclear materials to safeguard the environment from any inadvertent exposure. It has been proposed that a deep underground repository is suitable for storage of these nuclear materials. Selection of a unique site with appropriate ground water conditions is necessary; a site has been selected in Nevada from which electrolyte concentrations have been determined [1]. The spent nuclear fuel containers are generally referred to as waste packages. These waste packages consist of two concentric metal containers; the outer container is made of Alloy 22 (a highly corrosion resistant Ni-Cr-Mo alloy) and a thick inner container made of type 316 nuclear-grade stainless steel. The purpose of the inner container is to provide shield for radiation and mechanical integrity. The waste packages will be approximately 18 feet in length and 5 feet in diameter. Once the radioactive waste is placed in the waste packages, the lid will be closed by multipass gas tungsten arc welding with ERNiCrMo-10 filler metal, which is close to the composition of Alloy 22 (N06022). Completely sealed waste packages will be stored in the repository tunnels.

Alloy 22 (N06022) is a nickel based superalloy containing 22% chromium, 13% molybdenum, 3% tungsten by weight. This is used extensively for industrial applications because of its high corrosion resistance under various aggressive aqueous environments. The high corrosion resistance of Alloy 22 under both oxidizing and reducing conditions has led to the selection of this superalloy for use in outer shell of the radioactive disposal container in the Yucca mountain nuclear repository [2,3]. The corrosion resistance of this Ni-based superalloy is attributed to the alloying element chromium that increases the passive region and also reduces the passive current [4,5]. The alloying elements Mo and W lower the current for hydrogen discharge under reducing conditions [6]. The corrosion behavior of Alloy 22 has been the subject of intensive research since it has been selected for the waste package container for YM repository.

Rebak et al [7] have extensively studied the electrolytic behavior of nickel based alloys and reported that Ni-based alloys are susceptible to stress corrosion cracking. They [7] also observed increased corrosion rates with increases in electrolyte temperature and concentration. Cragnolino et al. [8] studied the passive corrosion behavior of Alloy 22 under different concentration of chloride ions. They determined that the passive current density that was independent of temperature and the passivity was almost independent of potential, Cl⁻ concentration and the pH. The susceptibility of Alloy 22 to localized corrosion in lead-containing solution was reported by Pan et al [9]. They observed that the
presence of lead species in a deaerated, super-saturated PbCl$_2$ solution with a pH of 0.5 promotes a pronounced anodic peak that increases the passive current density and simultaneously enhances the dissolution of Alloy 22. Evans et al [10] studied the anodic behavior of Alloy 22 in calcium chloride and calcium nitrate brines. The observed corrosion rates were lower in calcium nitrate containing solutions than in pure calcium chloride solutions. The addition of nitrate also decreased the anodic passive current density of Alloy 22. Day et al studied the corrosion behavior of Alloy 22 in oxalic acid and sodium chloride solutions and found that the corrosion rate of alloy 22 in 0.1M oxalic acid at 60°C was 200µm/year [11]. They also determined that Alloy 22 was not susceptible to localized corrosion in oxalic acid solution although, they found an increased corrosion rate as the temperature increased. Estill [12] et al studied the corrosion rate of Alloy 22 as a function of immersion time in six different mixtures of NaCl and KNO3 solution at 100°C. They reported that as the immersion time increases the corrosion potential increase and the corrosion rate decreases. They after 8 months observed a maximum corrosion rate of 50nm/year in concentrated brine solutions at 100°C.

In this study, we have assessed the corrosion behavior of Alloy 22 in simulated YM environment using electrochemical methods. The effect of various experimental parameters such as temperature of the electrolyte, aeration/deaeration on the corrosion behavior has also studied. Yilmaz et al have conducted a similar study of the corrosion behavior of carbon steel rock bolt in this simulated YM water [13]. The effect of temperature (from 25°C to 90°C) and the environment (aerated or deaerated) on the corrosion behavior of Alloy 22 has also been studied in 100x YM water. The composition of the simulated YM water is given in Table 1. The film formed on Alloy 22 at different potential at room temperature has been characterized by using SEM and EDX under deaerated conditions. Since the passive film formed on Alloy 22 is few nanometers thick, it is very hard to characterize the film by using SEM and EDX. So the X-ray Fluorescence Spectroscopy XPS and Auger Electron Spectroscopy (AES) are the best techniques for this kind of analysis.

**Experimental Procedure**

Alloy 22 specimens for electrochemical tests were prepared from commercially available mill annealed Alloy 22. The Alloy 22 from Haynes International was reanalyzed for chemical analysis at LTI Corporation. The nominal composition of the as-received alloy as well as analyzed composition is given in Table 1.

<table>
<thead>
<tr>
<th>Element (weight percent)</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>Si</th>
<th>Mn</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>V</th>
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<tbody>
<tr>
<td>Haynes</td>
<td>56.60</td>
<td>1.05</td>
<td>21.38</td>
<td>13.55</td>
<td>3.07</td>
<td>3.88</td>
<td>0.028</td>
<td>0.24</td>
<td>0.005</td>
<td>0.006</td>
<td>0.0057</td>
<td>0.14</td>
</tr>
<tr>
<td>LTI</td>
<td>56.86</td>
<td>1.00</td>
<td>21.20</td>
<td>13.50</td>
<td>3.00</td>
<td>3.90</td>
<td>0.050</td>
<td>0.31</td>
<td>0.002</td>
<td>0.010</td>
<td>0.0100</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Disc shaped test specimens were cut out from the plate sample. The test specimen was mounted in epoxy with ~1 cm$^2$ exposed surface area. After the molding, the electrical connection between the sample and the wire checked with a voltmeter. Before the experiment the specimens were polished down to 600 grit SiC emery papers. These prepared specimens were degreased with acetone and ultrasonically washed it with de-ionized water for 5 minutes before using them for electrochemical testing.

All the electrochemical experiments were conducted in a typical 1 liter Pyrex glass flask covered with a polytetrafluoroethylene lid. The lid had many ports containing working electrode, counter electrode (platinum), gas spurge, thermo couple, inlet and outlet for the gas, luggin probe connected to silver/silver chloride (Ag/AgCl) reference electrode through salt bridge (agar-agar solution) and a gas trap (ASTM G5) [14]. A schematic of the cell can be found in the work by Yilmaz et al [13] on carbon steel. A large (~10 cm$^2$) platinum sheet sealed to a glass capillary was used as a counter electrode. The reference electrode was saturated silver/silver chloride (Ag/AgCl) electrode, which has a potential of 199mV more positive than the standard hydrogen potential. The Luggin probe tip and Ag/AgCl reference electrode were connected via the electrolyte (YM water) in the bridge. Continuously purged gas (nitrogen or oxygen) in the sealed cell maintained constant pressure above the solution, and provided a slight positive pressure. A sealed glass capillary was used for the thermocouple for controlling the temperature of the electrolyte. A fritted glass capillary was used for continuous aeration/deaeration of the solution throughout the experiment at the rate of 100mL/min. An electric mantle heater surrounded the test cell and a PID (Proportional, Integral, Derivative) type temperature controller maintained the temperature of the solution. For high temperature experiments a condenser has been used to avoid electrolyte evaporation during the test. The electrolyte was purged continuously with nitrogen/oxygen for deaeration/aeration for ½ hour before immersing the test specimen. The specimen was then inserted into the cell and
maintained a constant distance (2-3mm) between the specimen and Luggin tip. After immersing the sample in the electrolyte for one hour the potentiodynamic tests were conducted at a scan rate of 0.2mV/sec using a commercially available Potentiostat. The corroded surface was characterized by using optical microscope for different temperatures and concentrations.

The composition of the simulated YM water is established by Yilmaz et al [13] and is given in Table 2 for 1X concentration. The electrolyte was prepared by mixing different kind of salts in distilled, de-ionized water. Table 3 shows the different salts that were used accordingly to make 1X YM water. After adding the salts to the de-ionized water the solution was stirred in a hot plate (50°C-60°C) for half an hour and then it is cooled down to room temperature. The excess or undissolved salts precipitated from the solution at the bottom of the flask. The clear solution was filtered before using as an electrolyte. In this study we used 1X, 10X and 100X YM solutions and the measured pH of the solution was 7.8, 8.2 and 8.4 accordingly.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Na⁺</th>
<th>SiO₂⁻</th>
<th>Ca²⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>F⁻</th>
<th>NO₃⁻</th>
<th>pH</th>
</tr>
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<tbody>
<tr>
<td>1XYM</td>
<td>61.3</td>
<td>70.5</td>
<td>101</td>
<td>8.0</td>
<td>17.0</td>
<td>200</td>
<td>117</td>
<td>116</td>
<td>0.86</td>
<td>-</td>
<td>7.8</td>
</tr>
<tr>
<td>100XYM</td>
<td>6130</td>
<td>7050</td>
<td>10100</td>
<td>800</td>
<td>1700</td>
<td>20,000</td>
<td>11,700</td>
<td>11,600</td>
<td>86</td>
<td>-</td>
<td>8.2</td>
</tr>
<tr>
<td>SCW</td>
<td>40,900</td>
<td>&lt;40</td>
<td>&lt;1</td>
<td>3400</td>
<td>&lt;1</td>
<td>70,000</td>
<td>6700</td>
<td>16,700</td>
<td>1400</td>
<td>6400</td>
<td>8.0</td>
</tr>
<tr>
<td>SAW</td>
<td>40,900</td>
<td>&lt;40</td>
<td>1000</td>
<td>3400</td>
<td>1000</td>
<td>0</td>
<td>24,250</td>
<td>38,600</td>
<td>0</td>
<td>23,000</td>
<td>2.8</td>
</tr>
<tr>
<td>J-13</td>
<td>45.80</td>
<td>61</td>
<td>13.0</td>
<td>5.04</td>
<td>2.01</td>
<td>128.90</td>
<td>7.14</td>
<td>18.4</td>
<td>2.18</td>
<td>8.78</td>
<td>7.4</td>
</tr>
<tr>
<td>BSW</td>
<td>231,225</td>
<td>9038</td>
<td>---</td>
<td>81,480</td>
<td>---</td>
<td>107,171</td>
<td>169,204</td>
<td>16,907</td>
<td>1616</td>
<td>177,168</td>
<td>13.0</td>
</tr>
<tr>
<td>SDW</td>
<td>440</td>
<td>24</td>
<td>&lt;1</td>
<td>33</td>
<td>&lt;1</td>
<td>---</td>
<td>74</td>
<td>144</td>
<td>8</td>
<td>60</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Table 3. YM water chemistry for 1X concentration per Liter

<table>
<thead>
<tr>
<th>No.</th>
<th>CHEMICALS</th>
<th>Weight (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Magnesium sulfate(MgSO₄.7H₂O)</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Magnesium chloride(MgCl₂.6H₂O)</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Calcium chloride(CaCl₂,2H₂O)</td>
<td>196</td>
</tr>
<tr>
<td>4</td>
<td>Calcium sulfate(CaSO₄.2H₂O)</td>
<td>210</td>
</tr>
<tr>
<td>5</td>
<td>Potassium Bicarbonate(KHCO₃)</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>Sodium Bicarbonate(NaHCO₃)</td>
<td>200</td>
</tr>
<tr>
<td>7</td>
<td>Sodium Silicate(Na₂SiO₃.9H₂O)</td>
<td>210</td>
</tr>
<tr>
<td>8</td>
<td>Sodium Fluoride (NaF)</td>
<td>2</td>
</tr>
</tbody>
</table>

Corrosion rate was calculated by following ASTM G59 [15] and ASTM G102 [16] procedures. During calculating the polarization resistance (R_p) solution resistance is neglected because it was shown by Yilmaz et al. [13] for the same electrolyte concentration to be zero for 1X, 10X and 100X concentrations. Tafel constants for both anodic reaction and cathodic reaction are assumed to be constant (0.12V/decade). From the polarization resistance (R_p) value the corrosion current density is calculated and using equation 1 corrosion rate is calculated.

\[
CR = K_i \frac{i_{corr}}{\rho} EW
\]

Where,

\[
K_i = 3.27 \times 10^{-3} \text{ mm.g/µA.cm.year}
\]

\[
i_{corr} = \text{µA/cm²}
\]

\[
\rho = 8.69 \text{ g/cm³ (ASTM G102)}
\]

\[
EW = 23.28 \text{ unit less (ASTM G102)}
\]

The sample for the SEM and EDX study was prepared by running the potentiostatic experiments at selected potentials. The potentials were chosen based on the potentiodynamic scan run at room temperature. The main objective was to characterize the film formed at different applied potential. The sample was prepared by running it at a fixed potential for 1 hour.
Results

1. Corrosion Behavior in de-aerated water
   A. Effect of Temperature

   Potentiodynamic polarization curves for Alloy 22 at different temperature in 100x simulated YM water are presented in Figure 1. The range for corrosion potential was approximately -700mV±50mV for all the temperatures. The repeatability of the tests at room temperature is shown in Figure 2. These tests were conducted on different days and also separately prepared simulated water to check for any systematic experimental errors. Experimental results showed that the corrosion potential of all these experiments were within the 50mV range. The corrosion potential reported in this study is lower that reported by previous researchers [9,10,11], a plausible explanation for this lower corrosion potential is given below. Evans et al. [10] reported a corrosion potential of -400 mV for the Alloy 22 in calcium chloride solution. It is well known that the corrosion potential is highly dependent on the electrolyte temperature and the immersion time. The electrolyte we used in our experiment is a mixed ionic solution of different species (composition given in Table 1). Corrosion potentials reported here are based on a relatively short-term test by stabilizing the solutions for approximately half hour and obtaining steady state conditions which was confirmed by repeatability tests (Figure 2). It should be noted that the corrosion potential of Alloy 22 may vary if these tests are performed after considerable prolonged period of time.

In the anodic regions we found transpassive behavior at higher potentials and concentration of electrolyte, so to make sure that this phenomenon is not due to the Platinum electrode, potentiodynamic scans were obtained using Pt as the working electrode, under the similar experimental conditions to determine if there any extraneous influence of electrolyte itself or electrode on the corrosion potential. The result of a potentiodynamic scan on pure Pt as working electrode in deaerated condition using 100X electrolyte is shown in Figure 3. This shows that Pure Pt has a lower potential (high exchange current density) for hydrogen reduction, Pt acts like a hydrogen electrode in this electrolyte. This experiment on pure Pt suggests that the observed low $E_{corr}$ for Alloy 22 in simulated electrolyte is not controlled or affected by other redox reactions of species in the electrolyte.
Figure 2. Repeatability of Potentiodynamic scans of Alloy 22 at room temperature in deaerated condition.

Figure 3. Polarization Curve of Pure Pt as working electrode in 100X YM water.
The potentiodynamic scan of Alloy 22 (deaerated condition in Figure 1) exhibits a distinct passive region at all the temperatures. Typically, the passivation starts at approximately -600mV and ends at +400mV; further localized variation in current density at higher potentials are due to presence of a transpassive region which occurs at specific temperatures. This transpassive region was also observed by other researchers using different electrolytes [17, 18]. The highest increase in current density is observed at 25°C and it decreases as the temperature increases. The potential at which we observed this transpassive phenomena decreases as the temperature increases. At the same time the critical current density also decreases. At 25°C the potential at which the redeposition occurs is +564mV, at 45°C +525mV, 65°C is +484mV and at 90°C is +434mV. Further discussion on this region of the potentiodynamic scan is given in the discussion section below.

The corrosion potential for all temperatures is between -700mV to -750mV (Figure 1). The observed $E_{corr}$ is ~-750mV at room temperature and increases with the temperature. At low temperatures (between 25°C to 45°C) the increase in $E_{corr}$ is not significant, but above 45°C there is a significant change; the highest observed $E_{corr}$ is -687mV at 90°C. The critical current density for passivation increases with the increase in temperature of the electrolyte (Figure 1). The room temperature critical current density is $5.26 \times 10^{-6}$ A.cm$^{-2}$ at -200mV applied potential. As the temperature increases the current density also increases at the same applied potential; varying the temperature from 45°C to 90°C the observed current densities vary from $8.26 \times 10^{-6}$ to $1.34 \times 10^{-5}$ to $5.02 \times 10^{-5}$ A.cm$^{-2}$, respectively. The range of potential of the passive region decreases as the temperature increases and the shortest passive region is observed at 90°C.

The corrosion rate is calculated by using the polarization resistance method and is discussed in the experimental section. The results of the corrosion rate in deaerated conditions using 100X electrolyte concentration are shown in Table 4.

Table 4. Corrosion Rates of Alloy 22 in Simulated YM Water in aerated and deaerated conditions

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Temperature(°C)</th>
<th>Conditions</th>
<th>$R_p$(ohm.cm$^2$)</th>
<th>$I_{corr}$(µA/cm$^2$)</th>
<th>Corrosion rate (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100X</td>
<td>25°C</td>
<td>Deaerated</td>
<td>3064</td>
<td>8.50E-06</td>
<td>74</td>
</tr>
<tr>
<td>100X</td>
<td>45°C</td>
<td>Deaerated</td>
<td>2015</td>
<td>1.29E-05</td>
<td>113</td>
</tr>
<tr>
<td>100X</td>
<td>65°C</td>
<td>Deaerated</td>
<td>1624</td>
<td>1.60E-05</td>
<td>141</td>
</tr>
<tr>
<td>100X</td>
<td>90°C</td>
<td>Deaerated</td>
<td>1404</td>
<td>1.86E-05</td>
<td>163</td>
</tr>
<tr>
<td>100X</td>
<td>25°C</td>
<td>Aerated</td>
<td>21708</td>
<td>1.20E-06</td>
<td>10</td>
</tr>
<tr>
<td>100X</td>
<td>45°C</td>
<td>Aerated</td>
<td>10971</td>
<td>2.37E-06</td>
<td>21</td>
</tr>
<tr>
<td>100X</td>
<td>65°C</td>
<td>Aerated</td>
<td>5432</td>
<td>4.80E-06</td>
<td>42</td>
</tr>
<tr>
<td>100X</td>
<td>90°C</td>
<td>Aerated</td>
<td>3540</td>
<td>7.36E-06</td>
<td>64</td>
</tr>
</tbody>
</table>

Also, these are graphically represented in Figure 4 showing the gradual increase in corrosion rates as a function of increasing temperatures. In the temperature range of 25°C to 45°C, the rate of increase in corrosion rate is relatively higher using this electrolyte. Yilmaz et al. [13] observed similar corrosion behavior on medium carbon steel (MCS) using the same electrolyte, but the corrosion rates were higher. At higher temperatures the rate decreases due to the reaction of the metal surface with anions in the electrolyte forming partially protective salt layer. This layer was evident in optical micrographs that were taken after potentiodynamic scans were made at different temperatures. It was found that there was no salt deposit on the metal surface at 25°C, as shown in Figure 5 (top), whereas there surface topography was quite different on the 90°C sample with abundant dispersion of salt layers of varying thickness on the surface of the sample (Figure 5, bottom). This behavior was also observed by Yilmaz et al [13] for medium carbon steel rock bolts. To understand the nature of interaction of this particular electrolyte with the materials surface, Deshukh et al. [19] performed X-ray photoelectron spectroscopy (XPS) and found a protective film of FeCO$_3$ and iron-oxide/hydroxide. The corrosion rate (CR) for the Alloy 22 was 74.49 and 163 µm/year at 25°C and 90°C, respectively. Although we did not indicate a linear behavior of corrosion rates in Figure 5, but to estimate the activation energy for the overall corrosion process we plotted ln CR vs 1/T (K) which is shown in Figure 6; the calculated activation energy was 10.70 kJ/mol (100X water).

At higher temperatures, > 65°C there was preferential etching of the sample surface, revealing the microstructure as shown in Figure 7, after the potentiodynamic test. The micrograph in Figure 7 (top) shows the surface as prepared, before conducting the experiment, the middle optical micrograph shows the condition after the test, and finally the microstructure after removing the surface layer (Figure 7- bottom). All the Alloy 22 samples examined above 65°C after
the potentiodynamic tests showed similar characteristics. It should be noted that that similar potentiodynamic tests performed below 65°C did not change the surface morphology at all. So the corrosion process involved in Alloy 22 in this electrolyte is localized corrosion or grain boundary corrosion.

B. Effect of Concentration of Electrolyte
Three different concentrations (1X, 10X and 100X) of electrolytes were used to evaluate the effect of concentration on corrosion rate. A room temperature potentiodynamic scan for the Alloy 22 under different electrolyte concentrations. The corrosion potentials for these three different concentrations are very close to each other as shown in Figure 8. The corrosion potential increases slightly as the concentration increases from 1X to 100X. The observed \( E_{\text{corr}} \) was -738mV in 1X, -729mV in 10X and -733mV in 100X water. The cathodic portions of the potentiodynamic scans were linear for all concentrations but overlapping. The linearity of the cathodic curve represents that there is no change in the reaction rate or in other words there is no limiting current for the cathodic reactions. The anodic portions of the potentiodynamic
Figure 6. Corrosion rate as a function of temperature in both aerated and deaerated conditions.

Figure 7. Optical Micrograph showing the surface of the sample after potentiodynamic scan at 65°C in deaerated condition (a) Before Experiment (b) After Experiment (c) After washing the Salt Deposit

scan are significantly different for all concentrations of electrolyte. It is interesting to note that there was no transpassive region observed for 1X and 10X concentrations due to lower levels of ions; this is vital role for the redeposition process beyond the transpassive region. The calculated corrosion rate was lowest in 1X water and highest in 100X water which is shown in Table 5. The observed room temperature corrosion rates are plotted as a function of concentration in Figure 9. From this plot, it can be observed that the corrosion rate increases as a function of concentration significantly as the concentration is increased from 1X to 100X in deaerated electrolyte. The highest corrosion rate of 163 µm/year is observed at 90°C in 100X water. Pulvirenti et al. [20] found a corrosion rate of 106µm/year in J13 (1000X) electrolyte at pH1, using weight loss method.

2. Corrosion Behavior in Aerated Electrolyte
A. Effect of Temperature
Potentiodynamic polarization tests on Alloy 22 in 100 X electrolyte (at different temperatures in aerated atmosphere) showed a distinct passive region in the anodic portion of the potentiodynamic plot; these are similar to those observed in Figure 8. Potentiodynamic Scan showing the effect of concentration of the Electrolyte in deaerated conditions at 25°C.

![Potentiodynamic Scan showing the effect of concentration of the Electrolyte in deaerated conditions at 25°C.](image)

Figure 8. Potentiodynamic Scan showing the effect of concentration of the Electrolyte in deaerated conditions at 25°C.

Corrosion rate as a function of concentration for both aerated and deaerated conditions at 25°C.

![Corrosion rate as a function of concentration for both aerated and deaerated conditions at 25°C.](image)

Figure 9. Corrosion rate as a function of concentration for both aerated and deaerated conditions at 25°C.
Table 5. Corrosion Rates of Alloy 22 in Simulated YM Water.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Temperature(°C)</th>
<th>Conditions</th>
<th>$R_p$(ohm.cm²)</th>
<th>$I_{corr}$(µA/cm²)</th>
<th>Corrosion rate (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>25°C</td>
<td>Deaerated</td>
<td>19856</td>
<td>1.31E-06</td>
<td>11</td>
</tr>
<tr>
<td>10X</td>
<td>25°C</td>
<td>Deaerated</td>
<td>4588</td>
<td>5.86E-06</td>
<td>50</td>
</tr>
<tr>
<td>100X</td>
<td>25°C</td>
<td>Deaerated</td>
<td>3064</td>
<td>8.50E-06</td>
<td>74</td>
</tr>
<tr>
<td>1X</td>
<td>25°C</td>
<td>Aerated</td>
<td>126139</td>
<td>2.07E-07</td>
<td>2</td>
</tr>
<tr>
<td>10X</td>
<td>25°C</td>
<td>Aerated</td>
<td>46041</td>
<td>5.66E-07</td>
<td>5</td>
</tr>
<tr>
<td>100X</td>
<td>25°C</td>
<td>Aerated</td>
<td>21708</td>
<td>1.20E-06</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 10. Polarization Curve of Alloy 22 in 100x aerated YM water at 25°C.

deaerated waters. In addition, it can be noted that the passivation corrosion current density increases from 25° to 90°C (Figure 10). As far as the corrosion potential is concerned, it can be noted that it is lower at 90°C than at 25°C, which again suggests higher corrosion rate at 90°C, this behavior is common in steels as reported by Yilmaz et al [13]. The observed corrosion potential was -285mV at 25°C, -422mV at 45°C, -424mV at 65°C and -429mV at 90°C. The transpassive region which was observed in using the deaerated electrolyte was also observed with the aerated electrolyte and occurs at around +600mV (Figure 10). Also, (only) in the aerated condition the transpassive region is not very prominent at higher temperature (65° and 90°C), noting that peak potential lowers slightly from +594 mV to +574 mV when the temperature increased from 25°C to 45°C.

The corrosion rates obtained using 100X electrolyte (aerated conditions) at different temperatures are presented in Table 4 and plotted in Figure 4. From Figure 4 it is clear that as the temperature increased the corrosion rate increased with nearly the same rate. The corrosion rate was 10.51µm/year at 25°C and it increased to 64.47µm/year at 90°C. Also note that the corrosion rates are lower than deaerated condition which is unusual as compared to common steels that we have extensively studied using the same electrolyte [13]; these are discussed in next section. In their study they reported that the corrosion rate reached highest value at 65°C and the rate decreased again at 90°C. The corrosion rate in aerated
condition was lesser at all temperatures compared to deaerated conditions. In aerated conditions, because of the presence of more dissolved oxygen in electrolyte it is more favorable to form \(\text{Cr}_2\text{O}_3\) as a protective film on the surface that inhibits the overall corrosion process. The activation energy was calculated by plotting \(\ln \text{CR} \) vs \(1/T \) (K) which is shown in Figure 6. The calculated activation energy was 25.67KJ/mol which is higher than the deaerated condition. Optical micrographs were taken after the potentiodynamic scan at all temperatures that show there was no significant attack at lower temperatures. Figure 11 shows a micrograph taken after the potentiodynamic scan at 90°C which are some attack (pits as well as grain boundary) on the surface of the sample, probably due to the high potentials applied during the scan.

Figure 11. Optical micrograph showing some pits as well as salt deposits after the potentiodynamic scan at 90°C in aerated conditions.

B. Effect of concentration of electrolyte

The potentiodynamic scans for the Alloy 22 show a similar behavior to those of deaerated condition with some variations (Figure 12). The effect of concentration of the electrolyte is pronounced in the aerated electrolyte as compared to the deaerated one with respect to the corrosion potential. The \(E_{\text{corr}}\) decreased as the concentration of the electrolyte increased which is opposite in case of deaerated conditions. The highest \(E_{\text{corr}}\) of +75.8mV is observed in 1X water whereas for 10X it was -180mV and for 100X it was -285mV. The anodic portion of the curve was quite similar in nature as in the aerated conditions. It is interesting to note that there was no transpassive region observed in case of 1X and 10X electrolyte; as observed in the deaerated

Figure 12. Potentiodynamic Scan showing the effect of concentration of the Electrolyte in aerated conditions at 25°C.
electrolyte. However, using 100X electrolyte the transpassive region is observed at approximately the same potential (~600mV) for both aerated and deaerated conditions. From Figure 12 it can be seen that the current density shifts as a function of concentration suggesting propensity for higher corrosion rates. These corrosion rates that increase from increased from 1X to 100X are tabulated in Table 5 and are shown graphically in Figure 9 (the x-axis is logarithmic). The observed corrosion rate was 1.81µm/year in 1X water, 4.96µm/year in 10X water and 10.51µm/year in 100X water.

3. Effect of Aeration and Deaeration
Two potentiodynamic scans, one in aerated and other in deaerated conditions are presented in Figure 13 in 100X water at 65°C. Figure 13 shows that the corrosion potential is higher in aerated condition that in deaerated condition. From the same figure we see that the corrosion current is higher in case of deaerated condition, which implies a higher corrosion rate. The passive current density is higher in aerated condition than deaerated conditions. In case of deaerated conditions we observed a pronounced re-deposition peak whereas for aerated condition there was hardly any peak. The corrosion current for deaerated condition is much higher than the aerated conditions which attributed to the higher corrosion rate in deaerated conditions. In the same plot we have presented the optical micrograph for this sample. The optical micrograph was taken after the potentiodynamic scans. The micrograph for the aerated conditions shows no visible corrosion but in the deaerated micrograph there was preferential attack on the grain boundary.

![Figure 13. Figure showing the effect of aeration and deaeration on Alloy 22 at 65°C.](image)

Discussions

1. Characterization of Passive films at Different Potentials Using Potentiostatic Tests
A room temperature potentiodynamic test was first performed on Alloy 22 (Figure 14) to set the potentials at -200, +400, +600, and +800 mV of interest. Then maintaining the same potential we observed the change in current density. In general, the current density decreased as a function of time. The potentials were chosen from different passive and transpassive regions of the potentiodynamic scan in deaerated condition (Figure 14). The corresponding potentiostatic scans were also conducted in deaerated condition. A plot of current as a function of time for potentiostatic scans are shown in Figure 15, the reduction in current indicates that there is formation of an oxide film on the specimen that
inhibits the flow of current. At -200mV and +400mV potential, the current drops rapidly due to the formation of impervious oxide film and hence the slope of current versus time is higher. It should be noted that the transpassive region at +600 mV and +800 mV show that current does not decrease substantially after about an hour, whereas in the passive region (-200 mV and +400 mV) is continued decrease in the current density as function. Figure 14. Polarization Curves showing the potentials at which the SEM and EDX was studied (for 100X YM water at 25°C).

The samples from the potentiostatic tests were characterized for changes in chemistry of the film and microstructure. The SEM micrographs and EDS analyses taken after constant potential of -200 mV and +400 mV charged samples shown in Figures 16(a) and 16(b) indicate no surface deposit. The chemical composition of the Alloy 22 matrix showed the oxygen peak indicating formation of a thin layer of passive film. However, SEM and EDS results from samples subject to higher potentials (+600mV and +800mV) as shown in Figure17(a) and 17(b) clearly show a surface salt layer containing Si, Mg, Ca species along with increased oxygen content providing evidence for the transpassive phenomena (formation of hydroxides of Si, Mg, Ca). We propose to conduct more work to characterization this film formed under both aerated and deaerated condition by using X-ray Photoelectron Spectroscopy (XPS). Szmodis et al. [21] also observed an abrupt change in current density (see Figure 15), but they observed two of these events; one of the event (~300 mV) was suggested to be due to the formation of a passive oxide layer and the other (~800 mV) due to the formation of porous oxide layer (using SCW-Table 1 waters at pH8). It should be noted that in our study the event of currently density change occurred at 600 mV which appears to be analogous to the one at ~800 mV in reference 21. Even though they reported the 800 mV peak is due to the formation of Mo, Cr, Ni oxide layer, yet we observed additional Mg, Si and Ca along with the Ni and Cr in our study (Figure 17).

2. Characterization of the Passive and Transpassive film Using Potentiodynamic Tests The dynamics of the progression of anodic attack on the Alloy 22 were followed to further explore if this transpassive region persisted at higher temperatures we performed in potentiodynamic tests at 65°C. As mentioned above that there is an abrupt increase and decrease in the current density in the anodic region as shown in Figure 18 (top). After completion of the experiment we found that the microstructure similar to that shown in Figure 18 (bottom). This abrupt change in current density results in re-deposition layer; noting the micrograph shown in the inset has that particular layer removed to show the microstructure. In another experiment performed under similar conditions, we stopped the scan at point A in Figure 18 (bottom) to observe the microstructure change and found that the layer was intact which prevented further attack on the surface of the Alloy 22. Comparing the micrographs in Figures 18 (a) and (b) it can observe that when the oxide layer
Figure 15. Potentiostatic scan of Alloy 22 in 100x deaerated YM water at 25°C.

Figure 16. SEM and EDAX results of the sample at different applied potential (a) -200mV (left), (b) +400mV (right)
was removed it revealed the underlying microstructure in Alloy 22 during the transpassive event. It should be noted that Alloy 22 after metallographic polishing does not display any microstructure (Figure 7a) unless it etched electrochemically in oxalic acid; the microstructure is similar to that observed in Figure 18(a) inset.

Figure 18. Potentiodynamic scan of Alloy 22 at 65°C in deaerated conditions along with optical micrographs at potential scan upto +1000mV (top), +400mV (bottom)
Next, we compare the CR’s for the Alloy 22 as a function of pH of the electrolytes, although the electrolytes were different and under aggressive environments (Figure 20-top). It can be seen that the CR’s are significantly higher or so from Gary et al. [22] and Day et al. [11] between 2000 and 3600 µm/yr at pH of 1 to 1.3 (~85°C). Rebak et al. [23] performed immersion tests on Alloy 22 for 4 days with 50% H2SO4 and found the CR to be ~550µm/yr at ~85°C, and the CR’s increased to ~1600 µm/yr at 110°C. It is interesting to note that Day et al. [11] showed a increase of rate from to ~200 to ~3200 µm/yr by increasing the temperature from 60° to 85°C; thus there is temperature dependence regardless of the electrolyte. Rebak et al. [23] found a steep increase in CR’s using immersion tests which are somewhat similar to those obtained by Day et al. [11] used polarization methods.

In this study, although under less aggressive environments (Table 1 100XYM electrolyte), the CR’s varied from 74 to 163 µm/yr under deaerated condition, and 10 to 64 µm/yr in aerated condition, between 25° to 90°C. This increased CR in deaerated is possibly due because an oxide film does not form readily as the oxygen in the electrolyte is depleted during constant bubbling of nitrogen. Examining the combined corrosion rate plot (Figure 20) it can be seen that CR’s obtained in this study (shown in Figure 20 middle) are much higher than those obtained by other investigators [10,12,24,25,28,29,30,31,32] as shown in Figure 20 (bottom) that include the work Rebak et al. [28-29]. They used different electrolytes and different test environment in their studies. In Table 2 we have shown some of the similar electrolytes other researchers [24,25,28,31,32] used in their studies. The reported corrosion rate is much lower Evans et al. [10] showed using CaCl2 electrolyte and polarization method the CR’s ranged from 3 to 10 µm/yr. between 40°C and 100°C; they showed that addition of Ca(NO)3 further reduced the CR to below 3 µm/yr; these rates are much lower than what we observed in this study using the electrolyte in Table 2. Brown et al. [24] performed experiments on ozone and aeration at room temperature and observed very low CR’s (below 8 µm/yr-see Figure 21 and Table 5). Pulvirenti et al. [20] used very aggressive solutions and showed CR’s ranging from 10 to 115 µm/yr at 160°C, pH 1 (Figure 20), however it is difficult to compare these are high temperature and low pH results. F. Hua et al. [25] studied the corrosion behavior of Alloy 22 in Nuclear Waste Repository environment and reported the range of corrosion rate from 0.07µm/yr to 0.30µm/yr in a temperature range of 60°C to 90°C using immersion tests.
In general, the corrosion rates of Alloy 22 using different methods and electrolyte show some temperature dependence at \(~\text{pH}8\) and up to 95°C, whereas, under acidic conditions (\(\text{pH}1\) or so) the CR’s are very high comparing to the data obtained in this study using 100X YM water. We suggest this may be due to the fact that there is more chlorine present and lack nitrates (Table 2) in our electrolyte, as compared to others.

**Table 6. Corrosion Rates of Alloy 22 in under Different Environments.**

<table>
<thead>
<tr>
<th>Author</th>
<th>Electrolyte</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>CR ((\mu)m/year)</th>
<th>Time</th>
<th>Test Method</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulvirenti et al. [20]</td>
<td>J13x1000</td>
<td>160</td>
<td>1</td>
<td>102</td>
<td>14 days</td>
<td>weight loss</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1N HNO₃</td>
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<td>16</td>
<td>14 days</td>
<td>weight loss</td>
<td></td>
</tr>
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<td></td>
<td>1N HCl</td>
<td>160</td>
<td>1</td>
<td>12</td>
<td>14 days</td>
<td>weight loss</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1N H₃PO₄</td>
<td>160</td>
<td>1</td>
<td>74</td>
<td>14 days</td>
<td>weight loss</td>
<td></td>
</tr>
<tr>
<td>Brown et al. [24]</td>
<td>Seawater</td>
<td>25</td>
<td>8.2</td>
<td>4.6</td>
<td>7 days</td>
<td>weight loss</td>
<td>aerated</td>
</tr>
<tr>
<td></td>
<td>Seawater</td>
<td>25</td>
<td>8.2</td>
<td>3.8</td>
<td>7 days</td>
<td>weight loss</td>
<td>ozonated</td>
</tr>
<tr>
<td></td>
<td>Seawater</td>
<td>25</td>
<td>8.2</td>
<td>0.4</td>
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<tr>
<td></td>
<td>Seawater</td>
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<td>6.8</td>
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<td>ozonated</td>
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<td>Estill et al. [12]</td>
<td>6 m NaCl+ 0.9 m KNO₃</td>
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<td>6 m NaCl+ 0.9 m KNO₃</td>
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<td>0.25</td>
<td>0.25</td>
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<td>aerated</td>
</tr>
<tr>
<td>Rebak et al. [23]</td>
<td>7.1 m 50% H₂SO₄</td>
<td>70</td>
<td></td>
<td>200</td>
<td>4 days</td>
<td>immersion</td>
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</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
<td>600</td>
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<td>immersion</td>
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<td></td>
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<td>Evans et al. [10]</td>
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<td>1.7</td>
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<td>deaerated</td>
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<tr>
<td>Gray et al. [22]</td>
<td>H₂SO₄+4m NaCl</td>
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<td>1</td>
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<td>1</td>
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<tr>
<td>Day et al. [11]</td>
<td>0.1M oxalic acid</td>
<td>30</td>
<td>1.3</td>
<td>50</td>
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<td>polarization</td>
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<td>Hua et al. [25]</td>
<td>BSW-12</td>
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<td>0.075</td>
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<tr>
<td>Corbett &amp; Agarwal et al. [26,27]</td>
<td>SAW Modified SAW 70,000ppm Cl-SCW</td>
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<td>Rebak et al. [28]</td>
<td>J-13</td>
<td>95</td>
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<td>Rebak et al. [29]</td>
<td>0.1% to 10% NaCl</td>
<td>95</td>
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<td>Dunn et al. [30]</td>
<td>0.028 M to 4.0 M NaCl</td>
<td>95</td>
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<td>Pathupathi et al. [31]</td>
<td>SAW, SCW, SDW</td>
<td>90</td>
<td>0.74</td>
<td>6 months</td>
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<tr>
<td></td>
<td>90</td>
<td></td>
<td>0.076</td>
<td>2 years</td>
<td></td>
<td>immersion</td>
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<td>Evans et al. [32]</td>
<td>SAW</td>
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<td>2.8</td>
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<td>aerated</td>
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<tr>
<td></td>
<td>SAW</td>
<td>90</td>
<td>2.8</td>
<td>1.03</td>
<td></td>
<td>polarization</td>
<td>aerated</td>
</tr>
<tr>
<td>Lloyd et al. [33]</td>
<td>1M NaCl+ 0.1M H₂SO₄</td>
<td>75</td>
<td></td>
<td>1.38</td>
<td></td>
<td>constant potential</td>
<td>deaerated</td>
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</table>

**Author Electrolyte Temp (°C) pH CR (\(\mu\)m/year) Time Test Method Conditions**
Figure 20. Summary of Corrosion Rate of Alloy 22 under different environment and conditions; top (CR’s from 50 to 3650 µm/yr), middle (10 to 200µm/yr), bottom (0 to 10µm/yr).
Conclusions

The corrosion behavior of Alloy 22 studied using potentiodynamic polarization method at different temperatures and concentrations of YM waters of aerated and deaerated electrolyte. In general, the corrosion rate increased as the temperature increased for both aerated and deaerated conditions. The short-term corrosion rates (determined by using potentiodynamic scans) in aerated electrolyte were less than those of the deaerated due to the formation of passive oxide film which is not a common trend. Microstructural details showed anodic dissolution contributing to the corrosion process in the deaerated condition and higher temperatures only. As the electrolyte concentration increases the corrosion rate of Alloy 22 increase more significantly in the deaerated condition. A transpassive region is observed at higher anodic potentials using 100X electrolyte, but this was not observed for the 1X and 10 X electrolytes, both in aerated and deaerated conditions. In addition, transpassive process takes place for both aerated and deaerated conditions at a potential of about +600mV but less pronounced at higher temperatures.

References

26. R. Corbett, ASTM G61 Cyclic Potentiodynamic Polarization Testing, 1999, Rupp VDM, June 3, Houston, TX