Sub-surface corrosion research on rock bolt system, perforated SS sheets and steel sets for the Yucca Mountain Repository — Quarterly technical report No. 9

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

Quarterly Technical Report No. 9 (4th Quarter of FY 2006)

Start Date of this Quarter, July 1, 2006 to Sept. 30, 2006

Task No: ORD-FY04-019 and Document No: SIP-UNR-040

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September 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 are also reported with analyses.

General Statements
High-strength low-alloy (HSLA) steels are commonly used in commercial rock bolts. We have performed corrosion tests on commercial rock bolts Mn-24 Swellex rock bolts, (Split Sets – SS46), 4340 steel that may be potentially used for rock bolts of different types, and related materials for ground support of the repository. In this report (#9) the corrosion rates have been determined in aerated (oxygenated) and deaerated (nitrogenated) conditions at different temperatures in simulated 10X YM waters for 4340 steel. To isolate the ionic species in the YM water that contribute to significant corrosion we have used individual salts to test the effect for Swellex rock bolts; important for understanding corrosion behavior. Characterization of reacted products by optical microscopy has also been performed during this quarter on other materials. Analyses and more experiments are in progress. In the last quarter we submitted one manuscript for publication to *Electrochimica Acta* on Alloy 22 corrosion. This quarter we have submitted another new manuscript to *Metallurgical Transactions A*.

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 on split sets and Mn-24 Swellex rock bolts, and 4340 steel.
Subtask 3: Electrochemical Impedance Spectroscopy (EIS) of 4340 Steel
Subtask 6: Dry Oxidation Tests by Thermogravimetric analyses on Mn-24 and Split sets at different temperatures
Subtask 7: Microstructure 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 in 10X YM waters at several temperatures
- EIS studies were performed on the 4340 steel
- Detailed studies on Swellex Rock bolts were performed by using individual ionic species found in the YM waters, such sulfate ions, bi carbonate ions etc.
- Corrosion studies completed on Split set rock bolts and manuscript written sent to *Metallurgical Transactions*. The title of the manuscript is “Electrochemical Behavior of Friction Type Rock Bolt in Complex Ionic Electrolytes authors” by Md Sazzadur Rahman, Suresh Divi, Dhanesh Chandra, and Jaak Daemen.” Submitted to *Met Trans (A)* Journal, which is attached as part of this report. Please note that in the manuscript we have not disclosed the rock bolt manufacturer’s name, instead the type of steel.
- Please also note that a manuscript, entitled “Electrochemical Evaluation of Passive Corrosion Behavior of Alloy 22. In complex Ionic Electrolyte,” was sent last quarter. This manuscript has been recently submitted to *Electrochimica Acta*, and is currently under review.
- Oxidation studies were performed on Split Set (SS46) rock bolts; majority of the analyses completed.
2.1. Study of effect of anions on the corrosion rate of Swellex Mn-24 by Potentiodynamic Scans

2.1.1 Introduction
As a part of sub-surface corrosion research on various materials, we have initiated a study on the corrosion behavior of Swellex Mn-24 rock bolts. Details of the swellex rock bolt are given in the previous reports. In the past reports, we reported the effect of 1X YM water on corrosion of Swellex Mn-24 rock bolt. In this quarter we initiated the study of individual salts on the corrosion of swellex Mn-24 rock bolt, rather than combination of salts (1X YM water). In the Table 2.1.1, chemicals and different concentrations of YM water are shown. Different salts of 100X concentration which were used for this study are highlighted in the third column of Table 2.1.1. We concentrated on the anions such as Chloride, Sulfate, Silicate and Bicarbonate to study its effect on corrosion swellex Mn-24. Chlorides and sulfates are bad for corrosion and silicate and bicarbonate are good inhibitors for corrosion. Pitting corrosion can be caused by different ions in steels. Chlorides and sulfates are very aggressive anions for localized corrosion like pitting. In these experiments we used salts MgCl₂·6H₂O to study the effect of chloride, MgSO₄·7H₂O to study the effect of sulfate, NaSiO₃·9H₂O to study the effect of silicate and NaHCO₃ to study the effect of bicarbonate at ambient conditions.

Table 2.1.1. YM water chemistry in different concentrations per liter

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>1x YM (mg/L)</th>
<th>10x YM (mg/L)</th>
<th>100x YM (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄·7H₂O</td>
<td>50</td>
<td>500</td>
<td>5000</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>100</td>
<td>1000</td>
<td>10000</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>196</td>
<td>1960</td>
<td>19600</td>
</tr>
<tr>
<td>CaSO₄·2H₂O</td>
<td>210</td>
<td>2100</td>
<td>21000</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>50</td>
<td>500</td>
<td>5000</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>200</td>
<td>2000</td>
<td>20000</td>
</tr>
<tr>
<td>NaSiO₃·9H₂O</td>
<td>210</td>
<td>2100</td>
<td>21000</td>
</tr>
<tr>
<td>NaF</td>
<td>2</td>
<td>20</td>
<td>200</td>
</tr>
</tbody>
</table>

2.1.2. Experimental Procedures for Corrosion Tests

2.1.2.(a). Specimen and Electrolyte Preparation: Swellex Mn24 samples were procured from commercial sources. Small circular discs of 1.88cm diameter were punched out from the tube without applying any heat, which can alter the properties of materials (Swelllex Mn 24 specimens). These discs were polished around the diameter to eliminate any cold working effects at the edges during punching. Discs of diameter 1.87cm were soldered to thick copper wire for good electrical conductivity and mounted in epoxy resin. The front side of the disc with area of 2.75cm² is exposed for testing. After molding, the electrical connection between the sample and the wire were checked with a voltmeter. Before the experiment the sample was grinded manually by using SiC emery papers ranging from coarse to fine until 600-grit. The sample was degreased with acetone and cleaned with de-ionized water immediately before the experiment.

Salts used for this study are MgCl₂, MgSO₄, NaSiO₃, NaHCO₃. The electrolyte preparation (100X) for the experiments were prepared by mixing above mentioned salts in 1 liter of distilled, de-ionized water as shown in the column of Table 2.1.1. These solutions were stirred for half-hour at ~60°C to dissolve the salts. After few hours, the solution was vacuum-filtered twice and stored for experimentation. pH for all four salt solutions was maintained in between 7 and 8.

2.1.2.(b). Test cell and Procedures: Electrochemical potentiodynamic scans were performed by using ASTM-G59. These tests were conducted in a typical 1 liter Pyrex glass flask covered with a polytetrafluoroethylene lid with many ports, which contains the working electrode, counter electrode (platinum), gas purge, thermocouple, inlet and outlet for the gas, Luggin probe connected to a silver/silver chloride (Ag/AgCl) reference electrode through salt bridge (agar-agar solution) and gas trap. A heating bath was used to control the temperature and thermocouple for monitoring the temperature. For high temperature experiments condenser was used to minimize the solution loss due to evaporation. This type of setup was adopted from the D.A. Jones textbook, Principles & Prevention of Corrosion.
All potentiodynamic scans were performed by using a commercially available Potentiostat and controlled by commercial electrochemistry software. The electrolyte was conditioned (de-aerated) by continuous purging of nitrogen gas for one hour before immersing the specimen. The polished and cleaned specimens were introduced into the cell. A distance of 1 mm was maintained between the specimen and Luggin probe to avoid variation in corrosion current ($I_{corr}$). When it reached a steady open circuit potential (corrosion potential), the potentiodynamic scans were started by sweeping the voltage from -$V$ to 0V and for some experiments to +$V$ at a rate of 0.2mV/sec. After the experiment, the corrosion current density ($i_{corr}$) was calculated by using the resistance polarization ($R_p$) technique by following the ASTM G592 and ASTM G1023 procedures, assuming Tafel constants for both anodic and cathodic to be 0.12V/decade.

2.1.2.(c) Corrosion Rate Calculations: Polarization resistance ($R_p$) is determined by calculating the slope of applied potential and the current density. The corrosion rate is calculated by using the given expression.

$$CR = K_i \frac{i_{corr}}{\rho} \cdot EW$$

(2.1)

Where, $K_i = 3.27 \times 10^{-3} \text{mm.g/µA.cm.y}$, $CR = \text{mm/year}$, $I_{corr} = \mu A/cm^2$, $\rho = g/cm^3$ (density of Swellex Mn-24 is 7.858 gm/cm$^3$), and equivalent weight ($EW$) is 27.24 gm/equivalent.

2.1.3 Results and Discussion on Swellex Mn-24 rock bolts

In this report we present individual effects of anions to understand the intrinsic behavior of the “ions” that are found in the YM waters being studied. This will give us an understanding of the ionic species that are beneficial or harmful with respect to corrosion of the rock bolts. Effect of Chloride, Sulfate, Silicate, and Bicarbonate results are presented.

2.1.3(a) Effect of Chloride Ions

Anion species like chloride are very aggressive and leads to pitting corrosion. Chloride is a relatively small anion with high diffusivity, interferes with passivation and hence acts as contaminant to breakdown the passivation. Potentiodynamic polarization scan of swellex Mn24 steel in MgCl$_2$ solution is given in Figure 2.1.1. Rest potential is observed to be at around 0.68V and $I_{corr}$ is around 3.6 x 10$^{-6}$. From the anodic region (upper portion from rest potential) of the curve we can see that there is no passivation and the anodic branch is linear. The corrosion current is increased as we go further in to the anodic region. As we know $I_{corr}$ is directly proportional to dissolution of metal, the metal dissolution in this experiment seems to be high as compared to other anions. Resistance polarization and other parameters along with corrosion rate are shown in Table 2.2.1. The corrosion rate calculated for this experiment is 44.96 microns per year. For the consistency we repeated three experiments and the plot for the three experiments are shown in Figure 2.1.2. From the graph we can see that the anodic and cathodic branches of three experiments are overlapping and hence there is good reputability of experiments.

Table 2.2.1. Corrosion rate and other parameters calculated for Swellex Mn24 in 100X MgCl$_2$ YM water.

<table>
<thead>
<tr>
<th>File Name</th>
<th>Rp (ohm)</th>
<th>Goodness of fit for Rp</th>
<th>$I_{corr}$ ($\mu A/cm^2$)</th>
<th>Corrosion Rate ($\mu m/\text{year}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SwMn24-PD-25C-100X MgCl$_2$-N-07-18-06.xls</td>
<td>7248.1</td>
<td>0.9916</td>
<td>3.58715E-06</td>
<td>40.675</td>
</tr>
<tr>
<td>SwMn24-PD-25C-100X MgCl$_2$-N-07-18-06(2).xls</td>
<td>6349.6</td>
<td>0.9797</td>
<td>4.09475E-06</td>
<td>46.430</td>
</tr>
<tr>
<td>SwMn24-PD-25C-100X MgCl$_2$-N-07-18-06(3).xls</td>
<td>6169.3</td>
<td>0.9735</td>
<td>4.21442E-06</td>
<td>47.787</td>
</tr>
</tbody>
</table>
2.1.3(b) Effect of Sulfate Ions

Sulfates are another aggressive anion after chloride anion. Potentiodynamic scan of Swellex Mn 24 in 100X MgSO$_4$ concentration of YM water is shown in Figure 2.1.3. Even in this polarization scan there is no passive layer observed. The resistance polarization measured for this scan is 6730.4 and the goodness of fit is above 90% and the $I_{corr}$ is around 3.8 x 10$^{-6}$ micro amperes per square centimeter. Corrosion rated observed for the first experiment is 43.8 microns per year. As similar to chloride ion experiments, here also we repeated three experiments. Parameters calculated for the all the three experiments are shown in the Table 2.1.3 and the potentiodynamic graphs are plotted in Figure 2.1.3. The three graphs look similar and the anodic and cathodic branches are overlapping and there is no passivation in all the three polarization graphs. Average corrosion rate of swellex Mn24 in 100X YM water is 43.87 microns per year. Similar to chloride ions sulfates also constantly dominates the re-passivation and results in dissolving the metal.

Table 2.1.3. Corrosion rate and other parameters calculated for Swellex Mn24 in 100X MgSO$_4$ YM water.

<table>
<thead>
<tr>
<th>File Name</th>
<th>Rp (ohm)</th>
<th>Goodness of fit for Rp</th>
<th>$I_{corr}$ ($\mu$A/cm$^2$)</th>
<th>Corrosion Rate ($\mu$m/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SwMn24-PD-25C-100XMgSO4-N-07-12-06(2).xls</td>
<td>6730.4</td>
<td>0.9525</td>
<td>3.86307E-06</td>
<td>43.803</td>
</tr>
<tr>
<td>SwMn24-PD-25C-100XMgSO4-N-07-14-06.xls</td>
<td>6667.1</td>
<td>0.9459</td>
<td>3.89975E-06</td>
<td>44.219</td>
</tr>
<tr>
<td>SwMn24-PD-25C-100XMgSO4-N-07-14(2)-06.xls</td>
<td>6761.5</td>
<td>0.9561</td>
<td>3.8453E-06</td>
<td>43.601</td>
</tr>
</tbody>
</table>
Figure 2.1.3. Potentiodynamic scan of Swellex Mn24 in 100X MgSO₄ of YM water.

Figure 2.1.4. Comparison Potentiodynamic plots of Swellex Mn24 in 100X MgSO₄ of YM water.
2.1.3(c) Effect of Silicate: Generally alkaline salts hydrolyze to form solutions of higher pH and acts as corrosion inhibitors. They passive iron in the presence of dissolved oxygen similar to NaOH. Some examples are Na$_3$PO$_4$, Na$_2$B$_2$O$_7$, Na$_2$CO$_3$ and Na$_2$SiO$_3$. In these experimental results of effect of silicate ions we can see from the figure 2.1.5 that there is no increase in current density with increase in voltage towards anodic region. Ions like silicate, In addition to passivation of iron by dissolving oxygen form corrosion-product layer of ferrous and ferric compounds. This kind of product layers act as more efficient diffusion barriers than hydrous FeO. In the Figure 2.1.5, we can see that the passive region started from -0.55V and went through 0.2V. Resistance polarization for the first experiment is observed to be 10544 ohms and the current density and corrosion rate for the first experiment are $2.4 \times 10^{-6}$ micro amperes per square centimeter and 27.9 microns per year respectively. For the reputability we conducted three similar experiments and the calculated corrosion rates for the first two are close and the third one is little bit less. The calculated parameters are given in Table 2.1.4. Plot of all the three polarization plots are given in Figure 2.1.6. In our experiments also there is chance of formation of ferrous or ferric layers.

Table 2.1.4. Corrosion rate and other parameters calculated for Swellex Mn24 in 100X Na$_2$SiO$_3$ YM water.

<table>
<thead>
<tr>
<th>File Name</th>
<th>Rp (ohm)</th>
<th>Goodness of fit for Rp</th>
<th>I$_{corr}$ ($\mu$A/cm$^2$)</th>
<th>Corrosion Rate ($\mu$m/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SwMn24-PD-25C-100Na2SiO3-N-07-26-06.xls</td>
<td>10544</td>
<td>0.9175</td>
<td>2.4658E-06</td>
<td>27.960</td>
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<tr>
<td>SwMn24-PD-25C-100Na2SiO3-N-07-26-06(2).xls</td>
<td>11588</td>
<td>0.965</td>
<td>2.2437E-06</td>
<td>25.441</td>
</tr>
<tr>
<td>SwMn24-PD-25C-100Na2SiO3-N-07-26-06(3).xls</td>
<td>19964</td>
<td>0.969</td>
<td>1.30234E-06</td>
<td>14.767</td>
</tr>
</tbody>
</table>

Figure 2.1.5. (Left) Potentiodynamic scan of Swellex Mn24 in 100X Na$_2$SiO$_3$ of YM water.
Figure 2.1.6. (Right) Comparison Potentiodynamic plots of Swellex Mn24 in 100X Na$_2$SiO$_3$ of YM water.

2.1.3(d) Effect of Bicarbonate

Bicarbonate anions are very good corrosion inhibitor for the steels by forming a good passive layer of iron carbonate. To see the effect of bicarbonate we used 100X of sodium bicarbonate YM water solution. The potentiodynamic polarization plot of one of the four experiments is shown in figure 2.1.7. From the literature the expected layer could be iron carbonate as shown in the below equation:

$$\text{Fe} + \text{HCO}_3^- = \text{FeCO}_3 + \text{H}^+ + 2 \text{e}^-$$

As expected the current density and the corrosion rate for this experiment is very low. The current density for the experiment shown in figure 2.1.7 is $1.9 \times 10^8$ micro amperes per square centimeter and the corrosion rate is 0.15 microns per year. All the parameters calculated for the four experiments are shown in table 2.1.5. Polarization plots for the three experiments are plotted in figure 2.1.8. From the graph we can see that there is good repeatability of data. E$_{corr}$ for the fourth is little bit off as compared to first three but the corrosion rate is very near to rest.
Table 2.1.5. Corrosion rate and other parameters calculated for Swellex Mn24 in 100X NaHCO₃ YM water.

<table>
<thead>
<tr>
<th>File Name</th>
<th>Rp (ohm)</th>
<th>Goodness of fit for Rp</th>
<th>Icorr (µA/cm²)</th>
<th>Corrosion Rate (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SwMn24-PD-25C-100XNaHCO3-N-07-21-06.xls</td>
<td>1350424.65</td>
<td>1</td>
<td>1.92532E-08</td>
<td>0.218</td>
</tr>
<tr>
<td>SwMn24-PD-25C-100XNaHCO3-N-07-21-06(2).xls</td>
<td>1389195.49</td>
<td>1</td>
<td>1.87159E-08</td>
<td>0.212</td>
</tr>
<tr>
<td>SwMn24-PD-25C-100XNaHCO3-N-07-21-06(3).xls</td>
<td>1283261.09</td>
<td>1</td>
<td>2.02609E-08</td>
<td>0.229</td>
</tr>
<tr>
<td>SwMn24-PD-25C-100XNaHCO3-N-07-22-06.xls</td>
<td>1948548.58</td>
<td>1</td>
<td>1.33433E-08</td>
<td>0.151</td>
</tr>
</tbody>
</table>

Figure 2.1.7. Potentiodynamic scan of Swellex Mn24 in 100X NaHCO₃ of YM water.

Figure 2.1.8. Comparison Potentiodynamic plots of Swellex Mn24 in 100X NaHCO₃ of YM water.
Comparison of Effect of anions
Among all the anions studied chloride has the dominant effect. The average corrosion rate of chlorides is seems to be 44.96 microns and the average corrosion rate for sulfates is 43.87 microns. As expected from the literature chloride and sulfates are the most aggressive anions for the corrosion of steels. Silicates have the third highest corrosion after chlorides and sulfates. There is a good passivation range for the silicates due to the formation of either ferrous or ferric compounds. Effect of bicarbonate on corrosion of Swellex Mn 24 is the least. A corrosion rate in the sodium bicarbonate solutions has decreased dramatically as compared to the rest. The average corrosion rate in the bicarbonate solutions is seemed to be 0.22 microns per year. This may be due to the formation of iron carbonate. Average corrosion rates are showed in Table 2.1.6 and the corrosion rate plot for the different ions is showed in figure 2.1.10. For the comparison a polarization plot for each salt is shown in Figure 2.1.9. From the plot we can see that the $E_{corr}$ for MgCl₂, MgSO₄ and Na₂SiO₃ are very near but for the NaHCO₃ the $E_{corr}$ is way above and mostly the more anodic the polarization goes more will be the chance for the dissolution of metal but in the case of bicarbonate due to the formation of iron carbonates there is good passivation. In the case of silicate also there is a passivation but not as much as bicarbonate. The explanation above mentioned is based the observation of plots. But the results required enough theoretical explanation along with good characterization to explain the mechanism behind the increase or decrease in corrosion rate due to the effect of above mention anions.

Table 2.1.6. Average Corrosion rates in different salts.

<table>
<thead>
<tr>
<th>Salts</th>
<th>Average Corrosion Rate (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl₂</td>
<td>44.96</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>43.87</td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>22.72</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Figure 2.1.9. Comparison of Potentiodynamic plots in 100X concentration of different salts.
Figure 2.1.10. Average corrosion rates of Swellex Mn24 in 100X concentrations of different salts of YM water.

2.1.4 References for Corrosion of Swellex Rock bolts

2.2 Corrosion of 4340 Steel for Rock bolts

2.2.1 Introduction

In an effort to investigate the behavior of the common commercial steel that are readily available, AISI-SAE 4340 steel is being studied as a potential material for use in rock bolts and I-beams within the Yucca Mountain Nuclear Waste Repository, northwest of Las Vegas, Nevada. Slotted and tapered steel tube rock bolts are 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 ten times the normal concentration (10X) in both aerated (oxygenated) and deaerated (nitrogenated) conditions. Please note that in the last quarter we studied corrosion effects using 1X concentration YM waters. The overall median corrosion rate (CR) increased from 25°C to 65°C – peaking between 65°C and 75°C – then decreased to 90°C, for both the aerated and deaerated conditions.

2.2.2 Experimental

Electrochemical tests were prepared from commercially available 4340 steel. The chemical composition of 4340 steel was analyzed by LTI2 (QA vendor for YM project) and is given in Table 2.2.1. The test specimens were disc shaped, approximately 0.25”. The test specimen was mounted in epoxy with its ~1.2 cm² bottom surface area and electrical connection wire exposed out of it. 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 2.2.1. Chemical Composition (wt%) of 4340 Steel analyzed by LTI²

<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>

Electrochemical experiments were conducted in a standard 1 liter Pyrex glass flask covered with a Polytetra-fluoroethylene lid (Quarterly report No. 5 has photos of the apparatus). The lid has several 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 platinum sheet was sealed to a glass capillary and used as a counter electrode. 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. Nitrogen or oxygen gas was purged in the sealed cell at a constant pressure and flow rate in 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. The test cell was placed in an electrically-heated water bath at a constant temperature. The electrolyte was purged continuously with nitrogen/oxygen for deaeration/aeration for at least 30 minutes before immersing the specimen for conditioning purposes. The specimen was placed in the cell and is maintained at a distance of ~2 to 3 mm, between specimen and Luggin probe tip to avoid any variation in corrosion current (Icorr) and corrosion potential (Ecorr). The potentiodynamic tests were carried out at a scan rate of 0.2mV/sec. The electrochemical impedance spectroscopy (EIS) tests were carried out between 10 kHz and 10 mHz at an ac voltage of 100 mV rms. 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 water¹ and measured the pH of the solution before and after each experiment.

ASTM G59-97³ and ASTM G102-89⁴ procedures were followed to calculate the corrosion rates. The polarization resistance (Rp) of the solution was neglected because it was shown by Yilmaz⁵ 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).⁶ From the polarization resistance (Rp) value, the corrosion current density was calculated.
using equation 2.2, where \( K_1 = 3.27 \times 10^{-3} \text{ mm-g/µA·cm·year} \), \( I_{\text{corr}} = \mu\text{A/cm}^2 \), \( \rho = 7.87 \text{ g/cm}^3 \) and \( EW = 27.95 \text{ gm/equivalent} \).

\[
CR = K_1 \frac{I_{\text{corr}}}{\rho} EW
\]

(2.2)

2.2.3 Results & Discussion
In this section we present the results of potentiodynamic and impedance spectroscopy studies of 4340 steel in YM 10X solution, as well as a comparison of the activation energies of 4340 & 1040 steels in 10X solution.

2.2.2.2A. Potentiodynamic studies - effect of temperature on the corrosion behavior (deaerated & deaerated YM waters)

**Deaerated YM Waters:** The corrosion rates for 1X were reported in the last quarterly report. In this report, the effect of 10X YM water concentration is studied. Potentiodynamic scans for the 4340 steel in 10X waters are presented in Figures 2.2.1 and 2.2.2. The calculated corrosion rates as a function of temperature are presented in Figures 2.2.3. The measured was \( E_{\text{corr}} \approx -0.698 \text{ V} \) at room temperature (25°C), increasing to \(-0.683 \text{ V} \) at 45°C, subsequently decreasing to \(-0.695 \text{ V} \) at 65°C and finally increasing slightly to \(-0.663 \text{ V} \) at 90°C. Figure 2.2.3 shows the median corrosion rate as a function of temperature. As can be seen, the corrosion rate increases to approximately 75°C, then decreases to 90°C, resulting in a second-order polynomial fit. It’s important to note that there was considerable scattering of data points, despite repeated experiments at higher temperatures (75°C and higher), as compared to lower temperatures (from 25°C to 65°C).

**Aerated YM Waters:** Potentiodynamic scans for 4340 in aerated system are shown in Figures 2.2.4 and 2.2.5. For 10X concentration, the observed \( E_{\text{corr}} \) is \(-0.404 \text{ V} \) at room temperature (25°C). At 65°C it decreases to \(-0.588 \text{ V} \), then rebounds to \(-0.576 \text{ V} \) at 75°C, finally dropping to \(-0.601 \text{ V} \) at 90°C. Figure 2.2.6 shows the median corrosion...
The corrosion rate increases to approximately 65°C, then decreases to 90°C. As observed in the deaerated environment, there was a considerable scatter of data points, despite repeated experiments at higher temperatures (75°C and higher). The average corrosion rates in aerated and deaerated YM 1X solution are shown in Table 2.2.2.

Table 2.2.2 Median corrosion rates (CR) 4340 steel at different temperatures in 10X YM water. Please note that 1X tests were reported in the last quarterly and are shown here for comparison. Purposes.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Environment</th>
<th>CR -1x (microns/yr)</th>
<th>CR -10x (microns/yr)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Deaerated</td>
<td>28.78</td>
<td>65.84</td>
<td>Steady increase in Corrosion rates in 1X waters. Slight decrease in rates in 10x at high temperatures</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>38.75</td>
<td>129.24</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td>53.26</td>
<td>131.07</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td></td>
<td>65.08</td>
<td>125.58</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td></td>
<td>81.55</td>
<td>140.29</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>100.62</td>
<td>136.24</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Aerated</td>
<td>244.12</td>
<td>234.14</td>
<td>Initial increase in Corrosion rates and subsequent decreases at higher temperatures</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>798.66</td>
<td>787.87</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td>1052.75</td>
<td>711.26</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td></td>
<td>1445.80</td>
<td>739.21</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td></td>
<td>1303.30</td>
<td>692.04</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>1296.06</td>
<td>696.02</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.2.4. Potentiodynamic scan for 4340 steel in deaerated, 10X YM water at 25°C, 45°C & 65°C.

Figure 2.2.5. Potentiodynamic scan for 4340 steel in deaerated, 10X YM water at 75°C, 85°C, and 90°C.
Nyquist and Bode plots for 4340 steel in aerated and deaerated conditions are presented in Figures 2.2.7 through 2.2.30. The plots show lower resistance is observed in the aerated condition indicating a higher corrosion rate as compared to deaerated condition. Arjunan\textsuperscript{6} reported similar results on Low Carbon Steel (LCS), and are consistent with 1X YM water\textsuperscript{7}. Nyquist plots show a slight Warburg component at 25°C and 45°C, which is more pronounced from 65°C to 90°C, diffusion-controlled.\textsuperscript{8} process at higher temperatures for the 10x YM waters, these results are comparable with 1X YM water\textsuperscript{7}. The corresponding Bode plots exhibit a single phase angle maxima at lower temperatures, but at 65°C begin to exhibit double phase angle maxima (in the aerated condition); indicating a passive film formed on the 4340 steel is porous, especially at higher temperatures. This type of behavior is consistent with spectra of polymer-coated metals.\textsuperscript{9}

Figure 2.2.7. Nyquist plot of 4340 steel at 25°C in deaerated, 10X YM water.  
Figure 2.2.8. Bode plot of 4340 steel at 25°C in deaerated, 10X YM water.
Figure 2.2.9. Nyquist plot of 4340 steel at 45°C steel in deaerated, 10X YM water.

Figure 2.2.10. Bode plot of 4340 steel at 45°C steel in deaerated, 10X YM water.

Figure 2.2.11. Nyquist plot of 4340 steel at 65°C steel in deaerated, 10X YM water.

Figure 2.2.12. Bode plot of 4340 steel at 65°C steel in deaerated, 10X YM water.

Figure 2.2.13. Nyquist plot of 4340 steel at 75°C steel in deaerated, 10X YM water.

Figure 2.2.14. Bode plot of 4340 steel at 75°C steel in deaerated, 10X YM water.
Figure 2.2.15. Nyquist plot of 4340 steel at 85°C steel in deaerated, 10X YM water.

Figure 2.2.16. Bode plot of 4340 steel at 85°C steel in deaerated, 10X YM water.

Figure 2.2.17. Nyquist plot of 4340 steel at 90°C steel in deaerated, 10X YM water.

Figure 2.2.18. Bode plot of 4340 steel at 90°C steel in deaerated, 10X YM water.

Figure 2.2.19. Nyquist plot of 4340 steel at 25°C steel in aerated, 10X YM water.

Figure 2.2.20. Bode plot of 4340 steel at 25°C steel in aerated, 10X YM water.
Figure 2.2.21. Nyquist plot of 4340 steel at 45°C steel in aerated, 10X YM water.

Figure 2.2.22. Bode plot of 4340 steel at 45°C steel in aerated, 10X YM water.

Figure 2.2.23. Nyquist plot of 4340 steel at 65°C steel in aerated, 10X YM water.

Figure 2.2.24. Bode plot of 4340 steel at 65°C steel in aerated, 10X YM water.

Figure 2.2.25. Nyquist plot of 4340 steel at 75°C steel in aerated, 10X YM water.

Figure 2.2.26. Bode plot of 4340 steel at 75°C steel in aerated, 10X YM water.
2.2.2.2C. Calculation of activation energies for 4340 steels with 10x YM waters

In this section we present the corrosion rates and their respective activation energies required to begin the corrosion process; this is dependent on the temperature and electrolyte concentration. High-strength low-alloy (HSLA) steels have higher hardness values than plain-carbon steels (of similar carbon content); HSLA steels tend to have lower activation energies than plain-carbon steels, with higher corrosion rates at the equivalent temperature and solution concentration.\textsuperscript{10} The corrosion rates of 4340 in YM 10 X waters are given in Figure 2.2.31 and 2.2.32. The corrosion rates of 1040 steel are also superimposed in these Figures for comparison (from our previous studies-Yilmaz\textsuperscript{5}) in both aerated and deaerated environments. The activation energies for 4340 steel in deaerated and aerated environments, respectively, are 8.7 and 12.4 kJ/mol, as compared to 1040 steel\textsuperscript{5} 18 and 30 kJ/mol, respectively. Figures 2.2.33 and 2.2.34 show the calculated activation energy (Q) values for both 4340 and 1040\textsuperscript{5,6} steels.
References for Corrosion of 4340 steel


2.3 Oxidation Kinetics of Mn24 and SS26 High Strength Low Alloy Steels Rockbolt Materials

2.3.1 Introduction. High temperature oxidation behavior of High Strength Low Alloy (HSLA) steels that are candidate Rockbolt materials for use as underground roof supports at Yucca Mountain nuclear waste repository have been studied. Results of oxidation tests done on Mn 24 and SS46 Rockbolt materials for 4, 9, 16, 100 hour isothermal holding in pure oxygen atmosphere are presented in this quarterly report. These results are correlated with previous results and corresponding kinetic parameters like the rate constant, pre-exponential factor and activation energy have been determined. Table 2.3.1 shows chemical composition of both the High Strength Low Alloy Rockbolt materials.

Table 2.3.1 Chemical composition of SS46 and Mn24 as received from LTI*

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Mn</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>V</th>
<th>Cb/Nb</th>
<th>Cu + Ni+</th>
<th>Cu + Cr+</th>
<th>Mo</th>
<th>Al</th>
<th>Cu</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS46 (ASTM A607-98, Grade 50)</td>
<td>0.06</td>
<td>0.02</td>
<td>0.03</td>
<td>-</td>
<td>0.68</td>
<td>0.07</td>
<td>0.01</td>
<td>0.01</td>
<td>V 0.038</td>
<td>Cb/Nb 0.007</td>
<td>Cu + Ni+ 0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swellex Mn24</td>
<td>0.05</td>
<td>0.042</td>
<td>0.027</td>
<td>0.24</td>
<td>2.36</td>
<td>0.16</td>
<td>0.013</td>
<td>0.004</td>
<td>Al 0.054</td>
<td>Cu 0.17</td>
<td>N 0.006</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* LTI: Laboratory Testing Inc., Hatfield, PA

High strength low alloy (HSLA) steels have specific alloying elements like C, Si, Mn, Cu, etc. to low carbon steels to achieve good mechanical strength, formability and weldability in the as-rolled or normalized conditions by modifying grain size and/or sometimes providing precipitation hardening [1-2]. As seen from the table, the carbon content of ~0.1 wt% in both the steels is well below the carbon contents at which the steels undergo decarburization [3].

2.3.2 Background (This was given in the last quarterly, report here for continuity)

Isothermal experiments were performed on SS46 and Mn24 at 825°C for varying time periods: 4, 9, 16 and 100 hr. in pure oxygen atmosphere. Data for oxidation kinetics of “linear-like” region based on isothermal studies on Mn24 at 675°C is also reported. Long term (100 hr) isothermal experiments were also completed for Mn24 at 900°C and the values of activation energy and kinetic parameters have been calculated accordingly. The changed values (as against to the values given in Quarterly Report 7) are given in this report. Figure 2.3.1 shows the weight gain versus time for SS46 at 825°C. In principle, both isothermal and non-isothermal kinetics given by reaction rate, (r) can be written as follows:

\[ r = \frac{d\alpha}{dt} = k(T).f(\alpha) \]  \hspace{1cm} (2.3)

where \( \alpha \) is the extent of reaction, \( t \) is the time, and \( k(T) \) is the temperature dependent rate constant (a constant value for isothermal experiments). The rate constant follows an Arrhenius expression:

\[ k = k_0 \exp\left(\frac{-\Delta E_a}{RT}\right) \]  \hspace{1cm} (2.2)

where \( k_0 \) is the pre-exponential factor (the intercept), \( R \) is the gas constant, \( T \) is the absolute temperature and \( \Delta E_a \) is the activation energy. A plot of \( \ln k \) versus \( 1/T \) yields the activation energy from the slope of the curve. The weight gain per unit surface area as a function of time can follow a linear, parabolic, logarithmic or cubic relationship and such behavior has been compiled for various metals and alloys [4]. In general, the rate law can be given by:

\[ y = \left(\frac{W}{A}\right) = kt^n \]  \hspace{1cm} (2.3)

where, \( k \) is the rate constant and \( n \) is the time exponent of the rate law.
2.3.3 Results

Based on the raw data obtained, three oxidation regions were established (similar to the ones shown in the last report): (1) a first stage oxidation region (2) a second stage with a linear-like oxidation behavior for times up to 9 hrs, and (3) a parabolic-type oxidation for longer oxidation time (>50.842 hrs for SS46 and > 51.504 hrs for Mn24). The raw data for SS-46 steel at 825°C is presented in Figure 2.3. Analyses showing oxidation regimes for the SS-46 are shown in Figure 1.2. There is a transient portion where the kinetics undergoes a transition from the “linear-like” to parabolic-type. The kinetic analyses for SS-46 in the linear like region are shown in Figure 1.3.

Kinetics of the “Linear-Like” Region
Calculations for rate constants and activation energies for the almost “linear-like” regions for SS46 and Mn24 were made by fitting a trendline through all the data (different time periods) for a given temperature. The fit of the linear regression for all the curves was found to be 0.98 for both Mn24 and SS-46. For “linear-like” region, an average index of rate law \( n = 0.7302 \) was determined for SS46 at 825°C with a rate constant of \( k = 2.3212 \times 10^{-4} \text{ kg m}^{-2} \text{s}^{-0.7302} \). For Mn24, the index of rate law was determined to be \( n = 0.7013 \) with corresponding rate constant of \( k = 7.122 \times 10^{-3} \text{ kg m}^{-2} \text{s}^{-0.7013} \) for 825°C. The index of rate law \( (n) \) was found to be 0.7859 at 675 °C for Mn24 and the corresponding rate constant is \( k = 1.60 \times 10^{-5} \text{ kg m}^{-2} \text{s}^{-0.7859} \). Table 2.3.2 lists these values systematically along with the values for the two alloys at 750°C and 900°C which were reported in the previous quarterly report, in this report the 900°C (100 hrs) experiment for SS-46 is included. The units of the rate constants \( “k” \), \( (\text{kg m}^{-2} \text{s}^{-n}) \) depend on the index of the rate law \( (n) \). In the Table 1.2 we have calculated the values of “n” for different temperatures. It can be seen that the “n” value varies from ~0.6 to ~0.8. The calculation of activation energy from ln \( k \) vs (1/T) plot; but this assumes a constant ‘n’ value to be the same for all temperatures. In order to keep the “n” value the same, we have approximated the value of n~0.7 and used it to calculate the rate constants and activation energy for a particular regime. Corresponding rate constants, activation energies and the pre-exponential factors are also listed in Table 2.3.2. The Table also includes the value for \( n \) and \( k \) for isothermal experiments done on Mn-24 for “linear-like” region at 675°C; which have not yet been reported.

![Figure 2.3.1 Weight percent vs time curve for SS46 oxidized at 825°C in pure oxygen atmosphere (raw data).](image-url)
Figure 2.3.2 Oxidation regions determined for SS-46 oxidized at 825°C.

Figure 2.3.3 Trend line fit for all the time periods at 825°C for SS-46 in the “linear like” region.
Table 2.3.2. Time constants (n), Rate constants (k), activation energies and pre-exponential factors (k_0) for the HSLA steels at 750 and 900 oC in the second regime of oxidation [Linear-like].

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Index of Rate Law (n)</th>
<th>Rate constant (k) (kg m^{-2}s^{-n})</th>
<th>Activation energy (kJ/mol)</th>
<th>k_0 (kg^2 m^{-4}s^{-0.7})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-46</td>
<td>750</td>
<td>0.7968 0.7</td>
<td>2.44 x 10^{-5} 6.72 x 10^{-5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>825</td>
<td>0.7302 0.7</td>
<td>2.3212 x 10^{-4} 1.433 x 10^{-4}</td>
<td></td>
<td>92.81^b 3.693^b</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.5828 0.7</td>
<td>9.35 x 10^{-4} 2.71 x 10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-24</td>
<td>675</td>
<td>0.7859 0.7</td>
<td>1.60 x 10^{-5} 4.05 x 10^{-5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.6685 0.7</td>
<td>9.27 x 10^{-5} 6.24 x 10^{-5}</td>
<td></td>
<td>75.04 0.417</td>
</tr>
<tr>
<td></td>
<td>825</td>
<td>0.7013 0.7</td>
<td>7.122 x 10^{-5} 6.5 x 10^{-5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.7709 0.7</td>
<td>2.22 x 10^{-4} 2.67 x 10^{-4}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^aThe units of the rate constant will change according to the index of rate law (n).

^bSince the index of rate law are actually different for the two temperatures (hence different units of k), to determine activation energy the index was assumed to be n = 0.7 for consistent units while plotting ln k versus 1/T

Kinetics of the “Parabolic Region”
Analyses for the parabolic region are based on 100 hour experiments at different temperatures for SS-46 and Mn-24. A trend line fit to a plot of y^2 versus t gives the value of parabolic rate constant (k_p). The k_p value for SS46 and Mn24 at 825°C in Figure 2.3.4 along with the parabolic rate constants. The higher value of the parabolic rate constant for SS-46 than that of Mn24 indicates the better oxidation resistance of Mn24 in the parabolic region. Table 2.3.3 lists the values of parabolic rate constants, activation energies, and pre-exponential factor for SS-46 and
Mn 24 at 750°C, 825°C, and 900°C. Figure 2.3.5 shows a comparison of parabolic rate constants for Mn24 at different temperatures. The parabolic rate constants ($k_p$) increase as the temperature increases.

The plot ($y^2$ vs $t$) for SS-46 is not shown for brevity, but the analyzed rate constant $k_p$, activation energy and pre-exponential factor are shown in Table 2.3.3.

Table 2.3.3  Parabolic Rate Constants ($k$), Activation Energies and Pre-exponential factors ($k_0$) for the HSLA steels in the Parabolic Oxidation Regime. It should be noted the analyses for 900°C are not complete at this time for SS-46. The activation energies of these may not be compared at this time, as the analyses are not complete.

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Parabolic Rate constant ($k_p$) (kg$^{-2}$m$^{-4}$s$^{-1}$)</th>
<th>Activation energy (kJ/mol)</th>
<th>$k_0$ (kg$^2$m$^{-4}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-46</td>
<td>750</td>
<td>3.25 x 10$^{-8}$</td>
<td>81.9</td>
<td>4.94 x 10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>825</td>
<td>6.23 x 10$^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-24</td>
<td>750</td>
<td>3.32 x 10$^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>825</td>
<td>5.36 x 10$^{-8}$</td>
<td>410.27</td>
<td>2.48 x 10$^{12}$</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1.62 x 10$^{-6}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.3.4 Comparison of Parabolic rate constants ($k_p$) for SS46 and Mn24 oxidized to 825°C.

Figure 2.3.5 Comparison of Parabolic rate constants ($k_p$) for Mn24 oxidized at 750°C, 825°C, and 900°C.

References
Electrochemical Behavior of Friction Type Rock Bolt in Complex Ionic Electrolytes
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Abstract
Friction type steel rock bolts are one of the most commonly used for reinforcing tunnels since the late 1970’s due to their ability to sustain large rock mass displacements. These ASTM A607 steel rock bolts are tubes slotted along the length with one end tapered for easy insertion into a drill hole and the other end with a welded ring flange to hold the bearing plate. It is more commonly used these days to reinforce tunnels, and also being studied for underground support for nuclear repositories. We studied corrosion behavior of this A607 steel rock bolts using electrolytes in three different concentrations; 1X, 10X, 100X, in aerated (oxygenated) and deaerated (nitrogenated) conditions from 298 to 363K for nuclear repository applications. The corrosion behavior for 1X and 10X concentrations for this rock bolt were similar in both aerated and deaerated conditions except the corrosion rates were a order of magnitude higher in the aerated condition; ranging from ~30 to 200mm/yr for deaerated and 150 to 1600 mm/yr for aerated. The corrosion behavior using 100X electrolyte was quite different in aerated condition showing initial increases in the corrosion rate between 298 to 338K (~210 to 2400 μm/yr) and an unusual steep decrease from 338 to 348K (~2400 to 750 μm/yr). General as well as pitting corrosion were observed for these steels. In this paper we report results from potentiodynamic polarization and potentiostatic tests in simulated electrolytes as a function of concentration, temperature and environment. We also compare corrosion behavior of the A607 rock bolt steel with 1040 and A36 steels using the same electrolyte and similar environment.

Key Words: Electrochemical, Potentiodynamic scans, rock bolts, slotted & tapered steel tube, corrosion rate

Introduction
Rock bolts made of different steels are used in mines, road tunnels, nuclear repositories, anchor support of large electrical towers and other applications. In the past, criterion for selection of rock bolts was mainly by comparing the mechanical properties with the radial stress load as a function of radial deformation of host-rocks. More recently, coupling of corrosion properties of steels with the above properties have become important for nuclear repositories for long term durability. Moreover, the repository environment is expected to range from 298 to 363K. In the future there may be temperature increases to 473K for the proposed US nuclear repository at Yucca Mountain in Nevada. Thus these studies are important as they have significance with an important nuclear repository environment in conjunction with commonly used steels in multi ionic electrolytes. In mining industries as well as underground nuclear repositories the steels investigated in this study have broader applications than the rock bolts themselves; for example I-beams and Bernold shields, wire meshes. Yucca Mountain (YM), a federal owned land, is located about 100 miles northwest of Las Vegas, Nevada. It has been extensively studied by the U.S. Department of Energy (DOE) for the disposal of spent nuclear fuel and other radioactive waste [1]. The radioactive waste will be contained in a waste package manufactured from Alloy 22 and will be placed in the underground tunnels of Yucca Mountain. The underground support for the YM site is different from other subsurface facilities due to the presence of heat from the spent nuclear fuel. This heat will introduce thermal mechanical stress along with the other loads involved in subsurface facilities. The underground support system, illustrated in Figure 1, shows a cross section of a typical emplacement drift with the proposed ground support and a perspective view of the drift with the slotted & tapered steel tube and welded-wire fabric details [2]. There are different kind of rock bolts that have been used for underground support materials. In the late 1970’s, Friction Rock Stabilizer (FRS) were introduced and have been widely used in mines and other underground support systems. Since then this type of material has been commonly used for rock reinforcement. It has a thin wall-wall tubular structure which exerts force for the entire length after it is placed inside the rock. This type of rock bolt can sustain large rock displacements due to slip at the interface between the device and the borehole wall. FRS holds the rock which prevents or minimizes shifts in the rock, whereas in the case of conventional rock bolts there is a chance of the rock bolts breaking or becoming loose within the rock itself.

Table 1. Types of slotted & tapered steel tube rock bolts

<table>
<thead>
<tr>
<th>Type</th>
<th>SS33</th>
<th>SS39</th>
<th>SS46</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Diameter (mm)</td>
<td>33</td>
<td>39</td>
<td>46</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>762-2438</td>
<td>762-3048</td>
<td>914-3658</td>
</tr>
<tr>
<td>Load Capacity (tons)</td>
<td>10</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>
Different kinds of FRS rock bolts have been used in industry. Slotted and tapered steel tube and expanded rock bolts are most commonly used. There have been quite a few studies on the corrosion behavior of plain steel FRS in underground mines under different mine water chemistries [3,4,5]. Inside, the mine water combines with the minerals in the rock and produce salts, which contribute to the corrosion of rock bolts. Therefore, the corrosion contribution to the failure of the FRS depends on the variations in the mine-site conditions. Ranasooriya [6] studied the behavior of slotted & tapered steel tube FRS rock bolts in different mines sites in Western Australia. He reported that there is about an average of 10% of mass loss in slotted & tapered steel tube using ASTM B117 tests [7]. He also reported that the maximum rate of mass loss was 81% in 11 months from one of the mine sites. In his study, he observed that there are three kinds of attacks: uniform, pitting and galvanic corrosion in the Western Australia mines. Tilman et al. [3] studied two types of high-strength low-alloy (HSLA) steels and galvanized steel in Missouri lead mine waters and iron mine waters. They reported the corrosion rate of these materials under aerated and deaerated conditions for 5 different mine waters. The corrosion rate in these lead mines were below 50µm/yr for both materials and in iron mines the corrosion rate was from 295 to 447µm/yr. Jolly et al. [5] also studied the corrosion behavior of split-set rock bolts in underground coal mine waters. They used electrochemical techniques as well as the weight loss method to calculate corrosion rate. The calculated corrosion rates for two different kinds of split sets in different coal mine waters were below 50µm/yr except in one mine, where the corrosion rate was 220µm/yr in aerated conditions. A medium carbon steel rock bolt (AISI 1040) has been studied by Yilmaz et al. under simulated YM water [8]. They studied the corrosion behavior of these rock bolts in 1X, 10X and 100X simulated water in aerated and deaerated environments. They reported a linear relationship between the corrosion rate (CR) and the temperature in 1X simulated YM water. However, at higher concentration there is a nonlinear relationship between them. They also reported that the corrosion rate increased as function of concentration at room temperature. This suggested that at higher concentrations and higher temperatures the corrosion rate decreased due to the precipitation of salts on the specimen surfaces. Similar behavior was also observed by Cragnolino et al. in J-13 water [9].

A slotted & tapered steel tube rock bolt consists of a slotted high-strength steel tube with a face plate. One end of the tube is tapered for easy insertion into a drill hole, and the other has a welded ring flange to hold the bearing plate. It is inserted into a hole slightly smaller in diameter than the tube, using a simple driver tool fitted to a pneumatic drill. As the tube enters the hole, its diameter is compressed and the slot partially closes. This exerts radial forces along the length of contact with the rock, providing the friction which holds the rock together. There are three common types of split-set rock bolts; specifications are given in Table 1.

In this current study, the corrosion behavior of slotted & tapered steel tube type ASTM A607 has been evaluated. We have systematically assessed the corrosion behavior of A607 steel in different concentration of simulated YM water in different environments using electrochemical methods. The effects of various experimental parameters such as temperature of the electrolyte, concentration of the electrolyte, and aeration/deaeration on the corrosion behavior have been studied.

![Figure 1. Underground support system for the proposed US nuclear repository [2]](image)

<table>
<thead>
<tr>
<th>Ions</th>
<th>$\text{Na}^+$</th>
<th>$\text{SiO}_2^{2+}$</th>
<th>$\text{Ca}^{2+}$</th>
<th>$\text{K}^+$</th>
<th>$\text{Mg}^{2+}$</th>
<th>$\text{HCO}_3^-$</th>
<th>$\text{Cl}^-$</th>
<th>$\text{SO}_4^{2-}$</th>
<th>$\text{F}^-$</th>
<th>$\text{NO}_3^-$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1XYM</td>
<td>61.3</td>
<td>70.5</td>
<td>191</td>
<td>8.0</td>
<td>17.0</td>
<td>200</td>
<td>11.7</td>
<td>116</td>
<td>0.86</td>
<td>-</td>
<td>7.2</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Element (weight percent)</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Nb</th>
<th>Mn</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.06</td>
<td>0.02</td>
<td>0.03</td>
<td>98.75</td>
<td>0.007</td>
<td>0.68</td>
<td>0.08</td>
<td>0.01</td>
<td>0.01</td>
<td>0.038</td>
</tr>
</tbody>
</table>
Experimental Procedure

Specimens for electrochemical tests were prepared from commercially available ASTM A607 slotted & tapered steel tube. The chemical composition of this steel was analyzed and is shown in Table 3. Disc shaped test specimens were cut out from the plate sample and mounted in epoxy with ~1 cm² exposed surface area. After the molding, the electrical connection between sample and the wire was checked with a voltmeter. Before the experiment the sample was polished manually using SiC emery papers ranging from coarse (240-grit) to fine (600-grit) finish to get an almost mirror finish. These prepared specimens were degreased with acetone and ultrasonically washed it with de-ionized water for 5 minutes before the electrochemical testing.

All the electrochemical experiments were conducted in a typical 1 liter Pyrex reaction vessel covered with a polytetrafluoroethylene (PTFE) lid. The lid had many ports containing the working electrode, counter electrode (platinum), gas spurge, thermocouple, inlet and outlet for the gas, luggin probe connected to silver/silver chloride (Ag/AgCl) reference electrode and a gas trap [11]. A schematic of the cell can be found in the work by Yilmaz et al. [8] on carbon steel. A large (~10 cm²) platinum sheet sealed to a glass capillary was used as the counter electrode. 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. 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 a constant pressure above the solution, and provided a slight positive pressure. A sealed glass capillary was used to house 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 ½ hour before immersing the test specimen. The specimen was then inserted into the cell and a constant distance (2-3mm) was maintained between the specimen and luggin tip. After reaching the steady state open circuit potential, potentiodynamic tests were conducted at a scan rate of 0.2mV/sec using a commercially available Potentiostat. The corroded surface was characterized using an optical microscope for different temperatures and concentrations.

Table 4. YM water chemistry for 1X concentration per liter

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>CHEMICALS</th>
<th>Weight (mg)</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>

The composition of the simulated YM water is established by Yilmaz et al. [8] and is given in Table 2 for 1X concentration. The electrolyte was prepared by mixing different kinds of salts in distilled, de-ionized water. Table 4 shows the different salts that were used to make 1X YM water. After adding the salts to the de-ionized water the solution was stirred on a hot plate (50°C-60°C) for 30 minutes and then cooled 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 it 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.

The corrosion rates were calculated using ASTM G59 [12] and ASTM G102 [13] procedures. For calculations, the polarization resistance (Rₚ) of the solution was neglected because it was shown by Yilmaz et al. [8] to be negligible for 1X, 10X and 100X concentrations. Tafel constants for both anodic and cathodic reactions were assumed to be constant (0.12V/decade). From the polarization resistance (Rₚ) value, the corrosion current density was calculated using equation 1, shown below.

\[ CR = K_j \frac{i_{corr}}{\rho} EW \]  \hspace{1cm} (1)

Where,

\[ K_j = 3.27 \times 10^{-3} \text{ mm·g/µA·cm·year} \]
\[ i_{corr} = \mu A/cm^2 \]
\[ \rho = 7.83 \text{ g/cm}^3 \]
\[ EW = 27.82 \text{ (unit-less)} \]

Results

Effect of Temperature in Deaerated Water:

Potentiodynamic polarization tests were carried out on A607 steel at different temperatures for three different concentrations of waters (1X, 10X and 100X). Figure 2(a) shows the potentiodynamic scan of A607 steel in 1X concentration of water at different temperatures. Since the corrosion potentials (Ecorr) for all the temperatures are close to each other only two temperatures are shown to maintain clarity. From this
figure, it is clearly observed that the corrosion current density increases as the temperature increases, which suggest a higher corrosion rate at 90°C. The corrosion potential is lower at 90°C than at 25°C which again suggests a more active material at 90°C. This kind of behavior is common for steel and is reported by Yilmaz et al. [8]. Figures 2(b) and 2(c) show the same kind of behavior for 10X and 100X water concentration. The corrosion potential range is from -0.74V to -0.76V in 1X, -0.725V to -0.742V for 10X and -0.705V to -0.709V for 100X water for all temperatures. The cathodic portion of the potentiodynamic plot is linear in 10X and 100X water and there is a slight change in the slope for 1X water for the applied potential range. The linearity of the cathodic curve represents that there is no change in the reaction rate; in other words there is no limiting current for the cathodic reactions. For all concentrations, there is a distinct passive region on the anodic portion of the potentiodynamic plot. It is clearly observed from Figure 2 that as the temperature increases, the passive current density also increases in the anodic region. For 1X water, the passive current density changes as the temperature increases. At 90°C, it becomes a vertical line, suggesting a thin protective passive film forms at this temperature. At lower concentrations (Figure 2), as the applied potential increases, the protective passive film starts to break down and the breakdown potential is higher at higher temperature. This may be due to a more protective oxide film formed at 90°C. At higher concentrations (10X and 100X), there was no vertical passive region at any temperature. The breakdown potential is lower at 90°C than 25°C for 10X and 100X waters due to a higher number of Cl\(^-\) present in the electrolyte.

The corrosion rate is calculated by the polarization resistance method as discussed in the experimental section. Table 5 shows the results of the corrosion rate in deaerated water for different temperatures and concentrations. A plot of corrosion rate as a function of temperature for different concentration of waters (1X, 10X and 100X) is shown in Figure 3. It is clear that as the temperature increases, the corrosion rate increases at all water concentrations; however the rate of increase is not linear. At all concentrations; the rate of increase in corrosion rate is higher between 25°C and 65°C, but as the temperature increases above 65°C, the rate of increase slows. Similar kinds of behavior were observed by Yilmaz et al. [8] in their study of rock bolts. When the temperature was raised above 65°C, the rate of increase in the corrosion rate promptly decreased due to the reaction of the metal surface with anions in the electrolyte, forming semi-protective salts. This effect may be more important in the 100X electrolyte. There is a lesser effect of O\(_2\) via the electrolyte when the solution is deaerated. The corrosion rate is 34µm/year at 25°C and 103µm/year at 90°C in 1X concentration. This same order of corrosion rate was observed by Yilmaz [8] in 1X YM water for medium carbon steel rock bolts which is 160 µm/year at 85°C. Jolly et al. [5] determined the corrosion rate of slotted & tapered steel tube (EX-TEN-H60 and KAI-WELL-55) in deaerated water in different mine waters at 17°C and the reported corrosion rate was around 10 to 48 µm/year for all mine waters. In another study, Tilman et al. [4] reported the corrosion rate to be around 40 to 71 µm/year in 4 different lead and iron mines.

Figure 2. Potentiodynamic polarization curves for A607 steel in deaerated water at different temperatures (a) 1X (b)10X and (c)100X concentration of electrolyte.
The corrosion rate of any material depends on time and on the environment, so the results reported in this study are different than the others [4,5]. In 10X YM water, the calculated corrosion rate at 25°C is 57µm/year, as the temperature increased the corrosion rate increased as well. The maximum corrosion rate of 214µm/year was observed at 90°C. Optical micrographs presented in Figure 4 show that at 90°C there are salts deposited on the sample (the white precipitates). This was also observed by Yilmaz et al. [8] for medium carbon steel rock bolts. A detailed study of the film formed on the medium carbon steel rock bolt was performed by Deodeshmukh et al. [14] using X-ray Photoelectron Spectroscopy (XPS). They determined the protective film consisted of FeCO₃ and iron-oxide/hydroxide. This same kind of behavior is observed in 100X YM water. The reported corrosion rate for 100X concentration is 93µm/year at 25°C and 211µm/year at 90°C. The activation energy for the corrosion process was calculated for three concentrations of electrolytes by replotting the corrosion rate data as a function of temperature and shown in Figure 5. The calculated activation energy for 1X was 10.77 kJ/mol, 10X was 18.29 kJ/mol and for 100X was 15.46 kJ/mol.

Optical micrographs were taken after the potentiodynamic scans at different temperatures in 10X and 100X water to understand the mechanism of corrosion. The micrographs are shown in Figure 6 for a qualitative study of the effect of the concentration and temperature on corrosion. In 10X water at 25°C, there is little attack (only a few pits), but at 90°C there are pits as well as uniform corrosion. In the case of 100X water, there are many pits present even at 25°C. At higher temperatures, the pit density increased, which indicates a higher corrosion rate because of the contribution of pitting corrosion along with the uniform corrosion (Figure 6).
**Effect of Concentration in Deaerated Water:**

Potentiodynamic scans for A607 rock bolts in different concentrations of electrolyte are presented in Figure 7(a) and 7(b). Figure 7(a) represents the potentiodynamic scan for A607 at 25°C for different concentrations. It shows that as the concentration increases, the corrosion potential, \( E_{corr} \), increases. At room temperature, in 1X water, \( E_{corr} \) was -0.76V. In 10X water \( E_{corr} \) was -0.73V and in 100X water, \( E_{corr} \) was -0.72V. The cathodic portions of the potentiodynamic scans were linear for all concentrations. The calculated corrosion rate was the lowest in 1X water and highest in 100X water, shown in Table 5. At higher temperatures, this behavior was also observed, and is shown in Figure 7(b). The cathodic portion of the potentiodynamic scan overlapped in case of 10X and 100X water and the \( E_{corr} \) were close to each other. This suggests an insignificant increase in corrosion rate for both 25°C and 90°C between 10X and 100X. This trend of corrosion rate is presented in Figure 8. The calculated corrosion rate is plotted as a function of concentration in Figure 8. This shows that the corrosion rate increases as a function of temperature and concentration. However, the increase in corrosion rate is not significant at higher concentration, especially at higher temperatures. At 25°C, the corrosion rate was 34µm/year in 1X water, increasing to 57µm/year in 10X water, and to 93µm/year in 100X water. This same kind of behavior was observed at 45°C. But at higher temperatures (65°C and 90°C), the highest corrosion rate was observed in case of 10X water. As the concentration increased from 10X to 100X, the corrosion rate didn’t change or decreased. At 100X water and higher temperatures, the ions that are present in the solution precipitated out from the solution onto the metal surface. These ions formed a protective film during the cathodic charging which inhibited the corrosion process. At higher temperatures, salt deposits were observed on the cell wall, as well as on the sample after the potentiodynamic scan.

**Effect of Temperature in Aerated Water:**

Corrosion behavior of A607 steel as a function of temperature was studied at all three concentrations of electrolyte (1X, 10X and 100X) in an aerated (oxygenated) atmosphere using potentiodynamic polarization. This is shown in Figures 9(a-c). These plots indicate that A607 steel exhibits active dissolution in aerated conditions at different temperatures and concentrations of electrolytes. There was no passive region observed under aerated conditions at all concentrations. The corrosion potential range was wider in aerated conditions than deaerated conditions. The lowest corrosion potentials were observed at 90°C for all concentrations of electrolyte. The measured corrosion potential was higher in the aerated condition compared to the deaerated condition as shown in Figures 9(a-c). The cathodic portion of the potentiodynamic scan shows linear behavior for all concentrations at all temperatures.
Corrosion rates of A607 steel at different temperatures and concentrations is shown in Table 6. A corresponding plot of corrosion rate as a function of temperature for different concentrations is shown in Figure 10. Overall, the corrosion rate is higher in aerated conditions than deaerated conditions. In general, an increase in temperature increased the corrosion rate for 1X and 10X concentrations. The corrosion rate didn’t increase in a linear fashion as was observed in deaerated conditions. In 100X concentration, the corrosion rate increased as the temperature increased from 25°C to 65°C, but started decreasing above 65°C. The corrosion rate was determined at more intermediate temperatures to observe trend more elaborately. There was a sudden drop in the corrosion rate from 65°C to 75°C and after that it decreased linearly. This has been confirmed by the optical microscopy, taken after the potentiodynamic scan. The micrographs are shown in Figure 11. At 25°C, hardly any pits are observed. As the temperature is increased to 45°C, the micrograph shows the topography of the corrosion, indicating higher corrosion rate. The highest pit was observed at 65°C, where the depth of the pits was also higher, compared to other temperatures. The corrosion rate is also highest at 65°C. At 90°C, the micrograph shows less attack on the surface of the sample, suggesting a lower corrosion rate. The lower corrosion rate at higher temperatures may be due to the lower solubility of oxygen. There is also evidence of salt precipitating out of the solution, onto the surface of the sample at higher temperatures, which render the corrosion process. It was also observed by other researchers that the higher corrosion rates increase to a maximum value at intermediate temperatures for carbon steel [6,9]. Similar kinds of behavior was observed by Yilmaz et al. [8] and Arjunan et al. [15] in the same kind of electrolyte for medium carbon steel and low carbon steel, respectively. They observed the maximum corrosion rates at 45°C in their studies, but in our current study we observed the maximum at 65°C.
Effect of Concentration in Aerated Water:

Potentiodynamic scans for A607 steel rock bolts in different concentration of YM water are presented in Figures 12(a) and 12(b). A decreased corrosion potential was observed, as the concentration of the electrolyte increased. This trend is opposite of what was observed in the deaerated condition, at the same concentration. At 25°C (Figure 12a), the corrosion potential was -360mV in 1X water, -423 mV in 10X water and -493mV in 100X water. The same trend was also observed at 90°C (Figure 12b). The cathodic portions of the potentiodynamic scans were linear for all concentrations. A plot of corrosion rate as a function of concentration is shown in Figure 13. In general, the corrosion rate increases as the concentration increases at 25°C, 45°C and 65°C. At 90°C, the corrosion rate increases as the concentration increases from 1X to 10X. However, in 100X water, the corrosion rate decreases significantly. This was discussed in the previous section.

Effect of Environmental Conditions:

The corrosion behavior was evaluated in aerated and deaerated conditions for the three different concentrations of water. Figure 7(a) shows the potentiodynamic scans for three different concentrations in the deaerated condition. Figure 12(a) shows the potentiodynamic scan for three different concentrations in an aerated (oxygenated) environment. According to Figure 12(a), as the concentration increases, the corrosion potential, \(E_{corr}\), decreases. At room temperature, in 1X water, \(E_{corr}\) was measured as -0.35V and in 100X water \(E_{corr}\) was measured as -0.48V. The calculated corrosion rate was also higher in 100X compared to 1X water, which is shown in Table 7, and is graphically represented in Figure 14. Overall, the corrosion rate is higher in the aerated condition than in the deaerated condition.

### Table 6. Corrosion rates of A607 steel in aerated conditions

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Temperature (°C)</th>
<th>Condition</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>aerated</td>
<td>8927</td>
<td>2.92E-06</td>
<td>158</td>
</tr>
<tr>
<td>1X</td>
<td>45°C</td>
<td>aerated</td>
<td>4626</td>
<td>5.63E-06</td>
<td>654</td>
</tr>
<tr>
<td>1X</td>
<td>65°C</td>
<td>aerated</td>
<td>3263</td>
<td>7.98E-06</td>
<td>1076</td>
</tr>
<tr>
<td>1X</td>
<td>90°C</td>
<td>aerated</td>
<td>2932</td>
<td>8.39E-06</td>
<td>1265</td>
</tr>
<tr>
<td>10X</td>
<td>25°C</td>
<td>aerated</td>
<td>5312</td>
<td>4.90E-06</td>
<td>197</td>
</tr>
<tr>
<td>10X</td>
<td>45°C</td>
<td>aerated</td>
<td>2350</td>
<td>1.11E-05</td>
<td>868</td>
</tr>
<tr>
<td>10X</td>
<td>65°C</td>
<td>aerated</td>
<td>1587</td>
<td>1.64E-05</td>
<td>1453</td>
</tr>
<tr>
<td>10X</td>
<td>90°C</td>
<td>aerated</td>
<td>1413</td>
<td>1.84E-05</td>
<td>1627</td>
</tr>
<tr>
<td>100X</td>
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<td>aerated</td>
<td>3240</td>
<td>8.04E-05</td>
<td>211</td>
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<tr>
<td>100X</td>
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<td>8.04E-05</td>
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<td>1.46E-05</td>
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<td>2182</td>
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<td>aerated</td>
<td>1607</td>
<td>1.62E-05</td>
<td>2393</td>
</tr>
<tr>
<td>100X</td>
<td>75°C</td>
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<td>1.46E-05</td>
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<tr>
<td>100X</td>
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<td>1437</td>
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<td>441</td>
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</table>
in deaerated condition. Under an oxygenated environment, in 1X water, the corrosion rate was 158µm/year. This increased to 197µm/year in 10X water and to 211µm/year in 100X water. At higher concentrations, the increase in corrosion rate is not as significant. This may be because there are more ions in the solution. Due to the higher concentrations of Ca$^{2+}$, Mg$^{2+}$ and CO$_3^{2-}$, there is a possibility of forming thin CaCO$_3$ film on the sample surface. This acts as a protective film and forms a barrier to the dissolved oxygen. This kind of behavior was also observed in medium carbon steel rock bolts by Yilmaz et al. [8].

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Temperature (°C)</th>
<th>Condition</th>
<th>$R_p$ (ohm.cm$^2$)</th>
<th>$I_{corr}$ (µA/cm$^2$)</th>
<th>Corrosion rate (µm/year)</th>
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Figure 12. Potentiodynamic polarization curve of A607 steel in different electrolyte concentration under aerated (oxygenated) condition (a) 25°C and (b) 90°C.

Figure 13. Corrosion rate of A607 steel as a function of electrolyte concentration at different temperatures.

Figure 14. Corrosion Rate of A607 steel as a function of concentration of YM water in deaerated and aerated conditions at 25°C.

Two potentiodynamic scans, one aerated and other deaerated, are presented in Figure 15, in 100X water at 65°C. The corrosion potential is higher in aerated condition that in deaerated condition. Also, it can be observed that the corrosion current is higher in the aerated condition, which implies a higher corrosion rate. There was no passive film formation, due to a continuous increase in current density in the anodic region as the potential increased. However, in deaerated conditions, the current density increased in the anodic region, with a small increase in potential beyond the $E_{corr}$. Observations showed that a passive layer began to
form at around -0.62V, and that there was no increase in current density up to -0.55V, where the passive film began to breakdown. At this potential, due to the breakdown of the passive layer, there is chance of localized corrosion, such as pitting corrosion. In the same plot, we have presented the optical micrograph for this sample. The optical micrograph was taken after the potentiodynamic scans. From these micrographs, it is clear that the corrosion rate is higher in the aerated condition than in the deaerated condition. This can be confirmed by the amount of pits that were observed for both cases.

Figure 15. Two potentiodynamic scans, under aerated and deaerated conditions in 100X YM water at 65°C along with micrographs taken after the experiment.

Corrosion behavior of A607 steel under deaerated conditions by using Potentiostatic method

The potentiostatic test is usually performed to determine the susceptibility of a material to pitting corrosion. In cyclic polarization method, the study of pitting corrosion depends on the sweep rate and also the pit stats to propagate before it starts to reverse sweep. With this technique, a constant potential is applied and the current is measured as a function of time. The use of individual samples held at potentials around the suspected pitting potential will allow the correct determination of the pitting potential. Dayal et al. [16] suggested that by using this method the pitting potential ($E_{pit}$), as well as critical potentials for stable and unstable pits, could be measured. The current transients of A607 steel under different applied potentials are shown in Figure 16. The potentials chosen for this experiment were selected from the active region, passive region and transpassive region. In general, decay in current is observed at all potentials due to the formation of an oxide layer. The current drops rapidly in the early stage of the polarization, followed by decay, reaching a low current density. However at -400mV, the current decreases at the beginning of the polarization and it continues to decay for 10 minutes. After that, the current starts to increase as a function of time, which suggests a stable pit is formed at this potential. The slope of the current vs. time is linear for +200mV, shows the passive layer formation at this potential; which can be attributed from the potentiodynamic scan (Figure 16). The passive behavior of glassy Ni_{55}Co_{55}Nb_{20}Ti_{10}Zr_{10} alloy was evaluated by using the potentiostatic tests by Pang et al. [17]. They used the slope of the current vs. time to describe the passive corrosion behavior of this material. Optical micrographs, which were taken after the potentiostatic scans, are shown in Figure 17(a-d). At -700mV, the micrograph didn’t show any pitting. Pitting started to initiate at -600mV, which is shown in Figure 17(b). N. Alonso-Falleiros et. al. [18] studied the potentiodynamic and potentiostatic tests for measuring the pitting potential of duplex stainless steels. He found that potentiostatic tests are more reliable for measuring the pitting potential as well as to understand the pitting nucleation mechanism. A stable pit was formed at -400mV which can be verified from the plot of current vs. time at -400mV. It shows a decrease in current density followed by a further increase of current. At lower potentials (-700mV and -600mV), the current fluctuates as a function of time. This fluctuation of current represents the metastable pit formation at these potentials. Y. F. Cheng et. al. [19] studied the metastable pitting of carbon steel by potentiostatic measurement at different applied potential. He concluded that the current fluctuation of the potentiostatic measurements is due to the formation of metastable pits.

Figure 16. Current transient of A607 steel at different applied potential in 1X electrolyte at room temperature.

To study the effects of temperature, we selected a fixed potential of -600mV and four different temperatures (25°C, 45°C, 65°C and 90°C). The current transient of the potentiostatic tests are shown in Figure 18. It is observed that the current decays as a function of time for all temperatures. The lowest current is observed at 45°C, suggesting a stable oxide layer formation at this temperature. The fluctuation of current at 25°C and 45°C suggests metastable pitting at these
temperatures. The slope of the current vs. time at 25°C is lower than at other temperatures. The highest slope is observed at 45°C. This is possibly due to the formation of an impervious oxide layer. At 90°C, the slope is the steepest. At the end of 1 hour, tests suggest a higher corrosion rate due to the pitting, as well as crevice corrosion, which was confirmed by the optical micrographs.

Figure 17. Optical micrograph of A607 steel taken after the potentiostatic experiments at different potentials shown in micrographs. The pitting initiation begins at -600 mV and is more pronounced at higher potentials.

Figure 18. Current transients in A607 steel taken at –600 mV as a function of temperature in 1X electrolyte

**Effect of Individual Salts on the Corrosion Rate under Deaerated Conditions**

Potentiodynamic polarization tests were carried out in individual salts to evaluate the effect of each salt on the corrosion rate. The electrolytes were prepared by using 100X concentration of each salt mixed with de-ionized water. To maintain clarity, only two salts are presented in each plot. Potentiodynamic scans for magnesium chloride and calcium chloride, presented in Figure 19, shows almost the same corrosion potential. The corrosion potential of calcium chloride is a little higher than magnesium chloride. Both cathodic and anodic current densities are also higher for calcium chloride. Potentiodynamic scans for the sulfate salts (CaSO_4 and MgSO_4) are shown in Figure 20. The corrosion potential is a little higher for the calcium sulfate, which suggest a similar trend, as in chloride salts. Figure 21 represents the potentiodynamic polarization plot for sodium bicarbonate and potassium bicarbonate. The corrosion potentials are almost the same for both salts. The only difference is in the cathodic and anodic current densities. The cathodic and anodic current densities are higher for sodium bicarbonate. Both bicarbonate salts show passive behavior in short, applied potential ranges. Sodium silicate showed a long, passive region, which is shown in Figure 22. Another study was carried out on similar ions of different salts, which is shown in Figure 23. All the potentiodynamic scans in combined salts of similar ions showed similar behavior, as was observed for individual salts. The corrosion rate was calculated by using the polarization resistance method, which was discussed in the previous section. The corrosion rates of individual salts, as well as the similar salts, are presented graphically in Figure 24. The lowest corrosion rate was observed for sodium silicate and the highest corrosion rate was observed for sodium bicarbonate.
Figure 21. Potentiodynamic polarization curves for A607 steel in KHCO$_3$ and NaHCO$_3$ obtained at room temperature.

Figure 22. Potentiodynamic polarization curve for A607 steel in NaSiO$_3$ obtained at room temperature.

Figure 23. Potentiodynamic polarization curves for A607 steel in similar salts obtained at room temperature.

Figure 24. Corrosion rates of A607 steel using different salt electrolytes obtained at room temperature.

Discussion

Comparison of Corrosion Rates of the A607 with other Steels

The corrosion rates of different materials (AISI 1040 steel and ASTM A36 steel) in 1X, 10X, 100X electrolytes studied by previous researchers in our group using polarization resistance is presented in Figure 25 [8,15]. In general, the corrosion rate for A607 steel is higher than 1040 steel and A36 steel except in 1X concentration in deaerated condition. The variation of corrosion rates in different steels may be affected by the manganese to sulfur ratio; A607 steel has Mn:S ratio of 68:1; whereas for A36 steel is 17:1, and 1040 steel it is 5:1, the lower 5:1 concentration yields lowest corrosion rates. Moreover, Mn, by itself, has a higher oxidation potential than other elements in the steel and is a very active metal, contributing to corrosion. In deaerated condition, there is an increase in corrosion rate as a function of temperature for carbon steels. However, there is a deviation of this behavior at higher ionic concentration (100X electrolyte in deaerated condition) for one type A36 as compared 1040 and A607 form this study, in the same temperature range.

In the aerated condition, the corrosion rate increases as a function of temperature for all materials in 1X and 10X concentration which is shown in Figure 26. The corrosion rate of A607 steel is higher than 1040 and A36 steel for all concentrations (1X, 10X and 100X). The corrosion rate maxima for 1040 and A36 steels in 100X electrolyte were observed at 45°C, whereas for the A607 steel it was observed at 65°C. In selecting the steels for the rock bolts, we have two major parameters to consider, (1) strength and (2) corrosion rates from metallurgical perspectives. In general, the 1040 steel exhibited lowest corrosion rate, and A607 has the highest corrosion rate in deaerated conditions. In aerated conditions the A36 steel has the
lowest corrosion rates and the A607 has the highest rate. Although we have not discussed mechanical property issues in this paper, but it is desired to have yield strengths of rock bolts well above the radial stress load exerted by rock displacements. If corrosion is a major consideration for long range durability of the rock bolts inserted in the rockmass, then an optimization has to be made between strengths and corrosion rates of steels used for rock bolts.

**Summary and Conclusions**

The corrosion rates of rock bolt steels that we have studied under multi-ionic as well isolated electrolytes are technologically important as it has significance with an important nuclear repository environment in conjunction with commonly used steels for the rock bolts. The understanding of the corrosion behavior of these generic steels have implications to other underground structural applications such as I-beams and Bernold shields wire meshes commonly used in mines and repositories.

The corrosion behavior of A607 rockbolt (1X and 10X) was similar in both aerated and deaerated conditions with the exception that the corrosion rates were an order of magnitude higher in the aerated condition. In deaerated electrolyte the corrosion rate ranges from 34 to 211 µm/yr between 298 to 338K encompassing all concentrations (1X,10X and 100X). For aerated conditions the 1X and 10X have similar behavior but higher corrosion rates as compared to the deaerated conditions. The behavior the 100X electrolyte is very interesting as the corrosion increase ~210 to 2400 µm/yr corrosion rate between 298 to 338K and beyond this decreases steeply decrease to 750 µm/yr from 338 to 348K.

The effect of concentration of electrolyte on the corrosion rate appears to be asymptotic. General as well as localized corrosion was observed. Potentiostatic scans showed formation of pits started at -600mV; above $E_{corr} -750$ mV at room temperature;
however the pitting potential varied with the temperature. The fluctuation of current in potentiostatic scans suggest metastable pits formation at lower temperatures. So far we discussed multionic salt solutions, but the study of individual ionic affect shows that the lowest corrosion rate using sodium silicate salts electrolyte.

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References