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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. 10

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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. 10 (submitted during 1st Quarter of FY 2007)

Start Date of this Quarter, October, 1, 2006 to December 31, 2006

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submitted to-

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January 10, 2007
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 Mn-24 rock bolts, and 4340 steel for Bernold shields or rock bolts, and Alloy 22. 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 on rock bolts and other materials in which radioactive waste is stored. During this period, we used potentiodynamic tests to obtain corrosion rates. We had to perform some TGA apparatus calibration and baseline tests for oxidation tests.

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, 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 No.10 the corrosion rates have been determined in deaerated (nitrogenated) conditions at different temperatures in simulated 100X 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.

This quarter, one student graduated with a Ph.D degree in our department working on our Task ORD 19 YM project research. (Dr. S. Rahman)- Advisor – D. Chandra

Metallurgical Transactions A .paper now in Print, (J. Lamb et al., Chandra’s group)

NACE Conference Proceeding paper No.06628 published in 2006 (S. Rahman et al. (Chandra’s group)

NACE Conference Proceeding paper No.06615 published in 2006 (S. Rahman et al ., Chandra’s group)

NACE Conference Proceeding paper No.06617 published in 2006 (A. Talekar et al., Chandra’s group)

NACE Conference Proceeding paper No. 06616  published in 2006 (S. Divi et al. , Chandra’s group)

Progress for the Period 10/1/06 to 12/31/06

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 Mn-24 Swellex rock bolts, Alloy 22, and 4340 steel.

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

Subtask 6: Thermogravimetric (TGA) recalibration for reliability test 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:

- Potentiodynamic tests were performed to determine corrosion rates (CR) of 4340 Steel in 100X YM waters at several temperatures in deaerated condition.
- EIS studies were performed on the 4340 steel at 100x YM waters
- Further studies on Swellex Rock bolts were performed by using individual ionic species found in the YM waters, such sulfate ions, bi carbonate ions etc.
- The TGA had to be recalibrated and the anomalies of the modulated data for oxidation studies were performed for determination of accuracy of the data.
II. Effect of Heat treatment on Corrosion Rate of Alloy 22 weld using Electrochemical Method
(10th Quarterly Report)

Summary

It is well known that Alloy 22 has excellent corrosion resistance in various environments. But the fabrication process of the container for nuclear waste involves welding of Alloy 22 to close the lid. This welding process will involve high temperatures, at which the topologically close packed (TCP) phases are stable. After welding the material, it will also go through heat treatment process for stress relief. In this paper, we present the corrosion rates of As Weld Alloy 22 material in the three different locations (weld, half weld and base metal) and compare the results with the solution heat treated (at 1121°C for 1 hr followed by quenching) conditions in 0.1M HCl solution at 66°C. We also present the microstructural changes due to the heat treatment process. Finally we present the micrographs of the corroded sample after the potentiodynamic polarization to observe the localized attack of the specimen. Results show that the corrosion resistance of the heat treated sample is higher for all three samples (weld, half weld and base metal) than that of as weld conditions.

2.1 Background

Alloy 22 (N06022) is a nickel based superalloy containing 22% chromium (Cr), 13% molybdenum (Mo), 3% tungsten (W) and 3% iron (Fe). It has excellent resistance to corrosion, as well as stress corrosion cracking under various environments [1-8]. The U.S. Department of Energy (DOE) is considering this material for the outer barrier of the nuclear waste containers for the proposed nuclear repository site at Yucca Mountain (YM), Nevada [9]. Since then the corrosion behavior of Alloy 22 has been the subject of intensive research. According to the DOE, the spent nuclear fuel will be stored in a container called waste packages. These waste packages consists of two concentric metal containers; the outer container is made of Alloy 22 and a thick inner container made of type 316 nuclear-grade stainless steel [10,11]. The spent nuclear waste will be placed in the waste package and the lid of the waste package will be closed by multipass gas tungsten arc welding with a filler metal (ERNiCrMo-10) close to the composition of Alloy 22 (N06022). After sealing the waste package, it will be placed inside the repository tunnels, during the operational phase of the first 50 years, followed by a monitoring phase up to 300 years, after which the repository will be closed.

Since the fabrication process of the waste packages involve the welding of Alloy 22, there will be formation of dendrites in the weld as well as interdendritic microstructures in the Heat Affected Zone (HAZ). There have been several studies published showing that Topologically Closed Packed (TCP) phases such as, \( \mu \), \( P \), \( \sigma \) etc. form in the weld as well as in HAZ of the weld [12-16]. It has been shown by other researchers that Alloy 22 goes through phase changes at aging temperatures ranging from 600°C to 900°C forming secondary TCP phases [16-19]. Pan et. al. reported that the phases (\( \mu \), \( P \), \( \sigma \) etc) preferentially precipitate out at the grain boundaries after aging at 870°C for 30 mins. As a result, it decreases the corrosion resistance of Alloy 22 in chloride containing solutions [20]. Rebak et. al. showed a decrease in corrosion resistance and mechanical properties of Alloy 22 aged at higher temperature because of the secondary TCP phase precipitation [21].

The welding process involves a post-weld annealing at high temperature (1121°C) for removing residual stresses and for removing the TCP phases recommended by manufacturer [22]. However, Pan et al. reported that the annealing process enhances the TCP phase precipitation after annealing it at various temperatures and times [23]. El-Dasher et. al. [24] in their study, reported that the solution annealing of Alloy 22 welds at 1121°C for 20 mins reduces the TCP phase precipitation but the sizes of the precipitates were much smaller. Rebak et. al. studied the corrosion behavior of Alloy 22 weld using the ASTM G28B procedure and reported a higher corrosion rate than the base metal [25]. Gorhe et. al. reported that aging of alloy22 \( \geq 650°C \) for more than 1 hr diminishes the Cr depletion [26]. They also reported that the corrosion rate increases as the temperature and aging time increases due to the TCP phase formation.
The purpose of this study is to study the corrosion behavior of Alloy 22 welds in different locations (weld, half weld and base metal) and make a comparison of the corrosion rates in 0.1M HCl solutions at 66°C. Effects of post weld heat treating on the corrosion rate will also be presented. This study also involve the examination of microstructural changes of the Alloy 22 weld after heat treatment using Scanning Electron Microscope (SEM) as well as optical microscopy.

2.2 Experimental Procedure

2.2.1 Specimen Preparation

A prototype weld of Alloy 22 was prepared by welding two plates of Alloy 22 with ERNiCrMo-10 filler using gas tungsten arc welding. The Alloy 22 weld was then polished and etched to reveal the welded area which is shown in Figure 2.1. Three different locations of the sample were chosen for this study (base metal, half weld and half metal, weld) to compare the corrosion rate at different locations (Figure2.2). Two sets of each disc-shaped sample were punched out from the Alloy 22 weld. The first set was used to study the as weld condition. The other set was heat treated in a air furnace at 1121°C for one hour and then quenched in water. The test specimen was mounted in epoxy with ~1 cm² exposed surface area. Before the experiment, the specimens were polished with 600 grit SiC emery papers. These prepared specimens were degreased with acetone and ultrasonically washed with de-ionized water for 5 minutes before electrochemical testing.

Figure 2.1. The welded specimen showing the weld area after etching.

Figure 2.2. Optical micrographs of the specimen taken from the sample.
2.2.2 Electrochemical Tests

A one liter Pyrex glass flask, covered with a polytetrafluoroethylene lid, was used for all the electrochemical experiments. The lid contained many ports for the working electrode, counter electrode (platinum), gas purge, thermocouple, inlet and outlet for the gas, luggin probe [connected to silver/silver chloride (Ag/AgCl) reference electrode through a salt bridge (agar-agar solution)] and a gas trap (ASTM G5) [19]. This same setup was used by Yilmaz et al. [27] on carbon steel. A Platinum sheet sealed to a glass capillary was 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. The Luggin probe tip and Ag/AgCl reference electrode were connected via the electrolyte (YM water) in the bridge. Nitrogen gas was continuously purged 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 monitoring the temperature of the electrolyte. A fritted glass capillary was used for continuous deaeration of the solution throughout the experiment at the rate of 100mL/min. A temperature bath (Fisher Scientific ISOTEMP 220) was used to maintain the temperature of the solution. A condenser was used to avoid electrolyte evaporation during the test. The electrolyte was purged continuously with nitrogen for 30 min 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 immersing the sample in the electrolyte for one hour, the potentiodynamic tests were conducted at a scan rate of 0.2mV/sec using a Gamry potentiostat. The electrolyte for this study was 0.1M HCl solution and all the experiments were conducted at 66°C.

2.2.3 Corrosion Rate Calculations

The corrosion rate was calculated by following ASTM procedures [28, 29]. During calculation of the polarization resistance ($R_p$), solution resistance was neglected. Tafel constants for both anodic reaction and cathodic reactions were assumed to be constant (0.12V/decade). From the polarization resistance ($R_p$) value the corrosion current density was calculated. Using equation (1), the corrosion rate ($\mu$m/yr) was calculated:

$$CR = K_i \frac{i_{corr}}{\rho} EW$$  \hspace{1cm} (1)

Where, \( K_i = 3.27 \times 10^{-3} \text{ mm.g/\mu A.cm.year} \)
\( i_{corr} = \mu A/cm^2 \)
\( \rho = 8.69 \text{ g/cm}^3 \)
\( EW = 23.28 \)

2.2.4 Metallographic Sample Preparation

The microstructure presented in this study was prepared by using metallographic polishing using consecutive 240, 400, and 600 grit emery paper, and then polished with 1, 0.3 and 0.05µm alumina powder. Electrochemical etching was performed by using in a solution of oxalic acid and hydrochloric acid mixture (5g oxalic acid in 95cc of 37% HCl solution) at 6V for a few seconds. The samples were then washed with acetone before viewed under the microscope. Samples were viewed right after the potentiodynamic scan, after a gentle wash with de-ionized water.

2.3 Results and Discussions

2.3.1 Microstructure

The microstructure of as-weld and heat treated specimens are shown in Figure 2.3. It has been observed from the figure that in the as weld specimens, the grains of Alloy 22 are very prominent in the base metal, and the dendrites are visible in the welded area. The heat-affected-zone was not distinguished from this optical micrograph. The micrograph of the heat treated specimen showed a change in the microstructure in the dendritic region. The dendrites recrystallize to more homogeneous grains throughout the weld area and continue to the base metal.
2.3.2 Corrosion Behavior of As Weld Specimens:

2.3.2.1 Potentiodynamic scans

Potentiodynamic scans of Alloy 22 as weld specimens (Base Metal=M-1; Half weld and Half metal=H-1, Full Weld=W-1) in 0.1M HCl solution at 66°C are presented in Figure 2.4.
The corrosion potential for all the specimens is very similar. The lowest corrosion potential of -263mV is observed for the weld specimen (W-1). All three specimens showed a larger passive region. However, the passive current density changes and highest passive current density was observed for W-1 specimen, suggesting a higher corrosion rate.

### 2.3.2.2 Corrosion Rate

The corrosion rates for above specimens were calculated by using the polarization resistance method previously discussed in the experimental section. The corrosion rate data are plotted in Figure 2.5. It is observed from the plot that the corrosion rates of the Base metal (M-1) and the Half and Half (H-1) are much lower than that of the weld (W-1). The observed corrosion rate for the as weld specimen (W-1) is approximately 300µm/yr. It has been shown by other researchers that welded Alloy 22 has a higher corrosion rate than the base metals in different environments [30, 31], due to the segregation of Mo and W in the inter-dendritic regions of the weld. Summers et. al. [32] studied the corrosion rate of Alloy 22 using ASTM G28B as a function of aging time and temperature. They reported that as the corrosion rate increased the ageing time and temperature increased, due to the formation of TCP phases in the grain boundaries, as well as within the grain. In another study, Summers et. al. [33] reported that the corrosion rate of weld samples were 30% higher than the base metal samples, in both boiling acidic ferric sulfate and hydrochloric solutions. Optical micrographs were taken after the potentiodynamic scans for these specimens are shown in Figure 2.6. All the specimens were observed under the microscope before and after the potentiodynamic scans. For specimens H-1 and W-1 [Figure 2.6(b) and 2.6(c)], it can be observed that both specimens revealed the weld dendrite structure due to the corrosion process, whereas the base metal (M-1) didn’t show any noticeable changes in microstructure [Figure 2.6(a)]. It has been shown by El-Dasher et. al. that the majority of the corrosion occurs in the weld dendrites and less corrosion in the interdendritic regions [34].

### 2.3.2.3 Effect of Immersion Time

A long term experiment was performed to observe the corrosion of these specimens. These tests involved the following steps: a) immersing the specimens in deaerated 0.1M HCl solution at 66°C for 1 hr, b) running three consecutive potentiodynamic experiments with potentials ranging from -1V to +1V, c) Continuing the immersion of
the specimens for 3 additional hrs and running three consecutive potentiodynamic experiments with potentials ranging from -1V to +1V. The corrosion rates for each of these tests were calculated using the polarization resistance method. Potentiodynamic scans for the Base Metal after 1 hr immersion is shown in Figure 2.7(a).

The first experiment shows a higher corrosion potential than the following experiments. It shows that the passive current density is lower for the first experiment suggesting a lower corrosion rate. After the first experiment, the passive film that formed on the specimen dissolved due to the higher applied potential. As a result, the following experiments required a higher current to form the passive film. However, the passive current does not change significantly after the first experiment. Figure 2.7(b), the potentiodynamic scans after continued immersion for 4 hours is shown.

![Figure 2.5. Corrosion rates of as-weld specimens (M-1, H-1 and W-1) and heat treated specimens (M-2, H-2 and W-2) in 0.1M HCl at 66°C.](image)

These show a similar trend as the previous experiments (after 1 hr immersion). Similar experiments were performed on specimens H-1 and W-1 are shown in Figures 2.8 and 2.9, respectively. It is interesting to note that the corrosion potential and the passive current do not change significantly for all experiments after 1 hr and 3 hr immersion.

Corrosion rates calculated using the polarization resistance method is shown in Figure 2.10. This shows a lower corrosion rate for specimens H-1 and W-1. The corrosion rate of the 1st experiment of specimen M-1 (base metal) after immersion for 1 hour, shows a significantly lower corrosion rate than the following experiments. This may be due to removal of the passive film after the first experiment, which makes the formation of passive films more difficult. It is interesting to note that the corrosion rate for H-1 and W-1 didn’t change significantly for both 1hr and 4 hrs immersion tests, and is lower than M-1.
Figure 2.6. Optical micrographs taken before (left) and after (right) the potentiodynamic scans for as-weld specimens (a) M-1 (top), (b) H-1 (middle) and (c) W-1 (bottom).
Figure 2.7. (a) After immersion of the specimen for 1 hr, (b) continue for another 3 hr of immersion and run another 3 consecutive tests for Base Metal (M-1) as weld.
Figure 2.8 (a) After immersing the specimen for 1 hr, run 3 consecutive tests; (b) continue for another 3 hr of immersion and run another 3 consecutive tests for Half and Half (H-1) as weld.
Figure 2.9 (a) After immersing the specimen for 1 hr, run 3 consecutive tests; (b) continue for another 3 hr of immersion and run another 3 consecutive tests for Weld (W-1).
Figure 2.10. Corrosion Rates measured by using polarization resistance method after immersing the sample for 1 hr (□) and after continuing for another 3 hrs (♦); (three consecutive experimental results) in 0.1M HCl at 66°C.

Figure 2.11. Potentiodynamic Scans of Heat Treated Specimens (M-2, H-2 and W-2) in 0.1M HCl at 66°C.
2.3.3  Corrosion Behavior of Heat Treated Specimens

2.3.3.1  Potentiodynamic scans

Potentiodynamic scans of Alloy 22 heat treated specimens (Base Metal=M-2; Half weld and Half metal=H-2, Full Weld=W-2) in 0.1M HCl solution at 66°C are presented in Figure 2.11. In this figure, the corrosion potential and the passive current density for all three specimens (M-2, H-2 and W-2) are very close to each other, which was not observed for the as weld specimens. It has been shown by the previous researchers that the aging of the weld and mill annealed Alloy 22 significantly changes the microstructure [12-16]. This change in microstructure also changes the corrosion behavior of these specimens after aging at different times and temperatures.

2.3.3.2  Corrosion Rate

The corrosion rates for the previously mentioned specimens were calculated by using polarization resistance method and plotted in Figure 2.5. As seen in the figure, the corrosion rate of the Base metal (M-1), Half and Half (H-1) and the weld (W-1) specimens are nearly identical. The corrosion rate of the weld specimen showed a significant reduction compared to the heat treated specimen (W-2). El-Dasher et. al. studied the effect of solution annealing of welded Alloy 22 and reported that the annealing process reduced the dendritic corrosion of welded Alloy 22 [34]. In another study, Summers et. al. showed that the corrosion rate of the base metal and weld, in both oxidizing and reducing atmospheres, has the similar corrosion rate after aging at 600°C for several hundred hours [33]. Micrographs taken after the potentiodynamic scans showed no significant differences for both H-2 and W-2 specimen which are shown in Figure 2.12.

![Heat Treated H-2](image1)  ![Heat Treated W-2](image2)

Figure 2.12. Optical micrographs taken after the potentiodynamic scans for heat treated specimens (a) H-2 (left) and (b) W-2 (right).

2.3.3.3  Effect of Immersion Time

The long term behavior of heat treated specimens showed a significantly different behavior than the as weld specimens. The potentiodynamic scans of M-2, H-2 and W-2 after 1 hour immersion and 4 hours immersions are presented in Figure 2.13 to 2.15. All of these specimens showed similar behavior in 0.1M HCl at 66°C. The first experiment showed a higher corrosion potential and a lower passive current. This was also observed for the M-1 (as-weld) specimen. The following experiments didn’t show any significant changes in the potentiodynamic scans. However, as the passive current density increased, the corrosion potential decreased, suggesting a higher corrosion rate. The higher passive current density is attributed to the breakdown of the passive film (after the first experiment)
and to a preexisting corroded surface of the specimens. The calculated corrosion rates from these potentiodynamic scans are plotted in Figure 2.16. It can be observed that the corrosion rates of these specimens were comparable, regardless of the locations of the specimens. Solution heat treating at 1121°C for 1 hour significantly changed the microstructure of the weld, as well as the base metal. This contributed to the corrosion process for these specimens in a similar manner.

Figure 2.13. (a-left) After immersing the specimen for 1 hr, run 3 consecutive tests; (b-right) continue for another 3 hr of immersion and run another 3 consecutive tests for Base Metal (M-2) Heat Treated

Figure 2.14. (a-left) After immersing the specimen for 1 hr, run 3 consecutive tests; (b-right) continue for another 3 hr of immersion and run another 3 consecutive tests for Half and Half (H-2) Heat Treated.
Figure 2.15. (a-left) After immersing the specimen for 1 hr, run 3 consecutive tests; (b-right) continue for another 3 hrs. of immersion and run another 3 consecutive tests for Weld (W-2) Heat Treated.

Figure 2.16. Corrosion Rates measured by using polarization resistance method after immersing the sample for 1 hr (■) and after continuing for another 3 hrs (♦); (three consecutive experimental results) in 0.1M HCl at 66°C.

2.4 Conclusions
1. Microstructures of the as-weld specimens and the solution-heat treated structure were different for both the base metal and the weld specimens.
2. The overall corrosion rate of the weld specimen is higher than that of the base metal for as welded condition. However, for the heat treated conditions, corrosion rate between base and welded specimens were comparable.
3. Corrosion rates of the heat treated specimens (M-2, H-2 and W-2) are below 100µm/yr and are very similar for M-1 and H-1 specimens. The corrosion rate of W-1 specimen was higher than 300µm/yr.
4. The microstructure of the weld corroded sample showed attacks on the dendritic region for as weld and also for the heat treated specimens. However, the attack is more severe for the as-weld condition than the heat treated condition.

References for Alloy 22

29. ASTM G-102, Annual Book of ASTM standards, Vol. 03.02.
III. Corrosion Studies on AISI-SAE 4340 Steel in Simulated YM Groundwater

3.1.1 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 one hundred times the normal concentration (100X) in deaerated (nitrogenated) conditions. The average corrosion rate (CR) reached a maximum at 45°C, then decreased to a minimum at ~ 78°C, stabilizing between 85°C and 90°C.

3.1.2 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 3.1. 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 3.1. Chemical Composition (wt%) of AISI-SAE 4340 Steel²

<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>Fe</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 ~ 15 standard cubic centimeters per minute (sccm) by using a flow meter. An electrically-heated water bath surrounded the test cell and maintained the temperature of the solution. The specimen is inserted into the electrolyte-filled cell and nitrogen is purged continuously for at least 30 minutes until the steady-state open circuit potential is reached. 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 at ~ 35°C. After adding the salts to the de-ionized water, the solution was stirred on a hot plate for 30 minutes without heat, and then allowed to cool down for approximately one hour. Upon cooling, the excess or undissolved salts precipitated out from the solution at the bottom of the flask. The solution was filtered twice before
using as an electrolyte. In this study we used 10X YM water and measured the pH of the solution before and after each experimental run.1

The corrosion rate was calculated by following ASTM G59-973 and ASTM G102-894 procedures. During calculations, the polarization resistance ($R_p$) 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 ($R_p$) value, the corrosion current density was calculated using equation 3.1, where $K_1 = 3.27 \times 10^{-3} \text{mm·g/µA·cm·year}$, $I_{corr} = \text{µA/cm}^2$, $\rho = 7.87 \text{ g/cm}^3$ and $EW = 27.95 \text{ gm/equivalent.}^1$

$$CR = K_1 \frac{I_{corr}}{\rho} EW$$

(3.1)

3.1.3 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 & 10405 steels in 10X solution.

3.1.3.1A. Potentiodynamic studies - effect of temperature on the corrosion behavior

Deaerated YM Waters: Representative potentiodynamic scans, as well as an average corrosion rate as a function of temperature, are presented in Figures 3.2 – 3.4. For 100X concentration, the observed $E_{corr}$ is -0.705 V at room temperature (25°C). As the temperature increases, the $E_{corr}$ value decreases, until it stabilizes at ~ -0.643 V between 75°C and 90°C. Figure 3.4 shows the average corrosion rate as a function of temperature. As can be seen, the corrosion rate maximizes at 45°C, then minimizes at approximately 78°C, stabilizing between 85°C and 90°C. Table 3.2 shows the average corrosion rates of 4340 steel at different temperatures in deaerated 100X YM water.

![Figure 3.2. Potentiodynamic scan for 4340 steel in deaerated, 100X YM water at 25°C, 45°C & 65°C.](image)

![Figure 3.3. Potentiodynamic scan for 4340 steel in deaerated, 100X YM water at 75°C, 85°C, and 90°C.](image)

![Figure 3.4. Average corrosion rate as a function of temperature in deaerated, 100X YM water.](image)
Table 3.2 Average corrosion rates of 4340 steel at different temperatures in deaerated 100X YM water.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Environment</th>
<th>CR (microns/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Deaerated</td>
<td>153.4161</td>
</tr>
<tr>
<td>45</td>
<td>Deaerated</td>
<td>307.818</td>
</tr>
<tr>
<td>65</td>
<td>Deaerated</td>
<td>155.4193</td>
</tr>
<tr>
<td>75</td>
<td>Deaerated</td>
<td>59.2672</td>
</tr>
<tr>
<td>85</td>
<td>Deaerated</td>
<td>69.0475</td>
</tr>
<tr>
<td>90</td>
<td>Deaerated</td>
<td>66.2375</td>
</tr>
</tbody>
</table>

3.1.3.1B. Impedance Spectroscopy studies - effect of temperature on the corrosion behavior (deaerated YM waters)

Representative Nyquist and Bode plots for 4340 steel in the deaerated condition, are presented in Figures 3.5 through 3.16. As can be seen from the scans, the Nyquist curves show a slight Warburg tail beginning at 45°C, with a more pronounced tail at 65°C and 75°C. This indicates a mixed kinetic/diffusion process occurs over the entire temperature range. The corresponding Bode plots exhibit a single phase angle maxima at lower temperatures, but at 75°C begin to exhibit double phase angle maxima. This shows that the 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, even though the film is brittle.
Figure 3.9. Nyquist plot of 4340 steel at 65°C steel in deaerated, 100X YM water.

Figure 3.10. Bode plot of 4340 steel at 65°C steel in deaerated, 100X YM water.

Figure 3.11. Nyquist plot of 4340 steel at 75°C steel in deaerated, 100X YM water.

Figure 3.12. Bode plot of 4340 steel at 75°C steel in deaerated, 100X YM water.

Figure 3.13. Nyquist plot of 4340 steel at 85°C steel in deaerated, 100X YM water.

Figure 3.14. Bode plot of 4340 steel at 85°C steel in deaerated, 100X YM water.
3.1.3.1C. Comparison of activation energies on the corrosion behavior of steels in deaerated 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. This is evident in a deaerated environment, as can be seen in Figures 3.17 – 3.18. The activation energy for 4340 steel in deaerated 100X YM water is 17.4 kJ/mol, compared with 18 kJ/mol for 1040 steel.

References on 4340 Steel for rock Bolts
IV. Study of affect of sulfates on the corrosion rate of Swellex Mn-24 using Potentiodynamic Scans

4.1.1. Summary
We had conducted the electrochemical potentiodynamic scans to study the affect of sulphate ions on the corrosion rates of Mn-24, that are discussed in this report.

4.2.1. 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 last report, affect of individual slat on the corrosion of Swellex Mn-24 rock bolt in 100X YM water was reported. In this quarter we are reporting the combined effect of sulfates on corrosion of Swellex Mn-24 rock bolt in 100X YM water. In the Table 4.1, chemicals and different concentrations of YM water are shown and the amount of sulfates used are highlighted in bold.

Table 4.1. 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>CaSO₄.2H₂O</td>
<td>210</td>
<td>2100</td>
<td>21000</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>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>

4.2.2. Experimental Procedures for Corrosion Tests

4.2.2.(a). Specimen and Electrolyte Preparation: Swellex Mn24 specimens 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 material at the edges. 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. Before the experiment the specimen was grinded manually by using SiC emery papers ranging from coarse (200 grit) to fine (600-grit) followed with disc polishing (if necessary). The specimen was degreased with acetone and cleaned with de-ionized water before the experiment.

Salts used for this study are MgSO₄.7H₂O and CaSO₄.2H₂O. The electrolyte (100X) for the experiments were prepared by mixing above mentioned salts in 1 liter of distilled, de-ionized water. These solutions were stirred for half-hour at ~60°C to dissolve the salts and cooled to room temperature. After few hours, the solution was vacuum-filtered twice and stored for experimentation. pH for the solution was maintained in between 7 and 8.

4.2.2.(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 and a gas trap. Luggin probe was connected to a silver/silver chloride (Ag/AgCl) reference electrode through salt bridge (agar-agar solution). A heating bath was used to control the temperature and
thermocouple for monitoring the temperature. 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 the 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, the potentiodynamic scans were started by sweeping the voltage from -0.8V to -0.2V 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 G59 and ASTM G1023 procedures, assuming Tafel constants for both anodic and cathodic to be 0.12V/decade.

**4.2.2.(c). Corrosion Rate Calculations**: Polarization resistance \((R_p)\) is determined by calculating the slope of applied potential and the current density.

\[
R_p = \left( \frac{\partial \Delta E}{\partial i} \right)_{i=0, \Delta E/\Delta t \rightarrow 0}
\]

By using the Stern-Geary coefficient, corrosion current \(i_{corr}\) is calculated. Where \(B = \frac{b_a \cdot b_c}{2.303(b_a + b_c)}\), anodic \((\beta_a)\) and cathodic \((\beta_c)\) slopes were assumed to be 0.12V/decade.

\[
i_{corr} = 10^6 \frac{B}{R_p}
\]

The corrosion rate is calculated by using the given expression.

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

Where, \(K_1 = 3.27 \times 10^{-3} \text{ mm.g/µA.cm.y} \), \(CR = \text{ mm/year} \), \(i_{corr} = \mu A/cm^2 \), \(\rho = g/cm^3 \) (density of Swellex Mn-24 is 7.858 gm/cm³), and equivalent weight \((EW)\) is 27.24 gm/equivalent.

**4.2.3 Results and Discussion on Swellex Mn-24 rock bolts**

*Effect of Sulfates*: Sulfate is an aggressive anion after chloride. Potentiodynamic scan of Swellex Mn 24 in 100X CaSO4.2H2O + MgSO4.7H2O YM water is shown in Figure 4.1. In this polarization scan there is no passive layer observed. The resistance polarization measured for this scan is 5071 and the goodness of fit is above 98% and the \(I_{corr}\) is around 5.17 x 10⁶ micro amperes per square centimeter. Corrosion rated observed for this experiment is 58.1 microns per year. For consistency, four experiments were done under similar experimental conditions. Parameters calculated for the all the four experiments are shown in Table 4.2 and the potentiodynamic graphs are plotted in Figure 4.2. All four graphs look similar and the anodic and cathodic branches are overlapping and there is no passivation in all the four polarization graphs. Average corrosion rate is 69.7 microns per year. Similar to chloride ions, sulfates also aggressive in dissolving the metal.

Table 4.2. Corrosion rate and other parameters calculated for Swellex Mn24 in 100X CaSO4.2H2O + MgSO4.7H2O 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-100X-CaSO4+MgSO4-N-07-28-06.xls</td>
<td>4040.9</td>
<td>0.941</td>
<td>6.4342E-06</td>
<td>73.0</td>
</tr>
<tr>
<td>SwMn24-PD-100X-CaSO4+MgSO4-N-07-28-06(2).xls</td>
<td>3632.4</td>
<td>0.9724</td>
<td>7.1578E-06</td>
<td>81.2</td>
</tr>
<tr>
<td>SwMn24-PD-100X-CaSO4+MgSO4-N-07-28-06(3).xls</td>
<td>4438.3</td>
<td>0.979</td>
<td>5.8581E-06</td>
<td>66.4</td>
</tr>
<tr>
<td>SwMn24-PD-100X-CaSO4+MgSO4-N-07-28-06(4).xls</td>
<td>5071</td>
<td>0.982</td>
<td>5.12719E-06</td>
<td>58.1</td>
</tr>
</tbody>
</table>
Figure 4.1. Potentiodynamic plot of Swellex Mn24 in 100X CaSO₄·2H₂O + MgSO₄·7H₂O YM water.

Figure 4.2. Comparison of Potentiodynamic plots of Swellex Mn24 in 100X CaSO₄·2H₂O + MgSO₄·7H₂O YM water.
References for Corrosion of Swellex Rock bolts


V. Characterization and Calibration of the Modulated TGA for Oxidation Studies

5.1 Introduction: Study of High temperature oxidation behavior of Alloy 22 using TA Instruments Thermogravimetric Analyzer (TGA) is planned. Thermogravimetric analysis is traditionally used to characterize any material that exhibits weight or phase changes as a result of decomposition, dehydration, and oxidation. In conventional TGA, two modes are commonly used for investigating thermal stability behavior in controlled atmosphere: (1) Dynamic, in which the temperature is increased at a linear rate, and (2) Isothermal, in which the temperature is kept constant. At UNR, we have a state-of-the-art Thermogravimetric analyzer from TA Instruments, Model Q500, with a continuous weighing capacity of 1.0 g, a sensitivity of 0.1 µg and a heating rate from 0.1 to 50°C/min. The TA Q500 is also equipped with the ability to perform Temperature Modulated TGA (MTGA) with a Hi-Res™ option.

5.2 Experimental: The TGA is weight and temperature calibrated appropriately in accordance with IPR-035. Alumina sample pans were used and flow rates of 10:90 ml/min to balance and furnace respectively of high purity Argon: Oxygen gas were maintained as the starting condition. Samples used were pieces cut out of Alloy 22 foil obtained from Lawrence Livermore National Labs., CA. The samples were cleaned with ethanol prior to oxidation tests. They were then introduced into the furnace on tared pans and the set-up was allowed to equilibrate for 20 minutes before starting the experiment. Isothermal experiments with different supporting segments (as described in Results section below corresponding to each figure) were run on the samples. Details of the oxidation procedures are listed in Quarterly Reports No. 4 and 5.

5.3 Results: Initial experiments showed an interesting hump in the weight gain curve and subsequent experiments were performed with and without actual samples under similar conditions to the first experiment to evaluate the discrepancy. Figure-1 shows weight gain, and temperature curves for an Alloy 22 sample heated and held at 900 °C for 4 hours. The temperature was modulated about the average temperature of interest (900 °C) at ± 5 °C for 200 seconds.

Figure 5.1. TGA curve for Alloy 22 held for 4 hrs. in oxygen gas, showing a discontinuity in the weight gain curve.
Figure 5.2 shows the TGA curve for another Alloy-22 sample. The sample was first held in Argon gas for 1 hour and later the purge gas was switched to oxygen. As can be seen from the curve, the hump was observed again. Another experiment without any sample (blank sample pan) was performed. Figure 5.3 shows the curve for this experiment; no discontinuity in the weight curve is observed. Total time of the experiment was reduced to 3 hours (1 hr in Ar + 2 hrs in O₂). The bump was thought to be a result of the inability of the instrument to hold a constant temperature after a fast rate of heating to reach 900 °C. Two experiments with Alloy 22 and one without sample were modeled with a fast heating to 800 °C (100 degrees below the temperature of interest), followed by a slow heating to 900 °C and holding initially in Argon gas and subsequently in Oxygen gas. Figures 5.4 to 5.6 show the TGA curves for these experiments. Another experiment was performed with Alloy 22 wherein the ramp segment was eliminated since it did not contribute in any way to the experiment and the corresponding data is shown in Figure 5.7.

![Graph showing TGA curves](image)

Figure 5.2. Weight gain curve for Alloy 22 held for 1 hr in Argon gas at 900 °C before switching the gas to Oxygen.

![Graph showing TGA curves](image)

Figure 5.3. Weight gain curve for blank sample pan at 900 °C.
Figure 5.4. Weight versus time curve for Alloy 22 ramped from 800 to 900 °C at 5 °C per min and then held at constant temperature of 900 °C.

Figure 5.5. Weight versus time curve for Alloy 22 ramped from 800 to 900 °C at 5 °C per min without modulations and then held at 900 °C with imposed temperature modulation.
Figure 5.6. TGA curve for blank sample pan; same experimental condition as in Fig. 5.

Figure 5.7. Weight gain curve for Alloy 22 held at 900 °C.

The above experiments have helped in better understanding the behavior of the instrument (Thermogravimetric Analyzer). Further experiments are being performed to decide the method segments to be followed for Alloy 22 oxidation studies.