Corrosion research on rock bolts and steel sets for sub-surface reinforcement of the Yucca Mountain Repository

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Final Technical Report

Corrosion Research on Rock Bolts and Steel Sets for Sub-surface Reinforcement of the Yucca Mountain Repository
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Task 19 YM Project
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EXEUCITIVE SUMMARY

Underground nuclear waste storage repositories generally use steels and super alloys for various structural members and storage containers. These materials are susceptible to corrosion due to seepage of water. We studied rock bolt materials for reinforcing tunnels and containment materials for storing nuclear waste materials. In general, the design of underground support materials for tunnels are mainly based on mechanical behavior of the materials, but not much was known about the interaction of the seepage YM waters with the structural members under various conditions in the tunnels. The sources of water in the Yucca Mountain (YM) repository are due to rain fall (~5%), perched and pore waters associated with the tunnel that contain various levels of chlorides, nitrate, sulfate, silicates and bicarbonates. The temperature of the tunnel is expected to increase initially and subsequently decreases after closure of the YM repository due to nuclear waste radioactive decay. Our tests for corrosion were under 100°C to obtain a wide range of data at different temperatures and electrolyte concentrations. The rock bolts are generally embedded 10 to 12 feet deep inside the host-rock of the tunnel and water seepage through the rock pores creates an interface between the bolt material and water making it conducive to aqueous corrosion. The issues related to corrosion of the rock bolts and other structural materials are: (1) variation in the temperature of the tunnel over the years, (2) concentration of the ions present in the YM waters, (3) combination of temperature and detrimental anions that cause structural damage.

This study was performed to understand environmental effects such as corrosion/oxidation of support structure of the underground Yucca Mountain repository. In broad terms, we conducted research on two classes of materials: (1) Rock bolts (Split Set Friction type Rock Stabilizers (SS-46), Swellex Mn-24 and AISI 4340 steel) to reinforce the tunnel, and (2) Super alloys, such as, Alloy 22(UNS N06022), Alloy 282, Alloy 263 for containers and other components for the underground repository.

- Electrochemical and conventional corrosion tests on rock bolts obtained from industry and also on other steels with desirable properties to make rock bolts. Corrosion tests were performed using the YM electrolyte water chemistry furnished by the Yucca mountain site, and in certain cases compared with other electrolytes with impurities. We used 1x, 10x, and 100x concentration of YM electrolyte, from room temperature to ~ 95°C. These tests were performed under nitrogenated and oxygenated conditions to obtain a range of corrosion rates for these materials.

- Oxidation kinetic studies were performed using thermogravimetric measurements on these rock bolt steels and super alloys at elevated temperatures to obtain the oxidation mechanisms. Both isothermal and continuous heating measurements were made to obtain the data between 600°C to 1100°C in pure oxygen atmosphere for predetermined periods of exposures (48 hours for the Super alloys and 100 hours for HSLA steels).

1. Corrosion Behavior of Double folded water expandable Mn 24 and Split Set Commercial rock bolts:

Friction rock stabilizers are very effective for underground tunnel support in specially formulated electrolyte. In this report we present findings from the electrochemical corrosion tests under aerated (oxygen/air) and de-aerated (nitrogen) conditions as a function of concentration and temperature using potentiodynamic, static, cyclic polarization, and polarization resistance methods. The key results are listed below:

A. Swellex Rock Bolts

- Corrosion Rate (CR) of Mn24 rock bolt steel under aerated (oxygen) conditions of YM-UNR water at all temperatures and concentration is higher (CR range 145-2269 microns/yr.) than in de-aerated (nitrogen) conditions.

- Presence of silicate ions in the YM-UNR electrolyte inhibited the corrosion of rock bolt steel under de-aerated conditions in YM-UNR water due to formation of passive film.

- Amongst all standard immersion corrosion tests (ASTM-G31), half-immersed rock bolt steel coupons under aerated (air) 1x YM water at 75°C, showed highest corrosion rate of 2598 microns/yr., due to oxygen concentration cell effect.

- Rock bolt steels showed highest CR of 429 microns/yr. in BSW electrolyte at 60°C, and 561.7 microns/yr. in SCW at 90°C under aerated (air) conditions. Also, under aerated conditions pitting corrosion is observed in SDW at 90°C.
B. Split set Rock Bolts:
Corrosion rates of friction type set rock bolts (split set) were measured at 25°C, 45°C, 65°C and 90°C using 1x, 10x and 100x concentration of YM electrolyte both in aerated and deaerated conditions. Key results are as follows:

- The corrosion behavior of rock bolts in 1x and 10x electrolyte showed similar temperature dependency in both aerated and deaerated conditions, except the corrosion rates were an order of magnitude higher in the aerated condition; ranging from ~30 to 200μm/yr for deaerated and 150 to 1600 μm/yr for aerated.
- The corrosion behavior using 100x electrolyte was quite different in aerated condition showing initial increases in the corrosion rate between 25°C to 65°C (~210 to 2400 μm/yr) and an unusual steep decrease from 65°C to 90°C (~2400 to 750 μm/yr).

2. Corrosion behavior of AISI 4340 steel for rock Bolts.
Corrosion tests were performed using simulated YM electrolyte in three different concentrations (1x, 10x, 100x) under aerated (oxygenated) and deaerated (nitrogenated) conditions to determine baseline corrosion rates from 25°C to 90°C. Important experiments were carried out to examine the potential corrosion inhibiting properties of the silicate and/or bicarbonate ions on the surface of the steel. The “passivity behavior” of 4340 steel in reducing conditions using combinations of sodium silicate (Na$_2$SiO$_3$) and sodium bicarbonate (NaHCO$_3$), in both pure water and simulated seawater (3.5% NaCl) showed very interesting results. In addition, general corrosion tests involving immersed test-coupons, with and without “pre-treatment” of sodium silicate, in simulated electrolyte to determine “real-world” conditions of the material are presented. Corrosion rates (CR) obtained from coupons tested under ambient, aerated and deaerated environmental conditions at four different temperatures are also presented. A summary of electrochemical CR’s and associated active-passive behavior of AISI 4340 steel in simulated, multi-ionic solutions is presented:

- Potentiodynamic polarization corrosion tests in simulated electrolyte for this 4340 steel showed a maxima CR$_{45°C}$~300 μm/yr (deaerated conditions), and a maxima of CR$_{65°C}$~2200 μm/yr (aerated conditions) in simulated electrolyte.
- Immersion corrosion rates under simulated electrolyte show that the steel corrodes at CR’s > 2500 μm/yr at 75°C (aerated and partially-immersed in solution condition). Corrosion rates are much lower, under deaerated, (fully-immersed in solution) conditions, the CR’s < 0.5 μm/yr at 25°C. In nearly all cases, corrosion rates were higher for partially-immersed samples than fully-immersed or water vapor-exposed samples. For the samples exposed under ambient (static-air) condition, the rates stabilized at near-constant CR ~15 μm/yr when the coupons were suspended above the solution, and CR~150 μm/yr for when the coupons were partially- and fully-immersed in the electrolyte.
- Silicate/bicarbonate experiments, results (Table 9.3 and Figure A-46) indicate that the steel corrodes CR < 70 μm/yr in solutions containing sodium silicate, but CR’s>2,000 μm/yr in solutions containing sodium bicarbonate.
- Pre-treatment of the steel coupon for immersion tests using sodium silicate increased the corrosion resistance by a factor of 1.2 to 4.7 when immersed in 1x YM solutions. (Figure A-46).

3. Oxidation Behavior of Mn-24 and SS-46 Rock bolts:
Temperature modulated thermogravimetry was used for studies on HSLA steels. Oxidation-weight gain curves for both SS-46 and Mn-24 show that there are three distinct oxidation regions for both the rock bolt steels (SS-46 and Mn-24): (1) an incubation period, (2) a first oxidation region, where the steels follow a rate law given by $y(kg/m^2)=k_0^{0.43-0.62}$ and (3) a parabolic oxidation regime thereafter. The rate constants determined for the first oxidation region for the steels show that the activation energies of both the HSLA steels is comparable at 82 kJ/mol for Mn24 and 102 kJ/mol for SS46. Activation energy was calculated assuming an average time exponent of the rate law of 0.52 for SS-46 and Mn-24.

- Parabolic rate constants for both the steels show considerable scatter on an Arrhenius plot. Activation energies of ~82 kJ/mol for Swellex Mn-24 and ~83 kJ/mol for SS-46 were determined based on calculated parabolic rate constants. The scatter on the rate constants is attributed to the observed blistering of oxide scales and breakaway oxidation, also noted by other researchers in oxidation studies in low alloy steels oxidized under high pressure oxidative environment from 700 to 1000°C for oxidation times between 10 to 250 hours.
The oxidation tests on SS-46 and Mn-2 rock bolts tested at 800°C showed the presence of noticeable fraction of Wustite along with hematite and magnetite phases; confirmed by in-situ micro-diffraction studies at ALS-Lawrence Berkeley laboratories.

4. Corrosion Behavior of Alloy 22

Alloy 22, with a composition of Ni-22Cr-13Mo-3Fe-3W, is a candidate alloy for the outer shell of spent nuclear materials storage containers in the Yucca Mountain High Level Nuclear Waste Repository because of its excellent corrosion resistance. The nuclear waste container fabrication involves welding of Alloy 22 adjacent to the end caps. Alloy 22 retains the high temperature single phase cubic structure near room temperature, but topologically close packed (TCP) phases such as μ, P, σ etc. and Cr rich carbides can form during welding as well as heat treatments. Another important material of significance to this subsurface repository is steel used for rock bolts to reinforce tunnels. The Alloy 22 containers as well as rock bolts have to resist environmental degradation.

The corrosion behavior of Alloy 22 as a function of temperature and concentration in complex multi-ionic YM related electrolytes using polarization resistance method in deaerated (nitrogenated) and aerated (oxygenated) electrolyte are presented. The corrosion rate of Alloy 22 was higher in the deaerated electrolyte as compared to the aerated. The presence of oxygen in the electrolyte during aeration is conducive to formation of passive films that inhibit the corrosion process. The temperature dependency of the corrosion rate was affected by aeration and deaeration of the electrolytes.

Another study related to corrosion behavior of weld Alloy 22 was undertaken to understand electrochemical behavior of welded structures. Corrosion studies were carried out in more aggressive electrolyte (0.1M HCl at 66°C) after solution annealed at 1121°C for 1 hr. Microstructure of weld showed dendritic growth in weld structure and after the solution annealed it showed a homogenization of the grains. Three different specimens were made out from a welded Alloy 22 plate with large welded surface; weld interface, half weld and base metal away from the weld and heat affected zone. The results showed that the corrosion resistance of solution-annealed Alloy 22, welded specimens, was lower than the base metal.

Simple corrosion tests on Alloy 22 in both dry and deliquescent salts at 200°C did not corrode in the dry out period.

XPS results showed that the passive behavior of Alloy 22 in mixture of corrosion product solution and in Fe³⁺ solution is due to formation of multiple oxide layers.

5. Oxidation Studies on Ni-base Super alloys - Alloy C-22, Alloy-263 (UNS N07263) and Alloy-282

Oxidation kinetics were determined by isothermal high temperature and continuous thermogravimetric measurements at temperatures ranging between 600°C to 1100°C in pure oxygen atmosphere for predetermined periods of exposures (48 hours for the Super alloys and 100 hours for HSLA steels). The super alloys were selected for comparison of their oxidation resistance with Alloy 22 as a baseline material with other underground structural materials. The three alloys investigated had similar Cr composition but varied in alloying concentration of Co and Mo, and are known chromia formers.

**Alloy 22:** Kinetic parameters and activation energies for these super alloys were calculated. Parabolic rate constants (RC) for Alloy-22 were: RC(700°C) = 6.85 x 10⁻¹³ kg⁻².m⁻⁴.s⁻¹, RC(800°C) = 2.72 x 10⁻¹² kg⁻².m⁻⁴.s⁻¹, RC(900°C) = 1.30 x 10⁻¹¹ kg⁻².m⁻⁴.s⁻¹, RC(980°C) = 5.83 x 10⁻¹⁰ kg⁻².m⁻⁴.s⁻¹, and RC(1100°C) = 7.13 x 10⁻⁹ kg⁻².m⁻⁴.s⁻¹. The activation energy for the parabolic regime of Alloy-22 is found to be 263 kJ/mol.

**Alloy-263:** The parabolic rate constants were found to increase with increasing temperatures with a value of 1.7 x 10⁻¹³ kg⁻².m⁻⁴.s⁻¹ at 700°C, 2.35 x 10⁻¹¹ kg⁻².m⁻⁴.s⁻¹ at 800°C, 1.06 x 10⁻¹⁰ kg⁻².m⁻⁴.s⁻¹ at 900°C, 7.68 x 10⁻¹⁰ kg⁻².m⁻⁴.s⁻¹ at 980°C, and 7.97 x 10⁻⁹ kg⁻².m⁻⁴.s⁻¹ at 1100°C. The activation energy for the parabolic regime of Alloy-263 is found to be 289 kJ/mol.

**Alloy-282:** This alloy showed an increasing trend in the parabolic rate constants with increasing temperatures also, with a value of 2.54 x 10⁻¹² kg⁻².m⁻⁴.s⁻¹ at 700°C, 1.37 x 10⁻¹¹ kg⁻².m⁻⁴.s⁻¹ at 800°C, 1.86 x 10⁻¹⁰ kg⁻².m⁻⁴.s⁻¹ at 900°C, 8.28 x 10⁻¹⁰ kg⁻².m⁻⁴.s⁻¹ at 980°C, and 9.94 x 10⁻⁹ kg⁻².m⁻⁴.s⁻¹ at 1100°C. The activation energy for the parabolic regime of Alloy-282 is found to be 232 kJ/mol. The slope of the curves on a plot of k_p as a function of (1/T) show Alloy-282 to have better oxidation resistance up to 980°C and thereafter the rate constants are similar for all three alloys, but when activation energies over the whole temperature range are calculated, Alloy-263 shows the best average oxidation resistance.
• Surface characterization by means of microscopy as well as X-ray photoelectron spectroscopy showed the nature of oxides formed. Based on the kinetics and the characterization, proposed mechanisms for oxidation of these alloys at high temperatures are discussed in the text.

**Graduate Students who earned their Ph.D or MS Thesis fully or partially Related YM Project Task 19**


**Researchers and Undergraduate Students who worked on the YM Task No. 19**

1. Dr. Wen Ming Chien Ph.D. (Metallurgical Engineering) at University of Nevada, Reno, YM Corrosion Project Task-18, Dissertation, (Worked on YM Corrosion Project Task 18 on micro structural and x-ray diffraction structural aspects),


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I. INTRODUCTION

1.1. Nuclear Power: Pros and Cons

With a conscious effort for energy production via cleaner, safer methods which meet the growing consumer and industrial demands while addressing climate change and reducing dependence on foreign sources, nuclear power is emerging as a viable alternative[1]. Nuclear power accounts for about 7% of the world’s energy and about 16% of the world’s electricity generation [2-4] with the United States generating about 19% of its electricity from nuclear sources[5, 6]. As of April 2008, the International Atomic Energy Agency (IAEA) reports a total of 439 nuclear power plants in operation in 31 countries worldwide producing about 372 Gigawatts [7] with 35 more reactors with a capability of producing about 30 GWe under construction[8]. The United States has 104 nuclear reactors running and generating about 100 GWe supplying about 19% electricity needs as shown in Figure 1.1[5, 9]. Not only are nuclear reactors used for civilian electricity generation, they are also used in space and marine applications by the government, for research and training, materials testing, or the production of radioisotopes for medicine and industry[10].

![Figure 1.1. Nuclear power units in operation in U.S.A. (April 2008) and the nuclear share of electricity. Adapted from ref.[9].](image)

With the use of nuclear reactors and their numerous pros, a few cons are also encountered. As the percentage of fission fragments and heavy elements formed as by-products of enriched Uranium-235 nuclear reactor fuel increases in the core of the reactor fuel assembly, the efficiency of the fuel bundle for energy production decreases. After a certain period of operation (about 3-4 years) the fuel bundles, now known as “spent fuel” are removed. Spent fuel is about 95% U-238 but it also contains about 1% U-235 that has not fissioned, about 1% plutonium and 3% fission products, which are highly radioactive, with other transuranic elements formed in the reactor[11, 12]. This spent fuel is still very radioactive and contains relatively high concentrations of both highly radioactive and extremely long-lived radionuclides. As of December 2005, the United States accumulated about 53,440 metric tons of spent nuclear fuel from nuclear reactors[13]. Since the end of the Cold War, efforts have been underway to close and clean up the then-operational weapons plants. This warrants dealing with and disposing of the highly radioactive material associated with weapons production, termed as High-Level Nuclear Waste (HLW)[12]. Apart from this, any other nuclear waste produced, which does not fit categorical definitions for high-level waste (HLW), spent nuclear fuel (SNF), transuranic waste (TRU), or certain byproduct materials known as 11e(2) wastes, such as uranium mill tailings, is known as Low Level Waste (LLW)[14]. LLW can range from anything including[15]:

- contaminated hand tools, components, piping, and other equipment from nuclear power plants and other industries
- research equipment from laboratories where radioactive materials are used
Presently in the United States, LLW is typically stored onsite until it has decayed to the point to which it can be disposed of as ordinary trash or until the quantity is large enough to ship to one of the three low-level waste disposal sites in operation in the nation\cite{16, 17}. The regulations for storage and disposal of spent fuel and HLW need stricter considerations. The accumulated radioactive waste since the mid-1940’s is presently stored in temporary facilities at some 121 sites in 39 states throughout the US located in a mixture of urban, suburban, and rural environments \cite{12, 18}. Since the 1950’s scientists have been trying to find ways of safe long-term storage or disposal of this spent fuel and HLW so as to shield the public from harmful radiation exposure. Again, in 1976 and 1977 President Ford and President Carter, respectively, issued directions for the U.S. to stay away from commercial nuclear spent fuel reprocessing. This was done for fear of nuclear proliferation by way of plutonium harvesting for weapons\cite{19}. All of this led to a consensual decision to find a permanent waste management and disposal site in a deep underground geological repository. Isolated in a deep underground repository, the waste would not be subject to the many environmental factors that on the earth’s surface would cause it to break down into radioactive particles that could be dispersed by air or water into the accessible environment\cite{12}.

1.2. Nuclear Waste Storage

In 1982, the U.S. Department of Energy (DOE), selected nine locations in six states to study as potential repository sites and performed preliminary environmental assessments of each. In 1986, the DOE published the results of these assessments, which documented the selection of five candidate sites from the original nine. And in 1987, under the amended Nuclear Waste Policy Act (NWPA), Congress directed the DOE to study only the Yucca Mountain site in Nevada as the nation’s first potential nuclear waste geological repository\cite{20}.

Yucca Mountain is located about 160 km (100 miles) northwest of Las Vegas on federal government owned land in remotely located Nye county in Nevada\cite{21}. Figure 1.2 \cite{21} shows the location of Yucca Mountain with respect to Reno and Carson City, Nevada. The crest of Yucca Mountain at the exact location chosen for the geologic repository is a maximum of 1400 to 1500 m (4600 to 4900 ft) above sea level. With no permanent residents within 14 miles of the Yucca Mountain, and 1.5 persons per square mile population density of the whole of Nye County, the repository would be far away from public interaction. Successive layers of volcanic rocks (called tuffs), approximately 14 to 11.6 million years old, comprise the Yucca Mountain. These tuffs were formed by eruptions of volcanic ash from calderas\cite{1} to the north side. Individual layers of tuff thin from north to south\cite{18}. The proposed Yucca Mountain repository will occupy about 230 square miles (150,000 acres) of federal land currently owned by the U.S. Department of Energy, the U.S. Air Force, and the Bureau of Land Management. A proposed layout of the repository is shown in Figure 1.3\cite{22}. Inside the tunnel the storage place is a series of emplacement drifts. Series of emplacement drifts are shown in Figure 1.4\cite{23}.

The repository is designed to be built 1000 feet below the surface and 1000 feet above the underlying water table at Yucca Mountain. This water table has been never known to have risen to the level of the proposed repository and so any water contamination by radioactive waste is not expected. Moreover this water flows into Death Valley and is never utilized for any direct or indirect human consumption. The area itself is thought to have a very stable geology since it has changed very little in millions of years. Yucca Mountain receives only about 7.5 inches of rainfall in a year and most of this evaporates, runs-off or is taken up by the nearby desert vegetation before ever reaching depths of the proposed repository. Banking on these and aforementioned potential advantages of the Yucca Mountain, DOE undertook the task of working towards building the geological repository here. It is expected to store up to 70,000 metric tons of High Level Nuclear Waste safely, once built.

---

1 Caldera is a volcanic feature formed by the collapse of land following a volcanic eruption. They are sometimes confused with volcanic craters. The word comes from Spanish, meaning "bowl".
Apart from relying on nature and the available natural barriers for shielding the escape of any radioactive material into environment, several man-made barriers have also been engineered and incorporated in the building of the repository.

Figure 1.2. Location of the Yucca Mountain Nuclear Waste Repository[21].

Figure 1.3. Yucca Mountain Repository layout[22].
1.3. Safe Storage of Nuclear Waste

To make sure that the radioactive waste is stored safely and away from human contact, engineered barriers will be used like[22]:

- Drip shields — which limit the ability of water to contact the waste package made of Titanium Grade 7 plates for the water diversion surfaces, Titanium Grade 29 for the structural members, and Alloy-22 for the feet
- Waste packages — which limit the water contacting the actual waste forms inside. These will have a double layered design
- Cladding (corrosion-resistant metal tubes that contain the ceramic fuel pellets) — which limits the water contacting the commercial spent nuclear fuel portion of the waste
- Solid waste forms — which limit the rate of radio nuclides picked up by any water that does contact the waste
- Inverts (the floors of stainless steel and crushed volcanic rock added to the emplacement tunnels) — which limit the rate of release of radio nuclides to the natural barriers

The waste packages as mentioned above will have a concentric double layered cylindrical design, a typical design of which is shown in Figure 1.5.[22] The inner cylinder will be made from stainless steel 316NG and the outer cylinder would be of corrosion resistant nickel base Alloy-22. The two layers work synergistically; the outer 20 mm thick layer made of Alloy-22 protecting the underlying structural material (SS316NG) from corrosion and the 50 mm thick stainless steel cylinder providing bulk and mechanical strength to Alloy-22 cylinder. The outer diameter of the waste package is ~ 1,644 mm and the outer length is 5,165 mm[24]. Figure 1.6.[25] gives and idea of the dimensions of the proposed waste packages with the different types of packages that will be used to store the different kinds of radioactive waste[25]. The materials chosen for the waste package are among the most corrosion resistant of engineering materials. They are used routinely under harsh conditions in the chemical process industry and at nuclear power plants and are expected to perform well in the expectedly more benign conditions within Yucca Mountain. Layout of the emplacement drift is given in Figure 1.7.[26] From the inside, the emplacement drift is supported by perforated carbon steel sheet. Rock bolts are used for rock reinforcement to prevent rock from falling on to the engineering features. Different engineering structure supports are shown in Figure 1.8.[23] Waste packages are placed on inverted steel structure. Gantry crane rail is used to transport the waste container in and out of the tunnel.
1.4. Alloy 22 – The Waste Package Material

Hastelloy® C-22® is a custom-developed Nickel-based corrosion-resistant alloy form Haynes International, Kokomo, IN. Commonly known as Alloy-22, or just C-22, it is touted as having better overall corrosion resistance in oxidizing corrosives compared to the other C-class alloys from Haynes International. The 56Ni-22Cr-13Mo-3W-3Fe superalloy designated UNS N06022, is known to have outstanding resistance to pitting, crevice corrosion, and stress corrosion cracking. It has excellent resistance to oxidizing aqueous media including wet chlorine and mixtures containing nitric acid or oxidizing acids with chloride ions. Also, C-22 has excellent resistance to a wide variety of chemical process environments [27] and hence has been suggested for use in the Yucca Mountain Repository. A known drawback of the alloy is that it is prone to formation of what are known as Topologically Close Packed (TCP) phases at elevated temperatures.

TCP phases tend to reduce the corrosion resistance of the alloy. TCP phases, rich in chromium and molybdenum are of the type μ, σ and P which are known to be stable at temperature ranges of 600-700°C, 700-800°C and 800-1000°C, respectively, and precipitate preferentially at the grain boundaries [28-32]. These temperatures are expected to be reached during the welding process for Alloy-22 waste packages. The depletion of corrosion-resistant Cr and Mo from the alloy substrate is bound to have a detrimental effect on the oxidation resistance of the alloy.

Figure 1.5. Typical design of the waste package proposed for YM Repository[22].
Figure 1.6. Dimensions of YM nuclear waste packages[25].

- Three generic waste package types
- All have Alloy 22 outer corrosion-resistant shell
- Type 316 nuclear-grade inner structural cylinder

Figure 1.7. Emplacement drift[26]
1.5. Rock Bolts That Stabilize The Emplacement Drifts In The Repository

Apart form the materials being actually used in the waste packages for storage, the tunnel itself will have an assortment of other structural materials that will be used as underground roof support system. Each of the emplacement tunnels or “drifts” will be lined with perforated steel plates and steel inserts that will be held in place by means of rock bolts. These rock bolts are 1 inch (2.54 cm) in diameter and range in length from 5 feet to 10 feet. They help to serve transfer load from the unstable tunnel, to the confined (and much stronger) interior of the rock mass. Rock bolts can be made from a wide variety of materials ranging from wood dowels, fiberglass and different metals. For the Yucca Mountain Repository rock bolts made of either low carbon steels or medium carbon steels or even high strength low alloy (HSLA) steels are proposed. Based on the anchoring mechanism of these rock bolts with the surrounding rocks, they are categorized as mechanically anchored bolts, grout anchored bolts, friction rock stabilizers (FRS) and strand anchors, etc. Since the first use of primitive slot-and-wedge rock bolts in 1927 and the proposed use of rock bolting as a systematic method for weak roof support by Weigel in 1943[33], rock bolting has become the most important support system in underground roof support system. Rock reinforcement is very important for mines, tunneling, etc. Development of internal roof support systems began in the early 20th century. In 1936, St Joseph Lead mine in Missouri used split wedge rock bolts for mine roof reinforcement[34]. In mid 1940’s the expansion anchor bolt was developed. In 1960, resin based grout rock bolts were used for underground rock reinforcement. By mid 1970’s the frictional rock stabilizers, deformable steel tubes, had been developed. Now around the world different types of rock bolts such as mechanically anchored, grout anchored, frictional stabilizer anchors, strand anchors and other secondary rock accessories are used for rock reinforcement in mining, tunneling, nuclear repositories, etc[35]. The widespread use of rock bolts was a result of the U.S. Bureau of Mines (USBM) advocating their merits to reduce the number of accidents caused by roof falls in 1947[36], their effectiveness in ground control and cost reduction. Table 1.1 shows the popular types of rock bolts in use in the U.S.[36, 37].

Friction Rock Stabilizers (FRS) are the easiest to install amongst the different kinds of rock bolts. FRS provide support to the structures by forming a frictional bond with the rocks they are inserted into. These FRS are generally known to be of two types: Split Set or Collapsed tube. Split-Set comprises of a length of a HSLA steel tube with a longitudinal split extending along its entire length and an accompanying bearing plate, as shown in Figure 1.9[38]. The inner section of the tube is tapered and a steel ring flange is welded to the tube outer end to retain the face plate (bearing plate), which maintains contact with the rock face when the device is completely inserted in the bolt hole. A hole of slightly smaller diameter than the fully relaxed split set rock bolt is drilled into the rock where the bolt needs
to be inserted. The rock bolt tube is driven into the hole using a drill. As the bolt is put in place, the whole length of the slot narrows, causing radial pressure to be exerted against the rock over the full contact length[38].

Table 1.1. Popular types of rock bolts in use in the U.S.  [36, 37]

<table>
<thead>
<tr>
<th>Types of bolt</th>
<th>Types of anchor</th>
<th>Suitable strata type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point-anchored bolts (tensioned)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slot-and-wedge</td>
<td>Hard rock</td>
<td>Used in the early stages</td>
<td></td>
</tr>
<tr>
<td>Expansion shell</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard anchor</td>
<td>Medium-strength rock</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bail anchor</td>
<td>Soft rock</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Explosive set</td>
<td>Lower-strength rock</td>
<td></td>
<td>Limited use</td>
</tr>
<tr>
<td>Resin grout</td>
<td></td>
<td></td>
<td>Increasing usage recently</td>
</tr>
<tr>
<td>Pure point anchor</td>
<td>All strata especially for weak rock</td>
<td></td>
<td>Resin length ≤24 in.</td>
</tr>
<tr>
<td>Combination system</td>
<td></td>
<td></td>
<td>Resin length ≥24 in.</td>
</tr>
<tr>
<td>Combination anchor (expansion shell and no mix resin)</td>
<td>Most strata</td>
<td>Good anchorage with &quot;no mix resin&quot;</td>
<td></td>
</tr>
<tr>
<td>Full-length-grouted bolt (untensioned)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement</td>
<td>Most strata</td>
<td>Disadvantages: 1. Shrinkage of cement 2. Longer setting time</td>
<td></td>
</tr>
<tr>
<td>Perfo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injection</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cartridge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resin</td>
<td></td>
<td></td>
<td>Increased use recently especially for weak strata</td>
</tr>
<tr>
<td>Injection</td>
<td>All strata</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cartridge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roof truss</td>
<td>Expansion shell</td>
<td>Adverse roof</td>
<td>Recommended for use at intersections and/or heavy pressure area</td>
</tr>
<tr>
<td>Cable sling</td>
<td>Cement anchor and full-length fraction</td>
<td>Weak strata</td>
<td>Substitute for timber, steel or truss support</td>
</tr>
<tr>
<td>Yieldable bolt</td>
<td>Expansion shell</td>
<td>Medium-strength rock</td>
<td>It is an expansion-shell bolt with yielding device</td>
</tr>
<tr>
<td>Pumpable bolt</td>
<td>Resin</td>
<td>Weak strata</td>
<td>Complex installation</td>
</tr>
<tr>
<td>Helical bolt</td>
<td>Expansion shell</td>
<td>Most strata</td>
<td></td>
</tr>
<tr>
<td>Split set</td>
<td>Full-length fraction</td>
<td>Weak strata</td>
<td>Cheap but need special installation equipment</td>
</tr>
<tr>
<td>Swellex bolt</td>
<td>Full-length holding</td>
<td>Water-bearing strata</td>
<td>Using high-pressure water to swell the steel tube</td>
</tr>
</tbody>
</table>
The most commonly known collapsed tube type of rock bolts were developed by the Atlas-Copco Company. They term their products as the *Swellex* Premium (Pm), Standard (Std.) and Manganese (Mn) lines, depending upon the
composition of the rock bolts. These bolts, usually 0.6 to 12 meters in length, are made form a folded thin-wall steel tube. The tube is collapsed and folded into a smaller diameter. A short sleeve is welded at each end of the steel tube. The top end sleeve is hollow and the opening continues into the reshaped tube. During installation, as with the split sets, Swellex rock bolts are inserted inside the drill holes, end bearing plates facing against the rock. The holes drilled are of a diameter that is a bit smaller than the expander diameter of the rock bolt tubes. Water under high pressure (max up to 4300 psi) is pumped into the tube opening to expand the rock bolt. Under the high hydraulic pressure the bolt conforms to any irregularities in the drill hole, thus interlocking the bolt to the rock mass. After installation, the water inside the tube is drained out. A schematic of the installation procedure of a typical Swellex rock bolt is shown in Figure 1.10 [39].

Researchers all over the U.S. are working towards studying the materials being proposed for the long-term storage repository, be it the materials used for actual storage containers or the structural materials supporting the underground tunnel and the roof support tunnels. Amongst all engineering materials, rock bolts are the one which will be exposed to any water run-offs, if at all, first, considering the arid conditions of Yucca Mountain. So the corrosion study of rock bolt is as important as corrosion study of nuclear waste containers. Corrosion is not only a problem for YM repository; even for the mines, with any mine water, rock bolt corrosion is a big problem. There has been extensive ongoing research on the corrosion of rock bolt materials in different water chemistries [40-56].

As part of research to improve mine safety, Tilman et al.[52] conducted research on the corrosion of friction rock stabilizer steels in five Missouri lead and iron mine waters in 1985; in this study they used electrochemical corrosion techniques and standard immersion corrosion tests to study general and localized corrosion such as pitting corrosion of steels in mine waters. In 1987, Jolly et al. studied corrosion susceptibility of friction rock stabilizer in seven Eastern and Midwestern United States coal mines. Accelerated electrochemical corrosion tests were used to estimate corrosion rates for two High Strength Low Alloy (HSLA) steels and long term static immersion weight-loss tests. Ranasoooriya et al. conducted a laboratory based program of studies to investigate the effect of corrosion on mechanical properties of FRS; In this study the focus is on the effect of corrosion on tensile strength of FRS and frictional resistance along the interface between FRS and the drill hole wall in western Australian mine waters. In other work, Ranasoooriya [56] studied salt-spray, uniform, Pull test of FRS (Swelllex, Split set and Cotter Pin) in 24 underground mines in Western Australia. B.Stimpson [41] conducted pull test of Split set in concrete; from the tests it is concluded that one major contributor to decrease in strength is corrosion of rock bolt over a period of time. Uniform corrosion rate of up to 1mm/month is observed for standard Swellex bolts under Canadian and US aggressive mine waters; also galvanic corrosion measurements were made for Standard Swellex bolts in massive sulfide environment by Charette et al[54]. Ram Singh et al.[50] performed a comprehensive corrosion study of several commercial alloys in six Canadian mine waters. Corrosion behavior was determined by anodic polarization scans, constant slow strain rate, crevice corrosion detection, field potential and noise measurements, and metallographic analysis of exposed specimens. Based on sample water from mine, synthetic water with varying concentrations of chlorides, sulfates, nitrates, etc., are generally used to study the effect of ions on the corrosivity of the mine water. In a study by Higginson et al.[49], effects of corrosivity of synthetic mine water was investigated by the variation of important properties such as dissolved oxygen concentration, pH, flow rate, temperature, and ammonium ion concentration on mild steel. Similarly, Mursalo et al.[55] studied the effect of chloride and sulfate from synthetic mine waters on mild steel and 316L stainless steel.

Throughout the last several years, researchers [2, 6, 7, 10, 11, 57-63] have tested different steels in simulated environmental conditions of Yucca Mountain. McCright et al.[60, 61] have tested a variety of carbon steels in order to assess their corrosion performance in the repository environment using various classical corrosion testing methods, both with and without the effects of radiation. Under these lab-simulated environments, the materials showed relatively low corrosion rates, even when samples were tested with a radiation source several meters away. Thompson and Beavers[7] conducted cyclic potentiodynamic polarization experiments on AISI 1020 steel rods to study the effects of different variables on the steel's corrosion performance in basalt ground water environments. They found that Fe, Cl, NO₃, CO₃²⁻, and the solution's pH had the largest effects on the corrosion performance of the steel. Brossia and Cragnolino[57] studied the effects that different chloride, carbonate and bicarbonate ion concentrations have on the localized corrosion behavior of ASTM A516 carbon steel. They reported that a critical pH range and a critical chloride concentration influence both the rate and type of corrosion behavior observed.

Many other researchers [10, 11, 58, 64, 65] have studied, or are currently studying, different types of carbon steels for the proposed use. For the YM repository tunnel, based on well water (J-13 water) at YM, different synthetic
waters were prepared for the corrosion study of rock bolt material and also the waste package material[66]. Lian and Jones[2] tested AISI 1016 steel in simulated, concentrated J-13 well waters from 25°C to 90°C. They reported maximum corrosion rates of 7.04 μm/yr at 90°C in deaerated conditions and 140.6 μm/yr at 25°C in aerated conditions. Additionally, they studied the pitting corrosion behavior of 1016 steel by varying the chloride and ferrocyanide ion concentrations in J-13 water.

To study the effect of various anions, similar to J-13 water, a dilute multi-ionic UNR-YM water chemistry was designed at the University of Nevada, Reno[67]. Under a UNR-YM water environment, Yilmaz[48] conducted standard immersion, salt spray, cyclic humidity and electrochemical corrosion testing of candidate structural materials – AISI 1144 (UNS G11440) steel [i.e. – Rock Bolt Carbon Steel (RBCS)] and ASTM A-36 low-carbon steel, as rock bolts and steel sets, respectively. In his study, the upper and lower bounds for the corrosion rates are 40 and 1000 microns per year for de-aerated and aerated conditions under UNR-YM water, respectively. In a real scenario at the repository, in addition to exposure to water, rock bolts and steel-sets are under constant stress over a period of time due to rock shifts. Yilmaz [48] also conducted Slow Strain Rate Tests (SSRT) of A-36 steel in UNR-YM water at different temperatures. Deodeshmukh [43] studied effect of silicate and bicarbonate ions on RBCS using potentiodynamic polarization. Results showed that addition of silicate ions with bicarbonates enhanced the passivity of RBCS by decreasing the passive current density.

The above-mentioned study of RBCS and ASTM A-36 steel are candidate structural materials for the YM repository. But due to the easy installation and low cost, FRS rock bolts, such as Split Set and Swellex, are considered as potential candidates for rock reinforcement at the Yucca Mountain emplacement tunnel over other types of rock bolts. Recently, at one of the Exploratory Study Facility (ESF) of the YM tunnel, approximately 20,000 Super Swellex bolts have been installed [68]. However, based on water seepage through the rock and coming in contact with these bolts, it is very important to perform corrosion study of these rock bolts in ground and simulated waters.

Another potential rock bolt material, AISI-SAE 4340 steel (UNS G43400), is an ultrahigh-strength low-alloy steel that “combines deep hardenability with high ductility, toughness, and strength, and is considered the standard by which other ultrahigh-strength steels are compared.”[69] These properties make the steel useful for industrial applications where “high strength in heavy sections is required.”[69]. However, there are not many reported works on the electrochemical, general and localized corrosion behavior of AISI 4340 steel in a similar repository environment. Myers and Saxer[14] studied the anodic polarization behavior of 4340 steel in sulfuric acid solutions, and Mansfeld et al.[15] studied the effects of 4340 steel using various sodium-based salt solutions in tap water, deionized water, and a mixture of phosphonic/polyacrylic acids with fatty amine as inhibitors. Most of the research on AISI 4340 steel has been devoted to stress corrosion cracking, hydrogen embrittlement and hydrogen-induced cracking (HIC), with and without induced strain, such as the work of Hirose & Mura,[13, 16, 17, 20, 70] Hillier & Robinson,[21, 22] S.M. Toy,[71-73] S.J. Ketcham[38, 74, 75] & D.A. Berman.[38, 76] This is mainly due to the material’s heavy use in the automotive and aerospace industries[69] and the need to understand the steel’s fracture mechanics and stress behavior under severe loading conditions.

The objective of the present research is to study the oxidation kinetics and corrosion resistance of several HSLA steels – Standard Swellex, Swellex Pm24, Swellex Mn24, Split Set rock bolt, AISI 4340 steel – and three other Ni-base superalloys – Alloy-22, Alloy-263 and Alloy-282 – proposed for use in the Yucca Mountain Nuclear Waste Repository. The purpose of studying oxidation kinetics is to evaluate the mechanism of the reactions occurring between metals (or alloys) and their environment and assess the reaction kinetics which serve as a pointer to the oxidation behavior of the material. Metals and alloys are thermodynamically unstable [77], and depending on their environment will form oxides, sulfides, carbides, nitrides, or mixtures of reaction products. Knowledge of oxidation kinetics is also an indicator of the useful lifetime of a given component under a given set of exposure variables like temperature, pressure, gas composition, etc.[78]. There are no studies done on Swellex rock bolts in simulated YM water or in any of the ground waters of Yucca Mountain. Since Super-Swellex is already installed at one of the ESF, it is very important to study this kind of material in different solutions. Also, there is a need to study the corrosion mechanism with respect to different ions at various concentrations and temperatures. AISI 4340 steel was also evaluated for general & localized corrosion behavior at various temperatures & concentrations in simulated Yucca Mountain solutions using potentiodynamic polarization and immersion corrosion techniques. The steel’s general corrosion rate values can then be used as a baseline to predict the aqueous corrosion behavior of other High-Strength Low-alloy (HSLA) candidate steels proposed for use as rock bolts and I-beams inside the repository tunnels. Also,
AISI 4340 steel was studied for its electrochemical corrosion behavior in solutions containing sodium silicate and/or sodium bicarbonate to determine if either of these chemicals could be used as a suitable corrosion inhibitor for the rock bolts and I-beams prior to tunnel installation. Using the information presented in this report, as well as results from available open literature, will help to determine the best direction for design of these underground structural materials.

II. BACKGROUND AND THEORETICAL ASPECTS

Corrosion phenomena are very well known in steels, and have been the subject of numerous investigations[79-85]. Corrosion of metal in aqueous environments is entirely electrochemical in nature, as it is governed by anodic and cathodic reactions that occur at the metal-electrolyte interface. Anodic reactions can cause dissolution of metals while cathodic reactions cause compound formations from the dissolved species in the electrolyte. Thus, metals usually lose weight because of their deterioration, while additional insoluble products may precipitate in the electrolyte. Therefore, these electrochemical reactions also change in the chemical composition of the reacting environment, which may influence further degradation, or deceleration of the weight loss of metals. Metallic forms are of higher Gibbs energy as compared to compounds or ores, and have a tendency to lower the energy[86]. It is necessary for metals to absorb and store energy when they leave their original natural compounds; this energy in turn, will be released by corrosion even at the room temperatures in a corrosive environment. The amount of free energy increased during the metallization process varies from metal to metal; it is relatively high for some metals such as magnesium or iron, and relatively low for noble metals such as gold or platinum. Consequently, magnesium and iron corrode faster than gold and platinum[87]. In some cases, metals have a tendency to return to their original compounds. For example, the most common iron ore, hematite, is an oxide of iron (Fe₂O₃). The energy required to reduce iron ore to metallic iron is absorbed when the iron corrodes to form the original compound.

2.1. Electrochemical Corrosion Mechanism

Two types of reactions occur electrochemically at the metal-electrolyte interface. One of these is the anodic (oxidation) reaction, which is dissolution of the metallic form into an ionic form at the interface, along with the release of valence electrons into the metal. It is the transformation of electrically-neutral metal atoms into discrete ions. These ions may remain in solution or react to form insoluble corrosion products. The anodic reaction (oxidation) of a metal M is generally expressed by the following equation:

\[ M \rightarrow M^{n+} + ne^- \]  \hspace{1cm} (2.1)

where ‘n’ represents the valence of the metal. The number of electrons released by the metal from its outermost shell, which can be used by a cathodic reaction, occurs over the same metal surface. Cathodic reactions (reductions) form compounds at cathodic sites of metal by consuming electrons, either released internally by anodic reactions, or supplied by an external source, or both. There are two fundamental cathodic reactions in neutral ground waters. If the environment is aerated, the cathodic reaction (reduction of oxygen) will be in the form of:

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  \hspace{1cm} (2.2)

If the water is deaerated and no other side reactions occur, then the cathodic reaction (reduction of deaerated water) at the metal-solution interface is given by:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \hspace{1cm} (2.3)

If the pH of electrolyte is low, then the cathodic reaction (evolution of hydrogen) in presence of extra H⁺ ions would be in the following form:

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (2.4)

It is possible to have any of these reactions for carbon steel-ground water corrosion systems depending upon the potentials over the steel, and the pH values of the environment. Ions in electrolytes can move and carry charges,
anions move from cathodic to anodic regions, and cations move in the opposite direction in an ioni-
cally conductive electrolyte. The absence of any one of them stops the electrochemical corrosion reac-
tions.

The extrapolation of the anodic and cathodic linear regions of the curve gives the corrosion cur-
rent density ($I_{corr}$), which is inversely proportional to the corrosion rate. The hypothetical cathodic and anodic polarization curves for electrodes show active and passive behaviors as seen in Figures 2.1 and 2.3[88-92]. The corrosion rate can be determined as follows:

$$CR = 3.27 \times 10^{-3} \frac{I_{corr} \cdot EW}{\rho}$$

(2.5)

where, $I_{corr}$ = Corrosion Current Density (A/cm$^2$)

EW = Equivalent weight of the metal

$\rho$ = Density of the metal (g/cm$^3$)

2.2. Corrosion of Steel in Water

Corrosion processes in steel due to ground water interactions are electrochemical in nature. Therefore, the mechanisms are anodic and cathodic reactions for corrosion of steel in water. Metallic Fe in anodic region oxidizes to ferrous Fe$^{2+}$ ions by the reaction in the form of:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

(2.6)

This reaction is balanced by the reduction of dissolved oxygen to hydroxyl ions (OH$^-$) via consuming the electrons released by the oxidation as given in Equation 2.2. Then the product of anodic reaction Fe$^{2+}$ and the hydroxyl ions (OH$^-$) formed by the cathodic reactions will react to form ferrous hydroxide precipitate Fe(OH)$_2$:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

(2.7)

Since the YM water would likely be aerated with approximately 10 ppm dissolved oxygen[2], it would be possible to represent the overall reactions for the corrosion system of interest as follows:

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$$

(2.8)

The corrosion mechanism of steel in neutral waters can be illustrated as shown in Figure 2.2.[93]
2.3. Faraday’s Law

The free energy change of a corrosion process in terms of the potential difference and the amount of transported charge is known as Faraday’s Law:

\[ \Delta G = -nFE \]  

(2.9)

where, \( F = 96,500 \) coulombs/equivalent, \( E \) is the measured potential, and \( n \) is the number of electrons transferred in the corrosion reaction[94]. An expression for penetration rate “\( r \)” (penetration per unit time) of a corroding metal can be derived from Faraday’s law as given in the following equation:

\[ r = 0.129 a/nD \]  

(2.10)

Figure 2.2. Electrochemical corrosion mechanism of steel in neutral waters.[93]

The penetration rate ‘\( r \)’ in Equation 2.9 is in the units of mils/year (mpy) when current density is \( I \) (\( \mu A/cm^2 \)), density \( D \) (g/cm³), and the atomic weight ‘\( a \)’ (g/mol). Consequently, it is possible to calculate the penetration rate equivalent of a current density measured from corrosion reaction of a metal by Equation 2.9.

2.4. Nernst Equation

Considering a reaction with reactants A and B, and products C and D, as in the following:

\[ A + B \rightarrow C + D \]  

(2.11)

Then Nernst equation for this particular reaction can be expressed as:
\[ \Delta G = \Delta G^\circ + RT \ln \left[ \frac{[C][D]}{[A][B]} \right] \]  \hspace{1cm} (2.12)

where ‘R’ is the gas constant (8.314 J/mol·K) and ‘T’ is temperature (K). The symbol (\( ^\circ \)) represents standard state parameters at 298 K and at the pressure of 1 atmosphere. The terms in the square brackets represent the concentrations of the species in the solution expressed in molarities (mol per liter). The Nernst equation may also be written by substituting Faraday’s free energy expression as follows:

\[ E = E^\circ - \frac{RT}{nF} \ln \left[ \frac{[\text{products}]}{[\text{reactants}] \right] \]  \hspace{1cm} (2.13)

The electrode potential ‘E’ changes as a function of concentrations of the participating substances. Therefore, this formula can be used to construct equilibrium potential-pH diagrams, also called Pourbaix diagrams[95].

2.5. Pourbaix Diagrams

Pourbaix used the Nernst equation (Equation 2.12) to develop potential-pH diagrams for a variety of metals considering all possible equilibrium reactions in water. The Pourbaix diagram for iron, for all dissolved species at electrolyte activity of 10^{-6} g-equiv/L, is given in Figure 2.3. Three main regions in the Pourbaix diagram describe the cases in which corrosion, immunity, and passivity occur. The hatched regions in Figure 2.3 show soluble products formed in a wide range of acidic conditions, and a narrow range of alkaline conditions, in which corrosion takes place. Between these two regions, an insoluble film forms giving rise to a passive region. The third region, immunity, shows that the metal is thermodynamically stable and neither corrodes nor passivates. Pourbaix diagrams provide a strong thermodynamic basis for understanding corrosion reactions for the metals of interest. However, it does not take into account the kinetics of reactions and how contaminated the water is. In practice, the corrosion processes are usually taking place in contaminated aqueous environments and, therefore, deviate from the thermodynamics.

![Pourbaix Diagram for Iron](image)

Figure 2.3. Pourbaix diagram for pure iron at the activity of 10^{-6} g-equiv/L.[95]

2.6. Polarization

The difference between the potentials of an electrode with and without current (measured in the external circuit via counter electrode) is called polarization. Polarization may also be referred to departure from equilibrium, or to over potentials. Positive over potentials are called anodic polarization, whereas negative over potential are called
cathodic polarization. Evans[96] introduced a method to represent the relationship between potential and current for a corroding metal in an environment, introducing a linear Tafel slope shown in Figure 2.4 (a) and (b), where the horizontal axis represents the logarithm of the current. The intersection of the anodic and cathodic curves represents the condition where the rates of those two reactions are equal, and no net current flows through the external circuit between anode and cathode. At this point, all of the electrons released by anodic reactions are consumed by the cathodic reactions. Therefore, the potential at the intercept of the cathodic and anodic curves defines the corrosion potential $E_{corr}$, and it will not change its value as long as the environmental conditions effective on reactions are the same. There are two types of polarizations effective on controlling the electrochemical reactions[87]: activation and concentration polarizations. These can occur simultaneously or individually at any time for any given corrosion system. Activation polarization is a type of reaction control that inherently comes from the reaction, such as limited speed of electron transfer in a certain metal, or temperature of the metal effective on the reaction. On the other hand, concentration polarization is caused by concentration changes of the species in bulk solution at the metal-solution interface. The reaction is delayed due to rapid depletion of species at the metal surface, due to low diffusivity of the electrolyte. Thus, the reaction rate cannot exceed a certain value, which is associated with the limiting current density. The limiting current density is the highest current density possible for a given metal-environment reaction due to diffusion limitations of the reaction particle in the electrolyte[97, 98]. The polarization plot representing the concentration controlled rate is given in Figure 2.4 (b), in which the $I_{corr}$ value is equal to the limiting current in this particular reaction control.

In the case of ‘activation polarization’, the relationship between polarization and reaction rate can be given in terms of Tafel constants $\beta_a$ and $\beta_c$[99], which are the slopes of the anodic and cathodic linear regions on the semi-logarithmic polarization plot:

$$\eta_a = \beta_a (\log i_{corr} - \log i_{a})$$  \hspace{1cm} (2.14)  

$$\eta_a = \beta_c (\log i_{corr} - \log i_{c})$$  \hspace{1cm} (2.15)  

where $i_a$ and $i_c$ are the equilibrium current densities for anodic and cathodic reactions respectively. The limiting current density is an important quantity as it is related to the concentration polarization. It is inversely proportional to the thickness of the diffusion boundary layer $\delta_n$[100], which can be expressed as:

$$i_{corr} \delta_n = \text{constant}$$  \hspace{1cm} (2.16)  

For a cathodic process, the concentration polarization is given in[101]:

$$\eta_c = 0.059/z \log \frac{c_e}{c_o} = 0.059/z \log \left(1 - \frac{i}{i_{corr}}\right)$$  \hspace{1cm} (2.17)  

where, ‘$c_e$’ is the concentration on an electrode, ‘$c_o$’ is bulk solution concentration, ‘$i$’ is applied current density, ‘$i_{corr}$’ is limiting current density, and ‘$z$’ is the number of exchange electrons.

2.7. Polarization Resistance

The determination of the corrosion rate by polarization method has been widely accepted because of its reliability and fast data acquisition as compared to classical long-term corrosion testing methods based on weight loss measurements[102]. Polarization resistance is defined as the slope of the $E = f(I)$ curve, given in Figure 2.4 (c), which is a typical plot of electrode potential vs. current in the linear axis. The slope is inversely proportional to the corrosion rate, or $i_{corr}$[99]. Therefore, the corrosion rate can be calculated using the equation:

$$i_{corr} = B/R_p$$  \hspace{1cm} (2.18)  

where $R_p$ represents the polarization resistance. $B$ is the proportionality constant obtained from the Tafel constants $\beta_a$ and $\beta_c$ as given by the Stern-Geary equation[100] given below:

$$B = \frac{\beta_a \beta_c}{[2.3(\beta_a + \beta_c)]}$$  \hspace{1cm} (2.19)
The anodic and cathodic reaction curves are shown in the same polarization plot[98]. Hypothetically, Evans’ diagrams may be obtained by potentiodynamic or galvanodynamic scans using a Potentiostat. A modern Potentiostat can analyze polarization curves [E vs. log(I)], and gives the polarization resistance values. In some cases, potentiodynamic scans are favored over galvanodynamic ones, or vice versa, depending on the test solution resistance, which always has a negative effect on measured currents.

2.8. Electrochemical Impedance Spectroscopy

Impedance spectroscopy is another method for calculating the corrosion rate of metals in aqueous environments. We can obtain the polarization resistance by applying a sinusoidal voltage of small amplitudes to the working electrode in an extensive frequency range[103-105]. The response in the circuit to every applied alternative voltage with different frequency is a sinusoidal current with different amplitude, and a phase shift relative to the input signal. The ratio of the applied and resultant signals through the circuit gives the impedance Z:

\[
Z = \frac{\Delta E}{\Delta I} = Z_r - iZ_c \quad (2.20)
\]

The impedance Z is a complex quantity, so it has real and imaginary components as opposed to a real resistance. The ‘Nyquist Plot’ shown in Figure 2.5 is obtained by plotting the imaginary part and the real part of complex Z as y and x axes, respectively.

It is useful to consider a hypothetical ‘equivalent circuit’, in order to realize the variations of the electrochemical impedance with changing frequencies. A combination of common circuit elements can behave in a similar manner like a corroding electrode in an electrolyte[106, 107]. The equivalent circuit proposed by Randles has been found to have wide application in many electrochemical systems[103]. Figure 2.5 shows the equivalent circuit of Randles type. In the case of steel and the YM water interface, we can employ the same equivalent circuit in order to analyze the electrochemical IS data.

The resistance R_o in the equivalent circuit represents the solution and the corrosion product film. R_t (charge transfer resistance) and C_{dl} (double layer capacity) both represent the corroding interface. R_t determines the rate of the corrosion reaction as it is the measure of electron transfer across the surface. Under an activation-controlled systems the R_t is always equivalent of R_p, the polarization resistance. As the R_t can be measured precisely from the intercept of semicircle with the real axis of Nyquist plot, this value can be substituted in the Stern-Geary equation to calculate the corrosion current density and the corrosion rate. The Stern-Geary equation will take the form as in the following:

\[
i_{corr} = \beta_a \beta_c / 2.3 \beta_a + \beta_c) \cdot [10^6] \cdot [1/R_t] \quad \mu A/Cm^2 \quad (2.21)
\]

where, \( \beta_a \), \( \beta_c \) are anodic and cathodic slopes in the polarization plot (E vs log I). In practice R_t and C_{dl} are non-linear elements. Their numerical value depends on the magnitude of the applied voltage. This difficulty can be overcome by considering the response of the electrochemical cell to a sinusoidal voltage of a single frequency, \( \omega \), and small enough amplitude for the non-linearity of the cell to be negligible. Figure 2.5 shows the behavior of the equivalent circuit in terms of a Nyquist plot. The horizontal axis in Figure 2.5 represents the real part of the cell impedance i.e. the resistive component, and the vertical axis the imaginary component, i.e. the capacitive reactance. At high frequencies (typically more than 10 kHz) C_{dl} conducts easily and shorts out R_t effectively. Therefore, only the film resistance R_o remains effective. As the frequency decreases C_{dl} conducts less and less and the response typically follows a semicircle. At low frequencies or as a DC voltage is approached, the capacitor stops to conduct and the cell impedance becomes the sum of R_t and R_o. In practice, the above situation (depressed semicircle) cannot be easily observed because of the activation controlled corrosion rate and the complications due to diffusion effects that are usually present. In order to model those effects, it is necessary to include an additional circuit element ‘W’, in series with R_t. This element is called Warburg impedance, which represents the concentration and diffusion related processes. By adding the Warburg impedance to the Randles circuit the complex plane response in Figure 2.5 changes from the depressed semi-circle to the gray curve denoted ‘W’, representing increased amounts in concentration controlled processes. In addition the Bode plot is represented in the Figure 2.6 with the equivalent circuit.
Figure 2.4. (a) Corrosion potential and rate ($I_{\text{corr}}$) under activation control; (b) Corrosion potential and rate under concentration control; (c) Linear portion of polarization curve at low overvoltage near $E_{\text{corr}}$. [96]
2.9. Passivation in Metals and Alloys

If the corrosion product is insoluble and adheres to the metal surface, it forms a very thin protective film on the metal surface, causing “passivity” because of its significant effect on decreasing the current density, as lowering the corrosion rate. A typical appearance of passivity on a hypothetical polarization diagram is given in Figure 2.7, showing the passive region with the passive current density. If there were no passivity, a steady increase in current would occur with increasing over-potentials as shown by the dashed line in Figure 2.7. The passivity due to film formation is of two types in general[107, 108], such as chemical passivity and precipitation related mechanical passivity. Chemical passivity occurs due to a thin and dense semi-conducting oxide film that adheres strongly onto metal surfaces. It is a type of coating, in which certain anodic and cathodic reactions form mainly metallic oxides with high adhesive forces. This type of passivity moves the working electrode potential strongly to the positive directions, to more noble values. Passivity by precipitation or mechanical passivation is the decrease in corrosion rate by accumulation of insoluble solid salts, already available in the solution, onto metal surfaces. These precipitates do not only form at the interface, but also in the electrolyte due to temperature and concentration effects and are deposited over the specimen leading to significant decrease in corrosion rates. The scale built up on the surface is a very thick salt layer but porous in nature, and most of the time it is not electrically conductive at all. Higher temperatures and concentrations increase the activity of aqueous environments and lead to more precipitation.
2.10. Pitting

Pitting is a type of localized corrosion that occurs on the passive surfaces of metals exposed to a corrosive environment\cite{109}. The passivity of metal i.e. the thin film formation is one of the requirements for pitting to occur over the metal surface. Another main factor for pit formations is the high chloride content of the environment\cite{101}. Pitting initiates by preferential attacks of aggressive ions, especially of chlorides in certain electrochemical conditions\cite{110}. Then, it starts to grow at an increasing dissolution rate to propagate through the metal while the other parts of the surface are still passive. Physical defects over the passive film such as cracks or pores also allow the pitting initiation and growth on the metal surface\cite{110}. Pitting initiation has been observed at certain electrode potentials for particular alloy-environment systems. This "critical pitting potential" is a function of the temperature as well as concentration of aggressive ions in the environment\cite{110}. Initiation and growth rate of pitting also depend on the properties of the passive film and crystal orientation of the metal grain on which pitting occurs. Particularly, the grain boundaries, inclusions, and heterogeneities are common sites where pits initiate. Generally, pitting can cause sudden unexpected failures, because of its localized nature. In localized corrosion, the dissoluti on takes place at an anode of preferably small surface area while cathodic areas are much larger. Then the exchanged current between anodic and cathodic reactions will cause more current density in the anodic areas due to that large surface area difference. Therefore, the corrosion rate becomes significantly higher resulting in a rapid dissolution and failure of metals and alloys. When a passive metal is under stress in an aggressive environment, it becomes more perilous, and more rapid failures become imminent due to local strain at the crack tip initiated by pitting. However, there are certain metal-environment systems that experience these types of failures, which will be a topic of the stress corrosion-cracking phenomenon.

2.11. High-temperature Oxidation and Kinetics

2.11.1. Oxidation of Metals

Figure 2.8 shows a schematic of the reaction between a metal/alloy and its environment. In its simplest form, the reaction between a metal and its environment can be written as:

\[
x M(s) + \frac{y}{2} O_{2(g)} = M_x O_{y(s)}
\]  \hspace{1cm} (2.22)

The reaction, simple as it looks, is influenced by factors like the composition of the metal/alloy, the surface conditions, microstructure of the substrate, pressure of the oxidizing atmosphere, etc. As the oxide film grows on the substrate, it effectively partitions the two reactants i.e. separates the substrate from the oxidizing atmosphere. For the
reaction to proceed further there has to be a solid-state transport of one or both of the reactants through the oxide so that the growth of the oxide occurs either at the oxide-metal or the oxide-gas interface. Reactions occurring at the oxide-metal interface require the faster transport of oxygen ions whereas those occurring at the oxide-gas interface need greater diffusive flux of the metal ions. Figure 2.9 [77] shows a schematic of the main aspects involved in the metal-oxygen reaction. The driving force for the transport of reactants is provided by electrical potential gradients for thin films due to the electrical fields present and due to chemical potential gradients in case of thick films, considering a non-porous, crack-free oxidation product is formed. When the oxide has physical defects present, it does not serve as a solid-state diffusion barrier between the two reactants. Since all oxides are ionic in nature, it is not practicable to consider the transport of metal and non-metal atoms through the oxide [78].

Figure 2.8. A schematic of the reaction between a metal/alloy and its environment.

Figure 2.9. Schematic illustration of aspects of metal-oxygen reaction[77].
Any oxidation process can be broadly divided into three stages; a schematic illustration of the stages is shown in Figure 2.10[111]. The first stage is an incipient or “transient” stage, characterized by the simultaneous formation of the oxides of all the alloying elements in the alloy; the second stage is the so-called “steady state” oxidation stage; and the final is the “breakaway” stage[112]. The second stage is typified by the formation and growth of protective scales. In this stage the diffusion of the ionic species through the oxide slows down and the reaction rates are significantly reduced. As the protective oxide grows and reaches a critical thickness, it starts to lose contact with the underlying alloy. The protectiveness of the oxide layer is lost and oxidation of the underlying alloy is accelerated as there is vigorous oxidation between the exposed alloy and the atmosphere.

During the first stage of oxidation, as a fresh surface is exposed to oxygen, adsorption of oxygen metals onto the surface takes place via the equation:

\[
\frac{1}{2} O_{2(g)} \rightarrow \frac{1}{2} O_2(ad) \rightarrow O(ad) \rightarrow O^-(chem) \rightarrow O^{2-}(lattice)
\]  

(2.23)

Oxide nuclei develop on the substrate surface as the above reaction proceeds. These nuclei may grow laterally and establish a thin continuous film on the surface; or they may nucleate as separate oxide particles. Surface preparation, impurity content, crystal defects at the surface and surface orientation are among the factors that affect the extent of oxygen adsorption and initial oxide formation[77]. As the oxide nuclei grow, they provide complete coverage over the oxide surface and at this stage formation of a protective oxide has started. The transport of the ionic oxidation reactants now proceeds through this layer as interstitial or substitutional jumps, vacancy jumps or via the grain boundaries. A good protective scale increases the oxidation resistance of the underlying alloy and should have the following characteristics:

a) It should have minimum physical defects like pores, cracks, or other paths that would allow short circuit diffusion of the ionic species  
b) It should be adherent to the underlying alloy under all conditions of use so that the breakaway stage of oxidation is not encountered  
c) Ionic defects that effect transport mechanisms should be low. The most commonly formed known protective oxides like SiO₂, Al₂O₃ and Cr₂O₃ have the lowest defect concentrations. Nickel oxide, which is known to be non-protective, gets its nature from the presence of small amounts of dissolved Cr, which increases the cation vacancy concentration and thus, increases Ni mobility  
d) Some heavy metals like Mo, Cr, and W are known to have low vapor pressures at high temperatures, causing oxide vaporization and poor oxidation resistance. Protective oxides should have low oxide evaporation.

Figure 2.10. A schematic of the various stages of oxidation on alloys that develop protective scales[111].
2.11.2. Thermodynamic Considerations

Whether a reaction takes place or not is determined by the second law of thermodynamics, which states that: “The total entropy of any isolated thermodynamic system tends to increase over time, approaching a maximum value”. When the temperatures and pressures in a system are constant (as encountered during high temperature reactions), the second law can be conveniently written in terms of the Gibbs free energy ($G'$) of a system:

$$G' = H' - TS'$$  \hspace{1cm} (2.24)

where $H'$ is the enthalpy and $S'$ is the entropy of the system.

The free energy change of a system has the following significance: $\Delta G' < 0$, spontaneous reaction expected; $\Delta G' = 0$, equilibrium; $\Delta G' > 0$, thermodynamically unfavorable reaction\[113\]. For the above equation 2.24, $\Delta G'$ can be expressed as:

$$\Delta G' = \Delta G^o + RT \ln \left( \frac{a_{M, O_x}}{a_M \cdot a_{O_2}^{y/2}} \right)$$  \hspace{1cm} (2.25)

where, $\Delta G^o$ is the standard free energy of formation of the oxide, $T$ is the absolute temperature, $R$ is the gas constant, and $a_i$ denotes the thermodynamic activity of species $i$.

At equilibrium, the equation 2.25 can be written as:

$$\Delta G^o = -RT \ln K_e$$  \hspace{1cm} (2.26)

where, $K_e$ represents the terms in the bracket and is known as the equilibrium constant. Assuming Raoultian behavior, activities of the metal and oxide are unity. For an ideal gas, the activity of gas can be given by its partial pressure ($P_{O_2}$)\[114\]. The equilibrium constant now can be expressed as:

$$K_e = \left( \frac{1}{P_{O_2}^{y/2}} \right)$$  \hspace{1cm} (2.27)

Combining equations 2.26 and 2.27, the equilibrium partial pressure of oxygen can be determined from:

$$P_{O_2}^{eq} = \exp \left( \frac{2\Delta G^o}{yRT} \right)$$  \hspace{1cm} (2.28)

A partial pressure in the reaction environment of more than the value calculated by equation 2.8 ensures the oxidation of metal according to equation 2.24.

Determination of the conditions under which a given corrosion product will form is made simpler by knowing the relative stabilities of the oxides which can be in part read off of an Ellingham diagram, as shown in Figure 2.11\[115\]. The diagram shows the values of $\Delta G^o$ in kJ per mole of oxygen and, hence, the lower the position of an oxide line on the diagram the more stable it is.
2.11.3. Kinetic Considerations

As mentioned earlier, the oxides formed are ionic in nature and their thickness increases with time. Usually, when a phase-boundary process is the rate determining step in a reaction, linear kinetics are observed. When diffusion through the oxides is the rate controlling step, parabolic kinetics are followed. Apart from this, linear, para-linear, logarithmic and inverse logarithmic laws are also encountered in alloy oxidation. Sometimes a combination of these laws is also observed for a system. It has been shown by numerous researchers [116-120] that metals and alloys demonstrate oxidation rate laws that deviate from the classic laws. The general form of the rate law can be given as:

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

(2.29)

where \( (W/A) \) is the weight gain per unit area at time \( t \), \( k \) is the rate constant and \( n \) is the time exponent of the rate law. The following discussion describes briefly how the rate law is derived[113, 121, 122].

Assuming a dense, adherent oxide scale formation on the metal/alloy, the rate of reaction controlled by diffusion of ionic species through this layer is given by Fick’s first law:

\[ J = -D \frac{dc}{dx} \]  

(2.30)

where \( J \) = flux of diffusing species through the product layer  
D = diffusion coefficient  
c = concentration of the diffusing species  
x = thickness of the oxide layer
Assuming thermodynamic equilibrium at the gas-oxide and oxide-metal interfaces, the outward cation flux, $j_{M^{2+}}$, is equal and opposite to the inward flux of cation vacancies. Figure 2.12 [113] shows the simplified model for diffusion-controlled oxidation. This can be represented as:

$$j_{M^{2+}} = -j_{V_m} = D_{V_m} \frac{C_{V_m}^c - C_{V_m}^v}{x} \quad (2.31)$$

where now, $C_{V_m}^c$ and $C_{V_m}^v$ are the vacancy concentrations at the oxide-metal and the oxide-gas interfaces respectively. At constant value of $C_{V_m}^c - C_{V_m}^v$, the equation can be written as:

$$j_{M^{2+}} = \frac{1}{V_{ox}} \frac{dx}{dt} = D_{V_m} \frac{C_{V_m}^c - C_{V_m}^v}{x} \quad (2.32)$$

where, $V_{ox}$ is the molar volume of the oxide.

Hence, we write:

$$\frac{dx}{dt} = D_{V_m} V_{ox} \frac{C_{V_m}^c - C_{V_m}^v}{x} = \frac{k'}{x} \quad (2.33)$$

which gives us the value of

$$k' = D_{V_m} V_{ox} \left( C_{V_m}^c - C_{V_m}^v \right).$$

Integrating the equation 2.21 over $t = 0$ to $t$ and $x = 0$ to $x$, we get:

$$x^2 = 2k' t = k'' t \quad (2.34)$$

which is the commonly known parabolic rate law, which is a specialized case of equation 2.17. Table 2.1 [123] lists the parabolic rate constants for the most commonly encountered base metals for alloys. Figure 2.13 [113] gives a visualization on the growth rates of known oxides as a function of temperature. The parabolic rate constant (or for that matter any rate constant) varies as a function of temperature and follows the Arrhenius equation given by:

$$k = k_o \exp \left( \frac{-\Delta E_a}{RT} \right) \quad (2.35)$$

where $k_o$ is the pre-exponential factor, $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature (K) and $\Delta E_a$ is the activation energy.

The theory of oxidation was initially developed by Wagner to explain the mechanism of oxidation. Wagner’s analysis lies in providing a complete mechanistic understanding of the process of high temperature oxidation under the conditions set out, and is elucidated in standard references [77, 113, 121, 124-126]. The assumptions made by Wagner can be summarized as below:

1. The oxide layer is compact and perfectly adherent
2. Migration of the ionic species through the oxide is the rate-controlling step
3. Thermodynamic equilibrium is established at both the oxide-gas and oxide-metal interface
4. Thermodynamic equilibrium is also established locally throughout the oxide
5. The oxide scale is nearly stoichiometric
6. The oxide layer is independent of the space charge effects
7. Oxygen solubility in the metal may be neglected

Table 2.1. Parabolic rate constant ($k_p$) values for Fe, Ni, Cr, Co at 1000°C and 1 atm. [123]

<table>
<thead>
<tr>
<th>Metal</th>
<th>$k_p$ (g².cm⁻⁴.s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>$4.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>Nickel</td>
<td>$2.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>Chromium</td>
<td>$1 \times 10^{-10}$</td>
</tr>
<tr>
<td>Cobalt</td>
<td>$2.1 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Figure 2.12. Simple oxidation model based on Wagner’s theory[113].
Figure 2.13. Order of magnitude parabolic constants for the growth of several oxides [113].

Figure 2.14. Hypothetical mass-gain versus time curve for an oxidation reaction and possible observable features[113].
Equipped with the thermodynamic and kinetic fundamentals, oxidation kinetics can be studied under a particular set of exposure variables. The simplest approach to this is to expose a specimen of known mass and dimensions to a known environment and record its mass gain for the time of exposure. Surface characterization of the specimen can be done by various techniques like optical microscopy, SEM, TEM, X-ray techniques, etc. The extent of reaction can be evaluated by:

- the amount of metal consumed
- the amount of oxygen consumed
- the amount of oxide produced

With the advent of modern continuous measurement and recording capabilities, it becomes easier to measure the amount of oxygen consumed by measuring continuously the mass gain of the samples as a function of time. Thermogravimetry is one of the principal techniques used in the investigation of the oxidation reactions. It can be easily used at high temperatures and with different exposure environments. Figure 2.14 [113] shows a hypothetical mass gain versus time curve for an oxidation reaction obtained via continuous thermogravimetry. Usually, isothermal thermogravimetry is the preferred means (as opposed to non-isothermal methods) of evaluating high temperature oxidation and corrosion of metals and alloys, since it is known to be more amenable to interpretation in terms of the kinetics and mechanisms of the reactions involved [122]. Details on the method used and the actual instrumentation employed for the study of the materials in this research are given in Section 3.8.

III. EXPERIMENTAL

3.1. Materials and Specimen Preparation

Alloy 22, AISI 4340 steel, and several types of rock bolts (Friction-type grouted rock bolts, Swellex, and Split-set) as well as Alloy-263 and Alloy-282, were procured and used as part of the YM research conducted. Alloy 22 was procured in both rod and plate forms. AISI 4340 steel was obtained in 1” and ½” diameter bar stock. The different types of rock bolts were obtained from the Yucca Mountain site or from commercial sources. Alloys 263 and 282 were received as 2 inch x 2 inch x 0.125 inch plates. The alloys and their compositions are shown in Tables 3.1(a) and (b), at the end of this section. Photographs of these different materials are shown in Figure 3.1. For polarization measurements, disc specimens were professionally machined from bar/plate stock for Alloy 22 and 4340 steel. However, for the rock bolts, disc specimens were professionally machined from the original rock bolts themselves. These specimens were mounted in epoxy resin with one end soldered to a copper wire for electrical connection. Electrical connection between the sample and the wire was checked with a voltmeter. The exposed side was subsequently polished using 240 & 600 grit SiC paper and finally cleaned in distilled water. Steps in sample preparation (for Swellex Mn 24) are shown in Figure 3.2.(a). For “effect of cold working” experiments, the sample preparation is shown in Figure 3.2.(b).

For the oxidation experiments, test specimens of nominal dimensions 2 mm x 3 mm x 5 mm were machined out of the received samples and are shown in Figure 3.1. These samples were machined on a Buehler IsoMet 1000 precision saw, using a diamond wafering blade. The machined test specimens were abraded successively on Buehler Carbimet® emery papers of grit size 240, 400 and 600, and then fine polished with Buehler Micropolish® II de-agglomerated alumina paste of 1 μm and 0.05 μm. After a preliminary wash in distilled-deionized (DDI) water, specimen dimensions were recorded using Mitutoyo Vernier calipers. The specimens were then cleaned ultrasonically in DDI water for 5 minutes and degreased with ethyl alcohol. They were allowed to dry in air for about 20 minutes and then placed in tared alumina pans in the respective TGAs.

For the immersion corrosion experiments, rectangular specimens were cut and machined from both the expanded Swellex Mn24 rock bolts and the 1” diameter 4340 steel bar stock. Dimensions of the test coupons for the aerated experiments were 40 x 17.5 x 3 mm, with a hole diameter of 3 mm, and 25 x 13 x 0.5 mm with a hole diameter of 3 mm for the deaerated experiments. Area of the sample was calculated by using the formula given in Equation 3.1, shown below.

---

2 The thermogravimetric experiments were performed using two different instruments.
\[ A(cm^2) = 2[(l \cdot w) + (w \cdot h) + (l \cdot h)] + \left[ \pi \cdot (h \cdot d) \right] - \left[ \frac{\pi}{2} \cdot d^2 \right] \] (3.1)

Where:
A = Effective Surface Area (cm²)
l = Length (cm);
w = Width (cm);
h = Height (cm);
d = Hole Diameter (cm)

Samples of Swellex Mn24 prepared for immersion experiments are shown in Figure 3.3.

For dry and deliquescent salt experiments, samples of Alloy 22, Inconel 825, 304L and 316L stainless steels, Swellex Mn24 and Standard Swellex, were mirror-polished similar to the specimens used in the oxidation experiments. A photograph of the polished samples prior to the experiments is shown in Figure 3.4.

Table 3.1(a). Chemical analyses of the Ni-base superalloys used in this study.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy-22\textsuperscript{a}</td>
<td>56.85</td>
<td>21.2</td>
<td>1.00</td>
<td>13.50</td>
<td>3.9</td>
<td>0.31</td>
<td>0.05</td>
<td>0.002</td>
<td>0.01</td>
<td>0.01</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy-263\textsuperscript{b}</td>
<td>52</td>
<td>20</td>
<td>20</td>
<td>6</td>
<td>2.4*</td>
<td>0.7*</td>
<td>0.6*</td>
<td>0.4</td>
<td>0.06</td>
<td>Al</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.6*</td>
<td>0.2</td>
</tr>
<tr>
<td>Alloy-282\textsuperscript{b}</td>
<td>57</td>
<td>19.5</td>
<td>10</td>
<td>8.5</td>
<td>2.1</td>
<td>1.5*</td>
<td>0.3*</td>
<td>0.15*</td>
<td>0.06</td>
<td>B</td>
<td>Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Maximum
\textsuperscript{b} Chemical analyses from LTI
\textsuperscript{b} Nominal composition from manufacturer’s website
Table 3.1(b). Chemical analyses of the steels used in this study.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Co</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+Cr+Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Split set (^a)</td>
<td>0.06</td>
<td>0.02</td>
<td>0.03</td>
<td>0.68</td>
<td>0.07</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
<td></td>
<td>0.038</td>
<td>0.007</td>
</tr>
<tr>
<td>(ASTM A607-98,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.22</td>
</tr>
<tr>
<td>Grade 50)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swellex (^a) Mn-24</td>
<td>0.05</td>
<td>0.042</td>
<td>0.027</td>
<td>0.24</td>
<td>1.16</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>
</tr>
<tr>
<td>Standard Swellex (^a)</td>
<td>0.024</td>
<td>-</td>
<td>0.01</td>
<td>0.008</td>
<td>0.39</td>
<td>0.10</td>
<td>0.013</td>
<td>0.013</td>
<td>Al 0.056</td>
<td>Cu 0.04</td>
<td>Cr 0.036</td>
</tr>
<tr>
<td>Swellex Pm24 (^a)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.012</td>
<td>0.46</td>
<td>0.078</td>
<td>0.012</td>
<td>0.011</td>
<td>Al 0.054</td>
<td>N 0.003</td>
<td>Nb 0.04</td>
</tr>
<tr>
<td>Williams Rock Bolt (^a)</td>
<td>0.06</td>
<td>-</td>
<td>0.03</td>
<td>0.27</td>
<td>1.57</td>
<td>0.44</td>
<td>0.013</td>
<td>0.31</td>
<td>Al 0.004</td>
<td>Cu 0.19</td>
<td>Cr 0.08</td>
</tr>
<tr>
<td>Low Carbon I-beam (^a)</td>
<td>0.09</td>
<td>-</td>
<td>0.03</td>
<td>0.12</td>
<td>0.84</td>
<td>0.08</td>
<td>0.02</td>
<td>0.05</td>
<td>V 0.02</td>
<td>Cu 0.34</td>
<td>Cr 0.08</td>
</tr>
<tr>
<td>AISI 4340 (^a)</td>
<td>1.86</td>
<td>-</td>
<td>0.26</td>
<td>0.26</td>
<td>0.77</td>
<td>0.43</td>
<td>0.015</td>
<td>0.020</td>
<td>Cr 0.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Balance Fe

\(^a\) Chemical analyses from LTI
Figure 3.1. Pictures of as received samples and machined test specimens: (a) Alloy-22 bars (b) AISI 4340 steel rods (c) Dimensions of a typical test specimen for oxidation tests (d) Swellex rock bolts (e) HSLA split sets

Figure 3.2(a). Sample Preparation for Electrochemical Experiments

All samples were cut to required TGA test specimen dimensions using a large flow rate of the coolant to prevent heating.
Figure 3.2(b). Sample Preparation for Electrochemical Experiments

Figure 3.3. Immersion samples used for the immersion experiments.
3.2. Cell Design and Experimental Set-Up for Electrochemical Corrosion Tests

For the electrochemical corrosion experiments, a schematic of a one-liter flask of Pyrex-brand glass, shown with the set-up in Figure 3.5, was used as the test cell of both polarization resistance and electrochemical impedance measurements. A disk shape lid constructed out of 2 cm thick Teflon to seal the cell by means of o-ring, was held in place by compression clamps. A tapered Teflon plug with two holes were machined for the middle opening of the lid, in which cylindrical receptacles for specimen and a Luggin probe were placed in the chamber. Several other receptacles on the lid sealed the entire cell elements via threaded o-ring fittings. The cell design was based on the design of Jones and Paul[127] and met ASTM G5[92]. A tapered Teflon stopper constructed for the larger central hole of the lid held both the specimen and Luggin probe in close proximity. The distance between the probe tip and the specimen surface was maintained at 2-3 mm in all cases, to eliminate any probe distance effect on the entire potentiodynamic polarization or impedance experiments.

A more detailed schematic of the overall arrangement is shown in Figure 3.6. In this, cylindrically shaped working electrodes (test specimens) were mounted in epoxy with their 1 cm² bottom surface area and electrical connection wire protruded out. 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 Luggin probe tip and Ag/AgCl reference electrode were connected via the test solution (YM water) in the probe, without using a salt bridge. Continuously purged gas (nitrogen or oxygen) in the sealed cell maintained constant pressure above the solution.

A heating mantle surrounded the test cell and, an auto-tune PID temperature controller (Ace Glass Econo Temperature Controller) maintained the temperature of the solution from 25°C to 90°C at any value to an accuracy of ± 0.1°C. An end sealed thin glass capillary was used as thermo-well to hold the thermocouple sensor in the solution. A fritted glass capillary was used for continuous aeration/de-aeration of the solution throughout the experiments with the rate of 150 ml/min. The fritted region supplied appreciable aeration and de-aeration for the test solutions. A water-cooled glass reflux condenser was used to minimize the loss of test solution by evaporation at elevated temperatures. The outlet of the reflux condenser was connected to an oxygen trap to avoid aeration/de-aeration fluctuations in the electrolyte. The overall construction required no complicated glass blowing while it already met the designations approved by ASTM G5.
Figure 3.5. Schematic of the apparatus used for Potentiodynamic and EIS tests.

A-Platinum counter electrode  
B-Specimen-working electrode  
C-Reference electrode  
D-Fritted glass purging element  
E-Heating mantle  
F-Water cooled condenser  
G-Oxygen trap  
H-Flowmeter  
I-Temperature controller  
J-Potentiostat  
K-Oxygen gas for aeration  
L-Nitrogen gas for de-aeration

Figure 3.6. Experimental set-up for potentiodynamic linear polarization and impedance spectroscopy.[6]
3.3. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) was performed at the corrosion potentials (open circuit potentials) of the test specimens using the same cell set-up and the same software as used in the polarization studies. Polarization resistance values can be determined from the real axis intercepts of the obtained semicircles of Nyquist plots of the impedance scans. These tests will be used to determine the electrochemical interface leading to activation and passivation events on the steel surfaces during polarization experiments. In general, impedance $Z(\omega)$, may be expressed in terms of real, $Z'(\omega)$ and imaginary $Z''(\omega)$, components.

$$Z(\omega) = Z'(\omega) + Z''(\omega)$$  \hspace{1cm} (3.2)

The Stern-Geary equation provides a direct relationship between the steady state corrosion current and the resistance across the interface, which can be expressed as follows:

$$i_{corr} = \left[ \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \right] \left( \frac{1}{R_p} \right)$$  \hspace{1cm} (3.3)

where, $\beta_a$ and $\beta_c$ are the Tafel constants for the anodic and cathodic partial reactions, respectively and $R_p$ is the polarization resistance. Polarization resistance is given by the difference of the measured impedance at sufficiently low and high frequencies:

$$R_p = |Z(j\omega)_{\omega \rightarrow 0} - |Z(j\omega)_{\omega \rightarrow \infty}|$$  \hspace{1cm} (3.4)

Gamry Potentiostats were used for impedance spectroscopy analysis (ASTM G-106). Nyquist and Bode plots were obtained for AISI 4340 steel in YM environments at different concentrations of ionic salts (1X to 100X).

3.4. Solution Preparation

Table 3.2 shows the composition of simulated Yucca Mountain water at normal concentration. The solutions were prepared by mixing A.C.S. reagent-grade salts at one times (1X), ten times (10X) and one hundred times (100X) the concentration in distilled, deionized water at a temperature of ~ 40°C. After adding the salts to the deionized water, the solution was stirred for 20 – 30 minutes without any applied heat, and allowed to cool down for approximately one hour or more. After cooling, the solution was filtered: once for 1X YM water, and twice for 10X & 100X YM water. The initial pH was approximately 8.2, 7.5 and 7.2 for 1X, 10X & 100X solution, respectively.

<table>
<thead>
<tr>
<th>No.</th>
<th>CHEMICALS</th>
<th>Weight (mg/L)</th>
<th>Molarity (moles/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Magnesium Sulfate (MgSO₄·7H₂O)</td>
<td>50</td>
<td>2.03 x 10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>Magnesium Chloride (MgCl₂·6H₂O)</td>
<td>100</td>
<td>4.92 x 10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>Calcium Chloride (CaCl₂·2H₂O)</td>
<td>196</td>
<td>1.33 x 10⁻³</td>
</tr>
<tr>
<td>4</td>
<td>Calcium Sulfate (CaSO₄·2H₂O)</td>
<td>210</td>
<td>1.22 x 10⁻³</td>
</tr>
<tr>
<td>5</td>
<td>Potassium Bicarbonate (KHCO₃)</td>
<td>50</td>
<td>4.99 x 10⁻⁴</td>
</tr>
<tr>
<td>6</td>
<td>Sodium Bicarbonate (NaHCO₃)</td>
<td>200</td>
<td>2.38 x 10⁻³</td>
</tr>
<tr>
<td>7</td>
<td>Sodium Silicate (Na₂SiO₃·9H₂O)</td>
<td>210</td>
<td>7.39 x 10⁻⁴</td>
</tr>
<tr>
<td>8</td>
<td>Sodium Fluoride (NaF)</td>
<td>2</td>
<td>4.76 x 10⁻⁵</td>
</tr>
</tbody>
</table>
3.5. Cell Design and Experimental Setup for Immersion Corrosion Tests

The experimental setup to measure the corrosion rate of Swellex Mn24 and AISI 4340 steels using weight loss measurements is shown in Figure 3.7. The top specimen marked A is not immersed, and is in humid air. The middle specimen is partially immersed (marked B) and the third specimen is fully immersed (marked C). Compressed air or nitrogen gas is purged continuously.

A-Non-immersed specimen
B-partially immersed specimen
C-Fully immersed specimen
D-fritted glass purging element
E-Plug specimen holder
F-Thermowell
G-Water cooled condenser
H-Flowmeter
I-Oxygen trap
J-Oxygen gas for aeration
K-Nitrogen gas for de-aeration
L-Temperature controller
M-Heating mantle

Figure 3.7. Laboratory setup at UNR used to perform dipping immersion tests to measure corrosion rates by measuring weight loss of the coupons after corrosion experiments. [6]

These experiments were conducted according to the procedures outlined in ASTM G31[128]. Experiments were performed at 25°C, 45°C and 75°C, under both aerated and deaerated conditions. Additionally, AISI 4340 steel was immersed for a period of 110 and 240 days, in an open-air environment to compare the material against previously published[6, 48, 63] results. The mass loss was converted into a corrosion rate using the following formula:

\[
CR = \frac{K \cdot W}{A \cdot T \cdot D}
\]

(3.5)

where, 
K= constant (8.76 x 10^7 for μm/year), 
T = time of exposure (hours), 
A = surface area (cm^2), 
W= mass loss (g), and 
D = density (g/cm^3)
3.6. Dry and Deliquescent Salt Tests

Equal-molar parts of NaCl, KCl, NaNO₃, and KNO₃, were mixed together using a mortar and pestle. These salts were placed on the polished coupons, and the coupons were exposed for a given time to a hot atmosphere. For the dry salt tests, the salt mixture was placed on the surface of the sample and allowed to react in an ambient atmosphere. For the deliquescent salt experiments, the salt mixture was placed on the surface of the sample and a coupon of Mn24 was placed over the salt, as shown in Figure 3.8. The samples were then exposed to an atmosphere of steam. Dry and deliquescent salt tests were performed for six weeks and three weeks, respectively.

![Figure 3.8. Experimental Setup for dry and deliquescent salt tests.](image-url)

3.7. High-temperature Oxidation Kinetics

The experimental data for this were collected by means of two state-of-the-art, highly sensitive thermogravimetric analyzers (TGAs). Oxidation data for all the superalloys were collected using a Seiko 220 horizontal furnace, TGA and data for the HSLA steels were collected using a TA Instruments Q500 vertical tube furnace.

3.7.1. TGA Q500 from TA Instruments

The TGA Q500 is equipped with a continuous weighing capacity of 1.0 g, sensitivity of 0.1 μg, and can handle heating rates from 0.1 to 50°C.min⁻¹. It has the ability to perform temperature Modulated TGA (MTGA). The weight gain as a function of time was recorded for HSLA steel specimens using data acquisition software provided with the instrument. The data acquisition allows recording of weight gain, modulated weight gain, temperature and modulated temperature continuously as a function of time. The gas flow into the balance and specimen chamber (furnace) is controlled by means of an automated Mass Flow Controller (MFC) with a high precision of ± 0.3 mL/min. Gas flows into both the chambers are adjusted as per the manufacturer’s specifications and ensure a positive inflow of the gas so that an environment of only the gas being used for the experiments is maintained. For all our experiments a gas flow of 10:90 mL/min to the balance and the furnace respectively was maintained. The furnace is made up of a quartz tube sealed in a stainless jacket and water cooled peripherally with the help of an attached chiller.

The mass calibration of TA Q500 was performed electronically by comparing with a known mass-set and the four point temperature calibration was performed by determining the curie transition temperature of Ni, Alumel, and two Ni-Co alloys. The mass calibration is performed and temperature calibration is checked every month or if there have been any changes in the operating conditions as per directions in DOE-NSHE regulated Implementing Procedure IPR-035[129]. The gas-outlet on the furnace is fitted with a simple tube the free end of which is placed in a mineral oil bath. This serves two purposes; the first to ensure that the outlet is not plugged and the second so that there is no backflow of laboratory air into the furnace. A cutout of this vertical furnace TGA is shown in Figure 3.9.
3.7.2. Seiko 220 horizontal furnace TGA

The Seiko 220 instrument is a very high precision machine with capabilities of performing simultaneous Thermogravimetry/Differential Thermal Analysis of inorganic materials such as ceramics and metals. The instrument comes equipped with ‘EXSTAR6000 Thermal Analysis & Rheology System’ data collection software. It has the capability to make measurements in the temperature range from room temperature to ~1100°C, and take test specimens up to a maximum weight of 200mg. The heating range is 0.01°C/min. ~ 200.00°C/min; the sensitivity of the instrument is 0.02 μg; it can handle gas flow rates of 1000 mL/minute max.[131]. The TG/DTA module uses a horizontal air cooled, differential system balance mechanism. The instrument works on the following principle:

The sample balance beam and reference balance beam are independently supported by a driving coil / pivot. When a weight change occurs at the beam end, the movement is conveyed to the opposite (rear) end of the beam via the driving coil / pivot, when optical position sensors detect changes in the position of a slit. The signal from the optical position sensor is sent to the balance circuit. The balance circuit supplies sufficient feedback current to the driving coil so that the slit returns to the balanced position. The current running to the driving coil on the sample side and the current running to the driving coil on the reference side is detected and converted into weight signals.

The measurement principle of thermogravimetry is shown in Figure 3.10 (a) and Figure 3.10 (b) shows a line diagram of the measurement system.
3.7.3. Procedure
Polished specimens (shown in Figure 3.1 (c)) were placed in tared alumina sample pans and Ultra-high purity (UHP) Argon gas was purged into the sample and the balance chamber for 20 minutes before starting the experiment. This also allows for enough time to steady any vibrations in the sample pans when the specimens are placed in them. The pans used were the largest available from the manufacturer(s). Sample pans of 500 μL capacity were used for all experiments in the case of TA-TGA, and 50 μL pans were used for the Seiko TGA. The initial weight of the specimen was recorded by the data acquisition software before the start of the experiments. The test specimens were heated at a very fast rate to the desired temperature (equilibrated). This takes at the most up to 30 minutes (for
Data recording was started when the isothermal hold cycle starts and oxidation time is counted from this point onwards. For the TA-TGA, the following test segments represent the isothermal oxidation tests for the HSLA steel samples confirming to the requirements of DOE-NSHE regulated Implementing Procedure IPR-036[132]:

1. Equilibrate \(^4\) from room temperature to the desired temperature of interest under UHP Argon gas
2. Switch gas to UHP Oxygen
3. Isothermal for 6000 minutes

The HSLA steels were held isothermally for periods of 100 hours at varying temperatures from 600°C to 900°C at 75-degree intervals. Only UHP Oxygen gas was used for all the experiments. The weight gain of the sample, temperature, time and other data signals from the instrument were recorded every 30 seconds. For these samples, a sinusoidal modulation of amplitude ±5°C was imposed for a period of 1 cycle per 200 seconds. This sinusoidal modulation creates an artificial perturbation around the mean isothermal temperature. Such a perturbation can also be interpreted as a structured uncertainty in the desired temperature. Results obtained and analyses obtained on the 100 hour data will be discussed in Chapter 5.

For the Seiko TGA, the following steps were used.
1. Ramp 40°C per minute from 27 to (X−55)°C in UHP Argon
2. Ramp 10°C per minute from (X−55) to X°C
3. Hold isothermally at X°C for 2880 minutes in UHP Oxygen

The Ni-base superalloys Alloy-22, Alloy-263 and Alloy-282 were held isothermally for 48 hours in UHP Oxygen. Data were collected every 0.5 seconds in the initial heating cycle and every 60 seconds during the second ramp and isothermal hold. Normalized weight change data of the specimens as a function of exposure time were used to examine the kinetics of oxidation.

3.8. X-ray Diffraction Studies

In-situ X-ray Diffractometer [133], model PW3040-PRO from PANalytical X’Pert PRO was used to characterize polycrystalline samples, oxide powder samples as well as for glancing angle diffractometry to identify the species and phase composition. Glancing angle analysis was done under following instrumental settings: Cu target, Ni filter, V=45kV, Current = 40mV, Scan range = 10 to 90°, Step Size = 0.050 and 0.020°, continuous scanning mode. This machine uses a Cu Long Line Focus (LLF) tube with \(\lambda = 1.54056 \text{Å}\), at a voltage of 45 kV and a current of 40 mA. A Proportional PW3011/20 detector with a Multi-Purpose Sample Stage (MPSS) was used in the thin film measurement, in combination with a parallel beam collimator. The MPSS can accommodate samples up to one kilogram with dimensions of 10 cm in diameter and 10 cm high.

3.9. Synchrotron X-ray Microdiffraction

These studies were performed on Beam Line 12.3.2 with high spatial resolution at the Advanced Light Source, Lawrence Berkeley National Laboratory to supplement the SEM results on HSLA steels. Both, white beam single-crystal Laue diffraction (energy range 6 – 22 keV), as well as monochromatic (E = 9 keV) powder diffraction was used. In white beam mode, the beam size was 1 x 1 micron. The monochromatic beam had a size of ~ 2 (v) x 3 (h) microns. In both cases linear scans perpendicular to the oxidation front were performed. The white beam scans had a step-size of 2.5 microns; monochromatic scans were done with 2 micron step-size. The diffraction experiments were performed in reflective geometry with the MarCCD 2-d detector at 2θ = 90°. The sample was held with the surface in bisecting geometry (i.e. at 45°). Sample to detector distance was determined using a Si-wafer as standard crystal mounted next to the sample [134].

\(^4\) Equilibrate command forces the instrument to ramp the temperature at the fastest rate achievable. No data is recorded during this time.
\(^\text{§}\) X = temperature of interest
3.10. Scanning Electron Microscopic (SEM-EDS) Studies

A Field Emission Hitachi scanning electron microscope (FE-SEM), Hitachi S-4700, with 1.5 nm resolution and operated between 15 to 20 keV was used for these studies. An Oxford INCA Energy 2000 energy dispersive system (EDS) system was used for X-ray microanalyses to characterize the corrosion products. The corrosion morphologies of I-beam or rock bolts, as a result of the incorporation of the above YM ions in the electrolyte and the change in electrode potential, were examined in this SEM in the secondary-electron imaging mode. The concentration of ions at the localized pit was analyzed by EDS. The SEM was normally operated at a voltage of 20keV.

3.10.1. Microstructures of As-received Ni-base Superalloys

Alloy-22, Alloy-263 and Alloy-282 were received from the manufacturer in mill annealed condition. Figures 3.11 and 3.12 show the microstructures for Alloy-22 and Alloy-263 as-received. All alloys were etched electrochemically with varying times with Alloy-282 being the most difficult to etch. The Alloy-282 samples were either over-etched or not etched at all, even after multiple re-polishing, re-etching tries, using recommended technique available from the manufacturer’s website. There is no microstructure available for the alloy at this time. The superalloys are henceforth referred to as Alloy-22, Alloy-263 and Alloy-282 (their compositions are given in Table 3.1 (a)).

Superalloy microstructures are usually typified by an austenitic Face-Centered Cubic (FCC) matrix phase known as gamma ($\gamma$) and a variety of secondary phases. The second phases may or may not be present at room temperatures but the alloys always have a tendency to precipitate all or some of these second phases at different temperatures and/or service conditions. The secondary phases are: carbides of the type MC, M$_2$3C$_6$, M$_6$C and the rare M$_7$C$_3$ which are found in almost all superalloys, and the gamma prime ($\gamma'$) phase which is typical of Ni- and Fe-Ni-base superalloys. The $\gamma'$ phase is a FCC-ordered Ni$_3$(Al,Ti)-type intermetallic compound[135]. The microstructure of superalloys (or for that matter any alloy) is a result of the alloying elements.

As seen in Figure 3.11 for Alloy-22, no grains boundaries are clearly observed and there are no second phases present. Alloy-22 in wrought mill annealed condition is a solution strengthened alloy with single phase austenitic structure[32, 136]. The alloying elements in these superalloys like Cr, Mo, Fe, W differ by about 1-13% in atomic diameter[137]. These additions cause lattice expansion in the base metal and lead to strengthening of the alloy. Addition of these elements also causes lowering of stacking fault energy to make cross-slip more difficult in the austenite and thus strengthen the alloy. The high content of chromium and molybdenum in all three superalloys (Table 3.1(a)) provides strong solid-solution strengthening, as also does the presence of tungsten (3%) in Alloy-22 and aluminum (1.5%) in Alloy-282. Annealing twins are observed in the Alloy-22 microstructure. Observation in SEM did not reveal any precipitates. Alloy-263 did not show any structure under optical microscope observation but when it was evaluated under SEM, Ti-rich precipitates were observed, as seen in Figure 3.12 (b). These are Ni$_3$Ti type $\gamma'$ precipitates.

Figure 3.11. Microstructure of as-received Alloy-22; electrochemical etch; optical microscope (100X).
Ni-base superalloys are categorized as predominantly alumina (Al₂O₃) or predominantly chromia (Cr₂O₃) formers. All three Ni-base alloys used in this study are predominantly chromia formers as seen from their composition. Alloy-22 has no aluminum whereas Alloy-263 has only 0.6% Al. Only Alloy-282 has 1.5% Al. Although thermodynamic calculations [138, 139] have shown that alumina and chromia both are expected to be stable in contact with alloys even with trace amounts of Al or Cr, the formation of continuous oxide layers of oxides on alloys depends on the relative diffusion rates of these elements in the alloys and the oxide[112, 140, 141]. Hindam et al. [112] say that the minimum solute concentration for establishing a continuous oxide film is around 1-8 wt% for Al and 13-25 wt% for Cr in 1 atm. oxygen pressures.

![Figure 3.12. Electrochemically etched microstructure of as-received Alloy-263 - (a) SEM image and (b) Chemical analysis on the precipitate using EDS.](image)

3.10.2. Microstructural Analyses of As-received High-Strength Low-Alloy Steels

High Strength Low Alloy (HSLA) steels (also known as microalloyed steels) are a separate steel category designed to provide better mechanical properties and/or greater resistance to atmospheric corrosion than conventional carbon steels. They are designed to meet specific mechanical properties without putting specifications on their exact chemical composition. Hence they are not considered to be alloy steels in the normal definition of the term. Figure 3.13 shows the microstructure of the as-received AISI 4340 steel. This microstructure shows a combination of ferrite, pearlite and spheroidized cementite. Figures 3.14 and 3.15 show the microstructures of the as-received Swellex Mn-24 and Split set (SS-46) steels, respectively. These steels show the typical ferritic-pearlitic microstructures [49, 142] with aligned grains showing the direction of rolling that the rock bolt tubes must have undergone during manufacture. EDS done on pearlitic grains also showed a very slight increase in carbon content. The microstructure of Mn-24 was fine grained as compared to the SS-46 sample. Precipitate-like growth was observed at the grain boundaries in the SS-46 sample and EDS done on these suggested increased Mn and C contents with Fe at the sites. Possible formation of (Fe,Mn)₃C is suggested since manganese enters readily into solid solution in Fe₃C but manganese carbide is not found in steels [50].

![Figure 3.13. Microstructure of AISI 4340 steel at 300X.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-Lα</td>
<td>28</td>
<td>17</td>
</tr>
<tr>
<td>Ti-Kα</td>
<td>37</td>
<td>46</td>
</tr>
<tr>
<td>Cr-Kα</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Co-Kα</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Ni-Kα</td>
<td>19</td>
<td>20</td>
</tr>
</tbody>
</table>
3.11. Optical Microscopy

Optical metallurgical microscopes, Olympus BH optical with an Olympus DP12 [143] camera and Olympus inverted research metallurgical microscope PMG3 [143] with DP 70 microscope controller, were used to perform qualitative microstructure analysis of all metal samples. Magnifications used for this study range from 50X to 400X.

3.12. X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed at Evans Analytical Group (EAG), San Jose, CA. Table 3.3 shows the parameters of the instrument used for XPS Survey and analyses performed at EAG.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>PHI Quantum 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray source</td>
<td>Monochromated Alkα, 1486.6eV</td>
</tr>
<tr>
<td>Acceptance Angle</td>
<td>±23°</td>
</tr>
<tr>
<td>Take-off angle</td>
<td>45°</td>
</tr>
<tr>
<td>Analysis area</td>
<td>1400μm x 300μm – all except as noted</td>
</tr>
<tr>
<td></td>
<td>200μm – Alloy-22/900°C depth profile and SS46 high resolution analyses</td>
</tr>
<tr>
<td>Charge Correction</td>
<td>C1s 284.8 eV</td>
</tr>
<tr>
<td>Ion Gun Conditions</td>
<td>Ar⁺, 4 keV, 4 x 4 mm raster</td>
</tr>
<tr>
<td>Sputter Rate in SiO₂</td>
<td>~48 Å/min</td>
</tr>
</tbody>
</table>

Depth profiles were obtained at EAG, by alternating an acquisition cycle with a sputter cycle during which material was removed from the sample using a 4 keV Ar⁺ source. In order to eliminate crater wall effects, the data were acquired from a smaller region in the center of the sputter area. In addition, Zalar rotation was used to help minimize sample roughening during the sputtering process. The sputter rate was calibrated using SiO₂.
3.13. Electrochemical Corrosion Tests on Annealing Alloy 22 Weld

3.13.1. 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 3.16. 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 (Figure 3.17). 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 an 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 3.16. The welded specimen showing the weld area after etching.

Figure 3.17. Optical micrographs of the specimen taken from the sample.
3.13.2. Microstructure
The microstructure of as-weld and heat treated specimens are shown in Figure 3.18. 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.

3.13.3. Metallography 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 being viewed under the microscope. Samples were viewed right after the potentiodynamic scan, after a gentle wash with de-ionized water.
PART ONE – NI-BASE SUPERALLOYS – RESULTS AND DISCUSSION

IV. ELECTROCHEMICAL CORROSION ON ALLOY 22

4.1. Overview and Summary of Electrochemical Corrosion Results of Alloy 22

In this study, the electrochemical corrosion behavior of Alloy 22 was investigated in four separate parts: (1) as a function of temperature and concentration under aerated and de-aerated conditions in simulated Yucca Mountain solutions, (2) welded Alloy 22 in 0.1M HCl at 66°C after solution annealing at 1121°C for one hour at three different positions – base metal, metal-weld interface and welded metal, (3) electrochemical corrosion of Alloy 22 in simulated seawater (3.5% NaCl), and (4) the electrochemical corrosion behavior of Alloy 22 immersed in corroded solutions containing various heavy-metal ions. In general, the corrosion rate of Alloy 22 increased as the temperature increased for both aerated and de-aerated conditions in simulated YM solutions. Corrosion rates in aerated electrolyte were less than those of the de-aerated due to the formation of a more protective, passive oxide film. As the electrolyte concentration increased the corrosion rate of Alloy 22 increased more significantly in the de-aerated condition.

For welded Alloy 22, results show that the overall corrosion rate of the welded specimen is higher than that of the base metal in “as-welded” condition. However, the heat-treated condition revealed that the corrosion rate between base and welded specimens were comparable. Corrosion rates of the heat treated specimens (M-2, H-2 and W-2) are below 100μm/yr and are very similar to those for M-1 and H-1 specimens. The corrosion rate of W-1 specimen was higher than 300μm/yr. The attack is more severe for the as-weld condition than for the heat treated condition. The microstructure of the corroded, welded sample showed attacks on the dendritic region for the as-weld and also for the heat treated specimens. However, after solution-annealing these dendrites were not observed, suggesting homogenization of the grains.

In simulated seawater (3.5% NaCl) at 25°C under de-aerated (nitrogenated) conditions, Alloy 22 showed a wide range of passivation, as well as a low corrosion rate of 8.7 microns per year. This corrosion rate was slightly higher than that for Alloy 22 electrochemically tested under potentiodynamic polarization in solutions containing “corrosion products” that could come in contact with the waste containment structure. Of the eight different solutions that were tested, Fe³⁺ solution showed the highest corrosion rate at ~5 μm/yr at 90°C. However, a mixture of all the corrosion products in solution (designated ALL solution) showed a corrosion rate 9 times higher, at ~54 μm/yr at 60°C. XPS depth profile analysis of Alloy 22 in ALL solution at 60°C showed thin layers of Ni-, Cr- and Mo-oxides. XPS analysis of Alloy 22 after cyclic polarization in Fe³⁺ solution at 90°C also showed a multi-oxide layer. However, this layer is relatively thick compared to the Fe³⁺ thickness observed from the ALL sample. This could be due to availability of ions in solution and oxygen from the purging gas. Approximately 340 nm of iron oxide was formed as the top oxide layer. Other oxide layers were produced underneath with thicknesses of 40 nm (Ni) and 60 nm (Cr, Mo), respectively.

4.2. Electrochemical Polarization Studies on Alloy 22 in Simulated Yucca Mountain Solutions

In this study, the corrosion behavior of Alloy 22 was investigated as a function of temperature and concentration in complex multi-ionic electrolytes. Alloy 22 samples were potentiodynamically polarized in 1X, 10X and 100X simulated Yucca Mountain solutions at 25°C, 45°C, 65°C and 90°C under a continuous purging of either nitrogen or oxygen gas. We found that the corrosion rate of Alloy 22 was higher in the de-aerated electrolyte as compared to the aerated electrolyte. The presence of oxygen in the electrolyte during aeration is conducive to formation of passive films that inhibit corrosion process. The temperature dependency of the corrosion rate was affected by aeration and de-aeration of the electrolytes. Results are presented below.

4.2.1. Effect of Temperature on Passivation of Alloy 22 in De-aerated YM water
Potentiodynamic polarization curves for Alloy 22 at different temperatures in 100X simulated YM water are shown in Figure 4.1. The corrosion potential ($E_{corr}$) was approximately -700mV±50mV for all temperatures. At 25°C, the observed $E_{corr}$ is approximately -750mV, and increases as the temperature increases. The highest observed $E_{corr}$ is -687mV at 90°C.
Corrosion rates in de-aerated conditions using 100X electrolyte concentration are shown in Table 4.1. At lower temperatures (25°C to 45°C), the corrosion rate increased more than 1.5 times, whereas at higher temperatures, the rate increased by a slightly lower amount (1.19 times), from 65°C to 90°C. The different rates of increase in the corrosion rate at different temperature ranges are associated with the different types of protective oxide films formed on the surface. Yilmaz et al. [63] observed similar corrosion behavior on medium carbon steel (MCS) using the same electrolyte, but these rates were higher than Alloy 22. Figure 4.2 shows an Arrhenius relationship between the corrosion rate and absolute temperature.

Samples after the potentiodynamic tests were characterized by an optical microscope at different temperatures. It was found that there was no salt deposit on the metal surface at 25°C, as shown in Figure 4.3 (a) (left), whereas the surface topography was quite different on the 90°C sample with abundant dispersion of salt layers of varying thickness on the surface (Figure 4.3 (b), right). This behavior was also observed by Yilmaz et al. [63] for medium carbon steel rock bolts. To understand the nature of interaction of this particular electrolyte with the materials surface, Deodeshmukh et al. [59] performed X-ray photoelectron spectroscopy (XPS) on carbon steel and found a protective film of FeCO₃ and iron-oxide/hydroxide.
At higher temperatures, > 65°C, there was preferential etching of the sample surface, revealing the microstructure as shown in Figure 4.4 (c), after the potentiodynamic test. The micrograph in Figure 4.4 (a) shows the surface as-prepared, before conducting the experiment; the middle optical micrograph (Figure 4.4 (b)) shows the condition after the test, and finally the microstructure after removing the surface salt layer (Figure 4.4 (c)). All the Alloy 22 samples examined above 65°C after the potentiodynamic tests showed similar characteristics. It should be noted that similar potentiodynamic tests performed below 65°C did not reveal the microstructure of the alloy.

4.2.2. Effect of Salt Concentration on Passivation of Alloy 22 in De-aerated YM water

Three different concentrations (1X, 10X and 100X) of electrolytes were used to evaluate the effect of concentration on corrosion rate. A room temperature potentiodynamic scan for the Alloy 22 under different electrolyte concentrations are presented in Figure 4.5. The corrosion potentials for these three different concentrations are very close to each other as shown in Figure 4.5. The corrosion potential increases slightly as the concentration increases from 1X to 100X. The cathodic portions of the potentiodynamic scans were linear for all concentrations but overlapping. The linearity of the cathodic curve represents that there is no change in the reaction rate or in other words there is no limiting current for the cathodic reactions. The anodic portions of the potentiodynamic scan are significantly different for all concentrations of electrolyte. It is interesting to note that there was no secondary passive region observed for 1X and 10X concentrations due to lower levels of ions. The calculated corrosion rate was lowest in 1X water and highest in 100X water which is plotted as a function of concentration in Figure 4.6. From this plot, it can be observed that the corrosion rate increased as a function of concentration significantly as the concentration is increased from 1X to 100X in the de-aerated electrolyte. The highest corrosion rate of 168μm/yr is observed at 90°C in 100X water. Pulvirenti et al. [144] found a corrosion rate of 106μm/year in J13 (1000X) electrolyte at pH=1, using the weight-loss method.
4.2.3. Effect of Temperature on Passivation of Alloy 22 in Aerated YM water

Potentiodynamic polarization tests on Alloy 22 in 100X electrolyte (at different temperatures in aerated atmosphere) showed a distinct passive region in the anodic portion of the potentiodynamic plot; these are similar to those observed in de-aerated waters. In addition, it can be noted that the passivation corrosion current density increases from 25°C to 90°C (Figure 4.7). As far as the short-term corrosion potential is concerned, it can be noted that it is lower at 90°C than at 25°C, which again suggests higher corrosion rate at 90°C; this behavior is common in steels as reported by Yilmaz et al. [63]. The observed short-term corrosion potential for Alloy 22 was -285mV at 25°C and -429mV at 90°C. The secondary passive region which was observed using the de-aerated electrolyte was also observed with the aerated electrolyte and occurs at around +600mV (Figure 4.7). Also, the secondary passive region is not very prominent at higher temperature (65°C and 90°C), noting that peak potential lowers slightly from +594 mV to +574 mV when the temperature increased from 25°C to 45°C. The passive current also increased as the temperature of the electrolyte increased.
The corrosion rates obtained using 100X electrolyte (aerated conditions) at different temperatures (Figure 4.6) show an increase in corrosion rate with temperature. The corrosion rate was 9.66 μm/ year at 25°C and it increased to 62.57 μm/ year at 90°C. Also note that the corrosion rates are lower in aerated conditions than in de-aerated condition which is unusual as compared to common steels that have been extensively studied by other researchers using the same electrolyte [10, 63]. The corrosion rate in aerated condition was lesser at all temperatures compared to de-aerated conditions. A plausible explanation for the lower corrosion rate in aerated conditions might be due to the presence of a more protective form Cr₂O₃ film on the surface that inhibits the overall corrosion process. The Arrhenius relationship is shown in Figure 4.2. It is apparent that the activation energy in aerated conditions is higher than in de-aerated conditions. Optical micrographs were taken after the potentiodynamic scans at all temperatures that show there was no significant attack at lower temperatures. Figure 4.8 shows a micrograph taken after the potentiodynamic scan at 90°C which show some attack (transpassively formed pits as well as grain boundary etching) on the surface of the sample, due to the high potentials applied during the scan.
4.2.4. Effect of Concentration on Passivation of Alloy 22 in Aerated YM water

The potentiodynamic scans for the Alloy 22 show a similar behavior to that of de-aerated condition with some variations (Figure 4.9). The effect of concentration of the electrolyte is pronounced in the aerated electrolyte as compared to the de-aerated one with respect to the short-term corrosion potential. The $E_{corr}$ decreased as the concentration of the electrolyte increased which is opposite in case of de-aerated conditions. The highest $E_{corr}$ of +75.8mV is observed in 1X water whereas for 10X it was -180mV and for 100X it was -285mV. The anodic portion of the curve was quite similar in nature as in the de-aerated conditions. It is interesting to note that there was no secondary passive region observed in case of 1X and 10X electrolyte; as observed in the de-aerated electrolyte. However, using 100X electrolyte the secondary passive region is observed at approximately the same potential (~600mV) for both aerated and de-aerated conditions. From Figure 4.9 it can be seen that the current density shifts as a function of concentration suggesting propensity for higher corrosion rates. These corrosion rates as a function of concentration are graphically shown in Figure 4.6 (the x-axis is logarithmic). The observed short-term corrosion rate was 1.54μm/year in 1X water, 5.69μm/year in 10X water and 9.66μm/year in 100X water.

![Figure 4.9. Potentiodynamic Scan showing the effect of concentration of the Electrolyte in aerated conditions at 25°C.](image)

4.2.5. Effect of Aeration and Deaeration

Two potentiodynamic scans, one in aerated and the other in de-aerated conditions are presented in Figure 4.10 in 100X water at 65°C. Figure 4.10 shows that the short-term corrosion potential is higher in aerated condition than in de-aerated condition. From the same figure we see that the corrosion current is higher in case of de-aerated condition, which implies a higher corrosion rate. The passive current density is higher in aerated condition than de-aerated conditions. In case of de-aerated conditions we observed a pronounced secondary passivation peak whereas for aerated condition there was hardly any peak. The corrosion current for de-aerated condition is higher than the aerated conditions which attributed to the higher corrosion rate in de-aerated conditions. In the same plot we have presented the optical micrograph for this sample. The optical micrograph was taken after the potentiodynamic scans. The micrograph for the aerated conditions shows no visible corrosion but in the de-aerated micrograph there was etching of the microstructure.
4.2.6. Characterization of Passive Films at Different Potentials Using the Potentiostatic Method

A room temperature potentiodynamic test was first performed on Alloy 22 (Figure 4.11) to set the potentials at -200, +400, +600, and +800 mV of interest. Then maintaining the same potential we observed the change in current density as a function of time. In general, the current density decreased as the time increased. The potentials were chosen from different passive and secondary passive regions of the potentiodynamic scan in de-aerated condition (Figure 4.11). The corresponding potentiostatic tests were also conducted in de-aerated condition. A plot of current as a function of time for potentiostatic tests is shown in Figure 4.12, the reduction in current indicates that there is formation of an oxide film on the specimen that inhibits the flow of current. At -200 mV and +400 mV potential, the current drops rapidly due to the formation of an impervious oxide film and hence the slope of current versus time is higher. It should be noted that the secondary passive region at +600 mV and +800 mV show that current does not decrease substantially after about an hour, whereas in the passive region (-200 mV and +400 mV) there is continued decrease in the current density as a function of time.

The samples from the potentiostatic tests were characterized for changes in chemistry of the film and microstructure. The SEM micrographs and EDS analyses taken after constant potential of -200 mV and +400 mV charged samples indicate no surface deposit. At these potentials the composition of the Alloy 22 matrix along with the oxygen peak indicate formation of a thin layer of passive film. However, SEM and EDS results from samples subject to higher potentials (+600 mV and +800 mV) clearly show a surface salt layer containing Si, Mg, Ca species along with increased oxygen content providing evidence for the secondary passive phenomena and a forced dissolution of the alloy for the high applied potentials (formation of hydroxides of Si, Mg, Ca). We propose to conduct more work to characterize this film formed under both aerated and de-aerated condition by using X-ray Photoelectron Spectroscopy (XPS). Szmodis et al. [145] also observed an abrupt change in current density, but they observed two of these events; one of the events (~300 mV) was suggested to be due to the formation of a passive oxide layer and the other (~800 mV) due to the formation of porous oxide layer (using SCW-Table 1 waters at pH=8). It should be noted that in our study the event of currently density change occurred at +600 mV which appears to be analogous to the one at ~+800mV[146]. Even though they reported the 800mV peak is due to the formation of Mo, Cr, Ni oxide layer, yet we observed additional Mg, Si and Ca along with the Ni and Cr in our study.
4.2.7. Comparison of Corrosion Rates of Alloy 22 under Different Environments

There are many reports on corrosion rates of Alloy 22 using different electrolytes, low and high pH’s, temperatures ranging from 25°C to 160°C, using different methodologies (for example using immersion testing or potentiodynamic testing). However the results have not been compiled in a single document. We compare CR’s of Alloy 22 obtained in this study with others from the literature (Figure 4.13). Gray et al. [146] reported CR’s in the range of 2200 and 3400 μm/yr at pH of ~1 at ~90°C. Day et al. [147] reported a wide range of CR’s between 50 and 3000 μm/yr between 30 to 90°C in 0.1M oxalic acid; these are shown in Figure 4.13 (top). Rebak et al. [148] performed immersion tests on Alloy 22 for 4 days with 50% H₂SO₄ and found the CR to be ~550μm/yr at ~85°C, and the CR’s increased to ~1600 μm/yr at 110°C. It is interesting to note that Day et al. [147] showed a increase of
rate from to ~200 to ~3200 μm/yr by increasing the temperature from 60° to 85°C; thus there is temperature dependence regardless of the electrolyte. Rebak et al. [148] found a steep increase in CR’s using immersion tests which are somewhat similar to those obtained by Day et al. [147] used polarization methods.

In this study, although under less aggressive environments (Table 3.2 – 100X YM electrolyte), the short-term CR’s varied from 74 to 163 μm/yr under de-aerated condition, and 10 to 64 μm/yr in aerated condition, between 25°C to 90°C. This increased CR in de-aerated is possibly due to because an oxide film does not form readily as the oxygen in the electrolyte is depleted during constant bubbling of nitrogen. The corrosion rate data reported in the current study are for short-term exposures and may not represent the values of corrosion rates for long time exposure [149]. Examining the combined corrosion rate plot (Figure 4.13) it can be seen that CR’s obtained in this study (shown in Figure 15 in the middle) that include the work of Rebak et al. [158, 159]. They used different electrolytes and different test methods and environment in their studies. In Table 2 we have shown some of the similar electrolytes other researchers [144, 150, 155, 158, 160] used in their studies. The reported corrosion rate is much lower comparing to the data obtained in this study using 100X YM water. We suggest this may be due to the fact that there is more chlorine present and lack of nitrates (Table 3.2) in our electrolyte, as compared to others, but the main factor could be the effect of time. Whenever a chromium rich passive film forms in the environment, the corrosion rate decreases as the time increases.

Evans et al. [154] showed using CaCl₂ electrolyte and polarization method the short-term CR’s ranged from 3 to 10 μm/yr. between 40°C and 100°C; they showed that addition of Ca(NO₃)₂ further reduced the CR to below 3 μm/yr; these rates are much lower than what we observed in this study using the electrolyte in Table 4.2. Brown et al. [151] performed experiments on ozone and aeration at room temperature and observed very low CR’s (below 8μm/yr-see Figure 4.13-bottom). Pulvirenti et al. [144] used very aggressive solutions and showed CR’s ranging from 10 to 115 μm/yr at 160°C, pH 1 (Figure 4.13), however it is difficult to compare these are high temperature and low pH results. F. Hua et al. [155] studied the corrosion behavior of Alloy 22 in Nuclear Waste Repository environment and reported the range of corrosion rate from 0.07μm/yr to 0.30μm/yr in a temperature range of 60°C to 90°C using immersion tests and weight-loss determinations after several weeks exposure. In general it is difficult to compare the corrosion rates from different sources at each temperature since there are too many other influencing factors changed at once, including time of immersion, electrolyte composition and solution pH.
Figure 4.13. Summary of Corrosion Rate of Alloy 22 under different environment and conditions; top (CR’s from 50 to 3650 μm/yr), middle (10 to 200 μm/yr), bottom (0 to 10 μm/yr).

4.3. Electrochemical Polarization Studies on Welded Alloy 22 in Simulated Yucca Mountain Solutions

In this study, the corrosion behavior of welded Alloy 22 was undertaken to understand the electrochemical and metallurgical behavior of welded structures. Three different specimens were made from a welded Alloy 22 plate with large welded surface – weld interface, half weld and base metal away from the weld and heat affected zone (HAZ). Corrosion studies were carried out in more aggressive electrolyte (0.1M HCl at 66°C) after solution annealing at 1121°C for 1 hr. The results are presented below.
4.3.1. Effect of Polarization on Corrosion Rate of Welded Alloy 22

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 4.14. 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 large passive region. However, the passive current density changes and highest passive current density was observed for W-1 specimen, suggesting a higher corrosion rate. The corrosion rate data are plotted in Figure 4.15. 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 ~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 [161, 162], due to the segregation of Mo and W in the interdendritic regions of the weld. Summers et al. [163] 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. [164] reported that the corrosion rate of weld samples was 30% higher than the base metal samples, in both boiling acidic ferric sulfate and hydrochloric solutions. Optical micrographs taken after the potentiodynamic scans for these specimens are shown in Figure 4.16. All the specimens were observed under the microscope before and after the potentiodynamic scans. For specimens H-1 and W-1 [Figure 4.16(b) and 4.16(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 4.16(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 [165].

Figure 4.14. Potentiodynamic Scans of as-weld specimens (M-1, H-1 and W-1) in 0.1M HCl at 66°C
Figure 4.15. 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.

Figure 4.16. 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).
4.3.2. Effect of Immersion Time on Corrosion Rate of Welded Alloy 22
A long term experiment was performed to observe the corrosion of these specimens. These tests involved the following steps: a) immersing the specimens in de-aerated 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 three 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 are shown in Figure 4.17(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 doesn’t change significantly after the first experiment. In Figure 4.17(b), the potentiodynamic scans after continued immersion for four hours are shown. These show a similar trend as the previous experiments (after 1 hr immersion). Similar experiments were performed on specimens H-1 and W-1, and are shown in Figures 4.18 and 4.19, 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.

Figure 4.17. (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 4.18. (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.

Corrosion rates calculated using the polarization resistance method are presented in Figure 4.20. 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 4.19. (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 4.20. 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.
4.3.3. Effect of Polarization on Corrosion Rate of Heat Treated Alloy 22

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 4.21. 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 were 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 [29, 166-169]. This change in microstructure also changes the corrosion behavior of these specimens after aging at different times and temperatures.

The corrosion rates for the previously mentioned specimens were calculated by using polarization resistance method and plotted in Figure 4.15. 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 annealed 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[165]. 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 [164].

Micrographs taken after the potentiodynamic scans showed no significant differences microstructurally for both H-2 and W-2 specimen which are shown in Figure 4.22.

Figure 4.21. Potentiodynamic Scans of Heat Treated Specimens (M-2, H-2 and W-2) in 0.1M HCl at 66°C.

Figure 4.22. Optical micrographs taken after the potentiodynamic scans for heat treated specimens (a) H-2 (left) and (b) W-2 (right).
4.3.4 Effect of Polarization on Immersion Time of Heat Treated Alloy 22

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 4.23 to 4.25. 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 4.26. It can be observed that the corrosion rates of these specimens were comparable, regardless of the locations of the specimens. The solution annealing 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 4.23. (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 Base Metal (M-2) Heat Treated.
Figure 4.24. (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-2) Heat Treated
Figure 4.25. (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-2) Heat Treated
4.4. Electrochemical Polarization Studies on Alloy 22 from Engineering Structures due to “Corrosion Products”

In this section, results are presented for uniform corrosion rates determined at two high temperatures (60°C and 90°C) for Alloy 22 in different corrosion products under aerated (air) conditions. Polarization resistance experiments at both temperatures were run after 24 hours of corrosion potential measurements. In all experiments, the corrosion potential reached equilibrium after 19 hours. XPS depth profile results for Alloy 22 in ALL solution (all corrosion products) at 60°C and XPS results for Alloy 22 in Fe³⁺ solution at 90°C are presented below. Additionally, results for Alloy 22 in simulated seawater (3.5% NaCl) are presented as well.

4.4.1. Effects of Individual Ions on Alloy 22

Corrosion rates at 60°C in base solution (HCl + NaCl) and all solutions with ions (corrosion products) are given in Table 4.1. Corrosion rates are plotted in Figure 4.27. Amongst all the solutions, the one with mixture of all ions (ALL solution) showed the highest corrosion rate of 54.3 microns. Addition of chromium ions showed the lowest corrosion rate of 0.167 microns per year. Solutions with Ni²⁺, Fe³⁺, WO₄²⁻ showed relatively higher corrosion rate than base solution.

Table 4.1. Corrosion rates of Alloy 22 in aerated (air) corrosion products at 60°C

<table>
<thead>
<tr>
<th>Ions</th>
<th>Corrosion Rate (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>54.3</td>
</tr>
<tr>
<td>WO₄²⁻</td>
<td>2.85</td>
</tr>
<tr>
<td>MoO₄²⁻</td>
<td>0.354</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.316</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.274</td>
</tr>
<tr>
<td>HCl + NaCl</td>
<td>0.227</td>
</tr>
<tr>
<td>Ti⁴⁺</td>
<td>0.209</td>
</tr>
<tr>
<td>CrO₄²⁻</td>
<td>0.167</td>
</tr>
</tbody>
</table>
Corrosion rates at 90°C are given in Table 4.2 and plotted in Figure 4.28. At 90°C, solution with Fe$^{3+}$ ions showed the highest corrosion rate of around 5 microns per year. MoO$_4^{2-}$, Ti$^{4+}$, Ni$^{2+}$ and CrO$_4^{2-}$ showed the lowest corrosion rates than in base solution. At both temperatures, WO$_4^{2-}$ showed higher corrosion rate than in base solution. Corrosion products like Ti$^{4+}$ ions from drip shield and other ions such as Ni$^{2+}$ and CrO$_4^{2-}$ are not detrimental to the Alloy 22. However, ions like Fe$^{3+}$ from steel set or rock bolts act as oxidizers and increases corrosion rate.

Table 4.2. Corrosion rates of Alloy 22 in aerated (air) corrosion products at 90°C.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Corrosion Rate (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>5.01</td>
</tr>
<tr>
<td><em>All</em></td>
<td>3.3</td>
</tr>
<tr>
<td>WO$_4^{2-}$</td>
<td>1.85</td>
</tr>
<tr>
<td>HCl + NaCl</td>
<td>0.977</td>
</tr>
<tr>
<td>MoO$_4^{2-}$</td>
<td>0.813</td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>0.673</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.435</td>
</tr>
<tr>
<td>CrO$_4^{2-}$</td>
<td>0.371</td>
</tr>
</tbody>
</table>
4.4.2. Surface Characterization of Alloy 22 in ALL solution

During potentiodynamic polarization test in ALL solution at higher potentials there was a passivation observed for a wide range of potentials. After the test, the sample surface is characterized by XPS depth profile. XPS depth profile showed a combination of three oxide layers on the top of the surface. Ni oxide layer up to around 10nm and then chromium oxide up to 5nm and molybdenum of around 5nm thickness. This type of combination of oxide layers was observed in NaCl solutions by Lorang[170] and also by Szmodis [171] in simulated water solutions. Depth profile and oxide layers are shown in Figures 4.29 and 4.30 respectively. Binding energy of Mo and Cr oxides are shown in Figure 4.31.
Figure 4.29. XPS depth profile plot of Alloy 22 sample surface after the potentiodynamic experiment in ALL solution at 60°C under aerated conditions.

Figure 4.30. Oxide layers formed on the surface of Alloy 22 (ALL).
4.4.3. Surface Characterization of Alloy 22 in Fe$^{3+}$ Solution

Since FeCl$_3$ is a good pitting corrosive agent, to see the pitting potential and repassivation potential, a cyclic polarization experiment was done at 90°C under aerated Fe$^{3+}$ solution. Cyclic polarization experiment is shown in Figure 4.32. In this solution, the pitting potential is just below repassivation potential. After the cyclic polarization scan, XPS depth profile is done on the surface of the sample. This is shown in Figure 4.33. Figure 4.34 shows a diagram of the different oxide layers, as well as their thicknesses, on the surface of Alloy 22. Unlike in ALL sample, the oxide layers in this sample are thick. Also, similar to ALL samples, multiple layers of oxides are formed on the surface. Due to presence of iron in the solution, a thick layer of 340nm iron oxide is formed as the top layer, and then a 40nm layer of Ni oxide, and 60nm of Chromium and Molybdenum oxide layers were formed underneath Ni oxide layer respectively. Binding energies of O, Fe, Cr, Ni and Mo are shown in Figure 4.35. After the experiment, a thick layer of iron oxide is also observed on the surface of the sample. A thick iron oxide may be formed due to presence of abundant amount of iron in solution and oxygen from purged air.

Figure 4.32. Cyclic potentiodynamic plot of Alloy 22 in Fe$^{3+}$ corrosion product solution at 90°C under aerated (air) conditions.
Figure 4.33. XPS depth profile plot of Alloy 22 sample surface after the cyclic potentiodynamic polarization experiment in Fe³⁺ solution at 90°C under aerated conditions.

Figure 4.34. Oxide layers formed on the surface of Alloy 22 (Fe³⁺).
4.5. Electrochemical Polarization Studies on Alloy 22 in Simulated Seawater (3.5% NaCl)

The corrosion rate of Alloy 22 in 3.5% NaCl at 25°C under de-aerated (nitrogenated) conditions was determined to be 8.7 μm/yr using potentiodynamic polarization methods. Please refer to Chapter 8, section 4, of this report for a more thorough explanation.
V. DRY AND DELIQUESCENT SALT CORROSION OF ALLOY 22 AND OTHER HIGH-Cr ALLOYS

In this section, results from the dry salt and deliquescent salt tests on Alloy 22, 304L SS, 316L SS and Inconel 825 are presented. As explained in the experimental section, these samples were exposed to dry and deliquescent salts to see the effect of salts on corrosion of structural materials in the dry out period (200°C).

5.1. Effect of Dry Salts on the Corrosion of Alloy 22, Inconel 825 and 304L/316L Stainless Steels

Results show that these alloys were not affected by dry salts, due to the formation of an outer chromium oxide (Cr$_2$O$_3$) layer present. Therefore, there is no effect of chlorides [172] on these alloys. Hence, under dry salt conditions at 200°C, the outer waste package container (Alloy 22) has no corrosion due to dry salts (chlorides, and nitrates). Similarly, for Inconel 825 and 304L/316L stainless steels, no dry salt corrosion was observed.

5.2. Effect of Deliquescent Salts on the Corrosion of Alloy 22, Inconel 825 and 304L/316L Stainless Steels

Results show that there is no corrosion for these alloys, even after a coupon of Mn-24 was placed on top of the salt-covered specimen. Alloy 22 was unaffected and is shown in Figure 5.1, with and without salt on its surface. From the Figure 5.1 (b), it can be observed that Alloy 22 was not affected by deliquescent salt. Figure 5.2 shows a SEM micrograph of the surface of Alloy 22 after removal of the salt. From the figure it can be observed that even in micro level there is no damage on the surface of Alloy 22. Hence, Alloy 22 waste container is immune to both dry salt and deliquescent salt test[172] with and without weights on the salt.

![Figure 5.1. Alloy 22 sample after deliquescent salt experiment: (a) before salt removal, (b) after salt removal.](image)

![Figure 5.2. SEM micrograph of Alloy 22 after the deliquescent salt test](image)
VI. OXIDATION KINETICS AND CHARACTERIZATION OF ALLOYS 22, 263 AND 282


Studies on Ni-based superalloys (Alloy-22, Alloy-263 and Alloy-282) were performed at 600°C, 700°C, 800°C, 900°C, 980°C and 1100°C for 48 hour exposure periods under pure oxygen atmosphere using isothermal continuous measurement thermogravimetry. To accelerate the dry oxidation process, we used high temperatures in this study. Alloy-22 was selected for study based on its potential use in the Yucca Mountain Nuclear Waste Repository. The two others superalloys, namely Alloy-263 and Alloy-282, were selected for comparison purposes with Alloy-22. Since the repository storage temperature is not expected to exceed 160-180°C [173] and the temperature of the storage components is expected to be in the range of 240-250°C [174], the calculated oxidation kinetics parameters are extrapolated to lower temperatures. These lower temperature parameters provide an estimate on the type of conditions to be expected, assuming that the same oxidation rate laws are followed even at low temperatures.

The Ni-base superalloys showed two distinct regimes, namely the initial transient period of extremely fast kinetics and the parabolic oxidation regime. Parabolic rate constant values determined for all the three superalloys increased from ~10^{-13} to 10^{-9} by increasing temperatures from 700 to 1100°C. Activation energies calculated for alloys from kinetic data were found to increase in the order: 232 kJ/mol for Alloy-282, 263 kJ/mol for Alloy-22 and 289 kJ/mol for Alloy-263. The slope of the curves on a plot of $k_p$ as a function of (1/T) shows Alloy-282 to have better oxidation resistance up to 980°C and thereafter the rate constants are similar for all three alloys. However, when activation energies over the whole temperature range are calculated, Alloy-263 shows the best average oxidation resistance. This is due to high amounts of Cr, Co and Ti in the alloy matrix. Cobalt and titanium are known to improve the oxidation resistance marginally and titanium is known to promote the formation of Cr$_2$O$_3$. This is suggested to be the reason for the highest oxidation resistance of Alloy-263 amongst the three superalloys.

6.2. Oxidation Kinetics of Alloys 22, 282 and 283

Oxidation tests were performed according to the test procedures outlined in Section 3.7.3 under 1 atm. of UHP oxygen atmosphere. Isothermal holding time was 48 hours at 1100, 980, 900, 800, 700 and 600°C. All the Ni-based superalloys used in this study followed a parabolic rate law after prolonged time of oxidation under 1 atm. of pure oxygen atmospheres. An initial period of faster (transient) kinetics was seen in all the alloys which extended not more than 25 to 35 minutes during the initial heating to the desired temperature of interest. Similar oxidation kinetics analyses on simpler alloy systems have shown the transient period to range from anywhere between one to five hours [175-177]. Figures 6.1, 6.2 and 6.3 show data for weight gain per unit surface area ($y = \Delta m/A$) for the superalloys at different isothermal hold temperatures. Although data were collected every 30-60 seconds, the figures show data at ~2 hours for clarity.

In general Alloy-22 showed a trend of increasing weight gains with increasing temperatures as seen in Figure 6.1. The isotherm at 600°C shows discontinuities in the mass changes at 21 and 24 hours. The first is an abrupt increase in weight and the latter is a sharp decrease. Such discontinuities in data have also been reported by Caplan et al. [178], Murris et al. [179] and assessed by Kofstad [77]. Murris et al. [179] explain these discontinuities by suggesting that the unrelieved growth stresses formed in oxides cause them to crack and spall. The oxides are unable to deform plastically and the exposed cracks in them react rapidly with the available oxygen reflecting a weight gain. The sharp decrease in weight at about 24 hours is attributed to a spalled oxide. After this sharp decrease the weight gain continues again, up to termination of the experiment. This seems to be the only plausible explanation since vaporization of any oxides is not expected at this temperature. Oxide volatilization increases exponentially with temperature and becomes pronounced at higher temperatures. The vaporization of Cr$_2$O$_3$ as CrO$_3$ is shown to be important during high temperature oxidation of chromium of chromia-forming alloys [77, 180-188]. Kofstad [77] mentions that as a rule of thumb, oxidative evaporation of CrO$_3$ becomes important only above 1000°C at 1 atmosphere oxygen. The discontinuities in the 600°C curve lead to a sequence of stages, each following parabolic kinetics [179]. But due to the difficulty of correlating the stage-wise parabolic rate constants to calculations of activation energies, this data set has not been used in any such calculations.
Figure 6.1. Weight gain per unit surface area as a function of time for Alloy-22.

Figure 6.2. Weight gain per unit surface area as a function of time for Alloy-263.
Figure 6.3. Weight gain per unit surface area versus time plot for Alloy-282.

Figure 6.4. Parabolic regime and rate constant for Alloy-22 at 980°C.
Oxidation kinetics of Alloy-22 at the rest of the temperatures follows a parabolic rate law with increasing kinetics with temperature. Oxidation kinetics at 900 and 1100°C show extremely increased values indicating that Alloy-22 had started to lose its protective behavior. In general, there is a rapid increase in kinetics during the initial period (25-30 min.) at all temperatures followed by the parabolic oxidation regime. The initial period of fast kinetics is associated with transient oxidation. As the temperature of the alloy(s) increases from room temperature, all the alloying elements in an alloy start to oxidize, forming an initial layer of complex oxides [77, 78, 187]. Linear least squares regression to the $y$ versus root $t$ data, to the function of type:

$$\left( \frac{\Delta m}{A} \right)^2 = k_p t \quad (6.1)$$

gives values for the parabolic rate constants for Alloy-22. $\Delta m$ is the oxidation weight gain, $A$ the surface area of the test specimens, $k_p$ is the parabolic rate constant and $t$ is the oxidation time. It has been shown by Pieraggi et al. [189] that a plot of kinetics data as $\Delta m$ versus $t^{1/2}$ is inherently superior to $\Delta m^2$ versus $t$ plot for accurate determination of steady state parabolic rate constant”. Figure 6.4 shows the parabolic regime and parabolic rate constant at 970°C for Alloy-22. The parabolic rate constant at 700°C was found to be $6.85 \times 10^{-13} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$, for 800°C it was $2.72 \times 10^{-12} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$, for 900°C it was $1.30 \times 10^{-11} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$, for 980°C it was $5.83 \times 10^{-10} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ and for 1100°C it was found to be $7.13 \times 10^{-9} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ as also tabulated in Table 6.1. The parabolic regime for 700°C starts at about 76 minutes, for 800°C starts at ~78 minutes, for 900°C at ~84 minutes and for 1100°C at ~100 minutes. The activation energy for the parabolic regime of Alloy-22 is found to be 263 kJ/mol.

As seen in Figure 6.2 for Alloy-263, oxidation kinetics follow increasing weight gains with increasing temperature except for the data at 600°C. Higher than expected weight gains are observed for 980°C, so that the curve falls above the 700°C. Either the sample forms a thick transient oxide right at the beginning giving it the above normal weight gains, or the other possibility which cannot be ruled out is that the differences reflected are a result of handling of the specimens at different temperatures, instrumental foibles, etc., even after all the care that was taken to maintain the same conditions of all the samples throughout measurements. As seen from the composition of Alloy-263 in Table 3.1(a), the alloy has the highest content of Chromium, Cobalt and Titanium with substantial amounts of Molybdenum. Transient oxidation causing the simultaneous oxidation of all the alloying elements is observed during the initial stages of oxidation in all alloys, as mentioned before. Another possibility is that these discrepancies in data are a result of reversal phenomenon where lower weight gains are recorded at higher temperatures or vice versa, although no corresponding results are reported for superalloys in open literature. Reversal phenomenon has been observed and recorded for steels and other Fe-base superalloys [119, 190-194]. The curve for 600°C again shows a discontinuity at about 21 hours. The issues of abrupt changes in weight (as observed for Alloy-22 and Alloy-263 in Fig. 6.1 and 6.2 respectively) for 600°C could also be probably due to momentary instrumental instability. A sudden increase observed is attributed to the formation of cracks, exposure of underlying fresh surface(s) to oxygen and a fast oxidation at these spots. Again, because of the difficulty of accommodating multiple parabolic constants for activation energy calculations, the data for 600°C has not been analyzed. As also seen in Figure 5.4, weight gains for 900°C are lower than those for 980°C only for the first 7.5 hours after which the rates increase and are higher than expected. Very fast oxidation kinetics are observed for temperatures of 980°C and 1100°C. The parabolic rate constants for the temperatures were found to increase with increasing temperatures with a value of $1.7 \times 10^{-13} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ at 700°C, $2.35 \times 10^{-11} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ at 800°C, $1.06 \times 10^{-10} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ at 900°C, $7.68 \times 10^{-10} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ at 980°C, and $7.97 \times 10^{-9} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ at 1100°C. The parabolic regime for 700°C starts at ~1.3 hours, for 800°C at ~6.3 hours, for 900°C at ~1.4 hours, for 980°C also at ~1.4 hours and for 1100°C at ~1.7 hours. The activation energy for the parabolic regime of Alloy-263 is calculated to be 289 kJ/mol. This activation energy is found to be the highest amongst the three alloys in this study. Maslenkov [195] et al. have shown that increasing the Co content of Ni-20Cr alloys from 0 to 40% increases their oxidation resistance. Co tends to stabilize the formation of Cr$_2$O$_3$ and thicker oxides are formed rendering better oxidation resistance. Alloy-263 has the highest Co content as mentioned before and the better oxidation resistance is in part attributed to this along with the presence of other alloying elements.

Figure 6.3 shows the mass gain per unit area as a function of time for Alloy-282 at different temperatures. Higher weight gains with increasing temperatures are observed for this alloy except for the 600°C. Isotherm at 873.15 K shows a series of discontinuities, at 4.4 hours, at 13.5 hours, at 22 hours, and at 25.5 hours suggesting continuous formation of cracks and healing oxides. After the initial transient period oxidation kinetics follows a parabolic law for all temperatures (except 600°C). Oxidation kinetics for 1100°C shows a very high weight gain as compared to the other temperatures. It also looks like the parabolic region is almost on the verge of breakaway oxidation as the
The slope of the weight gain per unit surface area against time starts to change towards the very end of the experiment. The alloy oxidized at 1100°C developed a very thick double layered oxide layer and hence the high weight gain. The alloy shows an increasing trend in the parabolic rate constants with increasing temperatures with a value of 2.54 \times 10^{-12} \text{ kg}^{2} \cdot \text{m}^{-4} \cdot \text{s}^{-1} at 700°C, 1.37 \times 10^{-11} \text{ kg}^{2} \cdot \text{m}^{-4} \cdot \text{s}^{-1} at 800°C, 1.86 \times 10^{-10} \text{ kg}^{2} \cdot \text{m}^{-4} \cdot \text{s}^{-1} at 900°C, 8.28 \times 10^{-10} \text{ kg}^{2} \cdot \text{m}^{-4} \cdot \text{s}^{-1} at 980°C, and 9.94 \times 10^{-9} \text{ kg}^{2} \cdot \text{m}^{-4} \cdot \text{s}^{-1} at 1100°C. The parabolic regime for 700°C starts at \sim 30 \text{ minutes}, for 800°C at \sim 3.32 \text{ hours}, for 900°C at \sim 0.6 \text{ hours}, for 980°C also at \sim 38 \text{ minutes} and for 1100°C at \sim 40 \text{ minutes}. The activation energy for the parabolic regime of Alloy-282 is found to be 232 \text{ kJ/mol}.

The \( k_p \) value for Alloy-263 is the lowest at 700°C and thereafter increases to the highest value at 800°C and 900°C as seen in Table 6.1. All the \( k_p \) values are similar at 980°C and 1100°C. At 700°C, Alloy-282 exhibits the best oxidation resistance, the slope of the curves in the Figure 6.5 suggesting a better overall oxidation resistance of Alloy-282 up to 980°C. Above 980°C, all three alloys seem to have similar oxidation resistance. As the activation energies are calculated over the whole temperature range of interest, the values reflect a combined oxidation resistance and in this respect the values of Alloy-282 fall below those of the other two alloys. Literature reported values of activation energies of superalloys tend to vary by two to three orders of magnitude, depending on the conditions of experiment. The parabolic rate constant values for all superalloys in this study vary by three to four orders of magnitude, depending on the conditions of experiment. Over the whole temperature range used in this study, based on the activation energies, Alloy-263 performs the best with the highest activation energy. Figure 6.5 shows the plots of parabolic rate constants as a function of \( 1/T \), used to calculate activation energies. The fit of linear regression for all the curves was found to lie between 0.92 and 0.98.

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Rate constant ( (k_p) ) (kg(^2)\cdot m(^{-4})\cdot s(^{-1}))</th>
<th>Activation energy (kJ/mol)</th>
</tr>
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<td>( 6.85 \times 10^{-13} )</td>
<td>263.01</td>
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<td></td>
<td>800</td>
<td>( 2.72 \times 10^{-12} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>( 1.30 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>( 5.83 \times 10^{-10} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>( 7.13 \times 10^{-9} )</td>
<td></td>
</tr>
<tr>
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<td>( 1.7 \times 10^{-11} )</td>
<td>288.65</td>
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<td>( 2.54 \times 10^{-12} )</td>
<td>231.93</td>
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<td>800</td>
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<td>1100</td>
<td>( 9.94 \times 10^{-9} )</td>
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6.3. Characterization of Alloys 22, 263 & 282 by XRD, Optical Microscopy, SEM and EDS

Glancing angle x-ray diffractometry was performed on Alloy-22 oxidized in pure oxygen at 1 atm. for 48 hours at 700°C. The pattern is shown in Figure 6.6; showing only the alloying elements in the base alloy. Since the samples sizes are so small, it was very difficult to get any good data from XRD and so further characterization has not been done.

The microstructure of Alloy-22 oxidized for 48 hours at 600°C showed no obvious continuous oxide layer, although protrusions of oxide spots were observed at some places, as seen in Figure 6.7. Grain boundaries do not indicate any oxidation or formation of precipitates. This result is also validated by Badwe [196] and Gorhe [173] who found no significant attack on the grain boundaries of their alloy C-22 samples aged at 610°C for 1 hour in air. Their microstructures also show the presence of annealing twins without any apparent formation of precipitates along them. However, Gorhe [136, 173] has shown in his modified electrochemical reactivation tests study that Cr depletion occurs during the initial stages of thermal aging for the Ni-Cr-Mo alloy. They attribute this depletion to formation of: (i) formation of Cr-rich carbides, (ii) formation of Cr-rich ordered phase of type Ni$_2$Cr [197], and/or (iii) formation of a Cr-rich μ-phase of the type (Ni, Fe, Co)$_3$(Cr, Mo, W)$_2$ [198] precipitates. Precipitation of carbides in this low carbon Ni-Cr-Mo alloy is possible since the kinetics of carbide precipitation were observed to be faster than μ phase precipitation[198]. Pan et al. [199] observed extensive carbide precipitation for Alloy-825 with three times more carbon content than Alloy-22 at similar temperatures. Both M$_6$C and μ phase showed almost similar chemistry [137, 198, 200].
Figure 6.6. X-ray diffraction data on Alloy-22 sample as received and oxidized at 700°C for 48 hours. Note that the Bragg peaks of the oxidized Alloy-22 are sharper than those observed for the as-received alloy suggesting some annealing of the specimen.

Figure 6.7. Optical image of Alloy-22 oxidized in 1 atm. oxygen at 600°C for 48 h. No visible oxide layer is observed, although annealing twins are seen in some grains.
At 700°C, there is a thickening of grain boundaries (grain boundary envelopes) but no precipitation is observed (Figure 6.8). A thin oxide layer of approximate thickness 0.7 μm also starts to form on the alloy, as seen in the figure. The oxide layers observed on Alloy-22 at all the temperatures irrespective of their thickness were found to have no void formations at the metal-oxide interface. At 800°C, there is a definite formation of grain boundary precipitates as seen in Figure 6.9 (a). EDS line scans along the grain boundary precipitates revealed the presence of higher concentrations of molybdenum and lower concentrations of Cr and Ni, as shown in Figure 6.9 (b). Badwe [196] has found similar results for his alloy C-22 samples aged at 800°C for 100 hours both by EDS and by SKPFM. Gorhe [136, 201] also found presence of a Mo-depleted region surrounding precipitates by using electrochemical potentiodynamic reactivation (EPR) tests and TEM. Our studies indicate that oxidation at 900°C increases the number of precipitates within the grains as well as thickening of grain boundary precipitates as shown in Figure 6.10. Mori [177] has shown that these precipitates are Mo-W mixed carbides of the type (Mo,W)6C. Figure 6.11 is representative of the morphology of the oxide scales formed on Alloy-22. The figure shows the scale after oxidation for 48 hours at 980°C along with the EDS results showing formation of Cr2O3 scale. Unfortunately the sample oxidized at 1100°C, was lost during sample polishing and no characterization data could be obtained for it. Mori [177] has mentioned that the amount of precipitated grain boundary carbides decreases on increasing the temperatures from 1000°C to 1100°C. Although there is an expected tendency for the precipitates to dissolve near the alloy surface, Mori found no diffusion layer either by optical microscopy or by EDS. They did find an internal oxidation layer of thickness about 20μm for Alloy-22 at 1100°C. In the case of other Ni-base alloys studied by them they found external scales formed to the order of 10 to 18 μm at 1100°C and internal oxidation zones of the order of 20μm for all three alloys.
Figure 6.10. Precipitate formation initiates within the grains at 900°C on Alloy-22.

Figure 6.11. Morphology of oxide formed on Alloy-22 at 980°C after 48 hours with EDS result showing the presence of Cr$_2$O$_3$. 
As shown in section 6.2, Alloy-263 has the highest activation energy and hence the best oxidation resistance amongst the three Ni-base superalloys in this study. At 600°C, no attack on the alloy was observed under optical microscope; no visible grain boundaries even after electrochemical etching for prolonged times, as shown in Figure 6.12 (a). The test specimen looked tarnished after oxidation at 600°C for 48 hours and a thin non-continuous oxide layer was resolved in SEM, but no grains. Figure 6.12 (b) shows the EDS for Alloy-263 at 600°C. The results show the formation of chromium oxide as well as an increase in titanium at the oxide. The image looked like amorphous globs of particles accumulated on the surface. The major precipitates at temperatures below 900°C are known to be gamma-prime and eta (Ni3Ti), with the eta phase starting to precipitate at the expense of the gamma-prime phase after prolonged annealing[202]. Figure 6.13 shows the oxide morphology of the oxide scale formed on the alloy at 700°C. Spot EDS done on the scale shows the presence of chromia with increased amounts of Ti and Co. Line scans done on the thin oxide layer formed on Alloy-263 at 700°C also confirmed the presence of Cr2O3 with amounts of increased Ti in the scale, Co was not observed.

Figure 6.14 (a) shows the optical micrograph of Alloy-263 showing the presence of a continuous oxide layer of about 10 micron thickness at 800°C. At this temperature, Alloy-263 showed definite signs of oxide spallation as seen in Figure 6.14(b). A magnified view of the oxide morphology is shown in Figure 6.14 (c), showing faceted crystals of mixed oxide: Cr2O3 + TiO2 + NiO as seen from the quantitative EDS spot analyses. Hance [111] showed the development of a thin layer of TiO2 over the chromia layer formed on IN 738 oxidized isothermally at 900°C. He performed oxidation tests in dry as well as wet atmospheres and found the presence of TiO2 films in both cases. Presence of this film is supposed to form a physical barrier between the chromia scale and the reactive gases, thus avoiding the loss of the protective layer by the formation of vapor species, which he observed to be more aggressive in air/H2O mixtures as compared to dry oxygen environment.

A relatively thick oxide layer is formed on Alloy-263 at 900°C. Uniform grains of size 100-150 µm are observed in an optical micrograph, as shown in Figure 6.15 (a). Pore formation and internal oxidation are also seen along with the external oxide formation (Figure 6.15 (b)). SEM image shows the pore formation leading to oxide scale separation from the base alloy at some regions with the presence of a definite Cr-depletion internal oxidation zone with large grains. This was confirmed by means of SEM-EDS line scans on the cross-section. Figures 6.15 (c) and (d) show the details. Increased Ti (fuchsia) amounts are seen in the oxide whereas the depleted zone is rich in Cobalt (green) and Molybdenum (yellow). The thickness of the depleted zone was found to be about 12.3 to 13 µm and the oxide thickness varied between 2.83 to 4.46 µm over the sample.

Layered scale structure is observed in the case of Alloy-263 oxidized for 48 hours in 980°C. Large depleted zone with a thick oxide layer is observed in optical microscope seen in Figure 6.16 (a). SEM evaluation shows the external layer to have a layered structure. EDS analysis shows the layer to consist predominantly of Cr2O3 with a spike in Ni pointing to NiO (at 1.2 µ on EDS graph) in the middle layer and the lowermost layer of TiO2 with adjoining depletion zone (which looks like a depression on the micrograph) with enrichment of Co and Ni, as shown in Figure 6.16 (b). As the temperature of isothermal holding increases, the thickness of the oxide layer is seen to increase whereas that of the depletion zone is reduced. Increasing diffusion rates of alloying elements with temperatures helps to heal the depletion zone faster. At this temperature of 980°C, the oxide thickness averaged 11.4 ± 1.2 µm and the depletion zone averaged 7.22 ± 0.8 µm.

Oxidized samples at 1100°C showed a thick oxide layer of thickness between 14.2 to 20.9 µm whereas the depleted zone had a thickness of about 13.2 ± 1.1 µm. EDS spot analyses on the oxide layer and adjoining flaky protrusions showed the presence of TiO2 islands near the mixed transient oxide layer of TiO2, CoO, NiO with adjoining chromia oxide and pockets of NiO at the chromia-oxygen interface. Details are shown in Figure 6.17. Such oxide protrusions have also been found by Orosz [203] on their CMSX-4 alloy specimen after thermal cycling.
Figure 6.12. (a) No visible attack is observed on Alloy-263 at 600°C; (b) SEM image shows the formation of a discontinuous oxide layer, EDS shows presence of TiO₂ and Cr₂O₃.

Figure 6.13. Oxide morphology and EDS for alloy Alloy-263 oxidized at 700°C for 48 hours: (a) oxide scale shows sharp faceted petal-like structure; (b) EDS scan confirms the presence of Cr₂O₃ with increased Co and Ti.
Figure 6.14. (a) Presence of oxide layer on Alloy-263 at 800°C in optical microscope; (b) oxide morphology showing spalled oxide; (c) faceted structure of the oxide.
Figure 6.15. (a) Optical micrograph of Alloy-263 at 900°C showing GB attack; (b) External oxide formation with internal oxidation and pore formation; (c) depleted zone; (d) EDS on depleted zone showing the presence of TiO$_2$. 
Figure 6.16. (a) SEM micrograph and EDS (in color) at the oxide layer showing the presence of TiO$_2$ beneath the Cr$_2$O$_3$ layer and enrichment of Co and Ni in the adjoining area. (b) Depletion zone in Alloy-263 at 980°C.
Alloy-282 is a wrought gamma-prime strengthened alloy developed for high temperature applications. This alloy has the highest Al content amongst the three alloys in this study. The effects of Cr, Si, and Al in an alloy are synergistic [204, 205]. These elements act as oxygen getters in the order of their increasing oxygen affinity. When one component in the alloy is depleted, the second acts to reduce the oxygen diffusivity through the oxide. Kaufman [206] summarized the effect of different alloying elements on Ni-15% Cr alloys. He suggested that aluminum increases the corrosion resistance greatly, cobalt and titanium increase it just slightly, and tungsten decreases it whereas tantalum has no effect on the resistance. On the other hand Bergman et al. [207] have found clashing results. They report that aluminum additions are detrimental in simple alloys but beneficial in complex alloys, cobalt increases the resistance and tungsten has no effect until 1038°C. Molybdenum additions become detrimental at higher temperatures and rare earth elements like yttrium and rhenium are supposed to have no effect. Thus it can be safely said that the overall composition of the alloy and the complementary action of all the alloying elements together determines the final oxidation behavior of an alloy or superalloy.

An optical micrograph of a sample oxidized at 700°C is shown in Figure 6.18. The sample had to be over etched before any features came into view. But as seen in the figure, a lot of annealing twins are observed. An extremely thin oxide layer was observed in the cross-sectional examination and there were precipitates seen forming along the twins. Annealing twins have lower energy as compared to the grain boundaries and so the precipitates start nucleating at these sites first. The black spots seen in the figure could be just etching pits or etched spots where the dislocations meet the surface of the sample. Figure 6.19 shows the optical micrograph of the alloy oxidized at 800°C. A definite layer of alloy depletion is observed along with a thick external oxide and an internal oxidation zone. Similarly, the optical micrograph of oxidized sample at 900°C shows a large depleted zone with extensive internal oxidation (Figure 6.20). The oxide looks warped and broken at places. There could even be a double oxide layer. Unfortunately this oxidized sample was lost during repolishing and so EDS analyses could not be performed. Based on available literature [111, 176] and the XPS surface scans done on the sample (see section 6.4 below), it looks like there is an outer layer of TiO$_2$ and an inner layer of chromia. The internal oxidation could be alumina formation. Giggins [176] has shown the presence of an alumina subscale in a Ni-20Cr-2Al alloy oxidized in oxygen for 21 hours at 1100°C. Figure 6.21 and 6.22 show the optical micrographs of oxidized samples at 980 and 1100°C respectively. At higher temperatures, the depth of internal oxidation is larger as also is the thickness of the middle oxidation layer. The thickness of the depletion layer was smaller at higher temperature due to healing of the depletion layer. Both the scales look adherent and no separations from the base alloy are observed.

In all of these studied Ni-base superalloys, which are predominantly chromia formers, it can be easily seen from the EDS spot spectrum scans that the Cr content at the alloy-scale interface is about or above 9 wt% which is necessary to maintain a predominantly Cr$_2$O$_3$ formation rather than formation of a spinel and/or NiO [204]. This would mean...
that the bulk alloy would need to have higher Cr concentrations so that depletion of Cr near the alloy-scale interface does not hinder chromia formation. Croll [208] has shown the presence of 9.6 weight percent interfacial Cr in a Ni-20Cr alloy and Wood et al. [209] have shown the concentration to be 9.4 weight percent Cr content in a Ni-15.9 weight percent alloy. Wallwork [204] summarizes that a chromium concentration of more than 20 atomic percent in the bulk alloy is necessary for formation of chromia scales so that a continuous supply of Cr is maintained by the required Cr content of 10 atomic percent at the alloy-scale interface.

Figure 6.18. Presence of annealing twins is clearly observed for Alloy-282 oxidized at 700°C in pure oxygen atmosphere for 48 hours.

Figure 6.19. Depletion zone observed in Alloy-282 at 800°C with internal oxidation and thin external oxide layer.
Figure 6.20. Extensive internal oxidation and a large depletion zone are observed in Alloy-282 at 900°C. External oxide layer looks warped and broken in places.

Figure 6.21. Oxide layer on Alloy-282 at 980°C. There is a decrease in the thickness of the depletion zone and increase in internal oxidation zone as temperature increases.
Figure 6.22. Increase in the internal oxidation zone as well as external oxide thickness is observed at 1100°C for Alloy-282. The external oxide layer looks double layered. The internal oxidation could be Al₂O₃ as literature references point, but because of the loss of sample in polishing, this cannot be confirmed for a fact. Alloy-282 has Al content of 1.5 wt %.

6.4. Characterization of Alloys 22, 262 & 283 by X-ray Photoelectron Spectroscopy

XPS surface survey and depth profile analyses were done on some of the superalloy samples, namely: Alloy-22 oxidized at 800°C for 48 hours, Alloy-22 oxidized at 900°C and Alloy-282 oxidized at 900°C also. The purpose of this study was to determine the surface composition and chemistry of the samples. Depth profile analyses characterized the oxide layer(s) present. Figure 6.23 shows the surface scan data for Alloy-22 oxidized at 800°C. It shows presence of strong peak signals for Ni and O and weak signals of Cr. Figure 6.24 shows the surface scans for Alloy-22 oxidized at 900°C showing strong Cr and O signals but weak Ni signals. Peaks for Mo, W, Na were also detected on both the samples. The presence of Na is attributed to skin oils due to poor handling of the specimens during some stage of analyses. Figure 6.25 shows the binding energies of the elements surveyed on the Alloy-22 samples. The sample showed significantly high levels of molybdenum, the binding energy shifted to somewhat lower levels, but not too low to be consistent with literature values for MoO₂. Based on this it seems like the sample formed some intermediate oxide phase between MoO₃ and MoO₂. Figure 6.26 shows surface scan for Alloy-282 oxidized at 900°C. Peaks indicate the presence of a chromium oxide on the sample. Figure 6.27 shows a comparison between the binding energies of Alloy-22/800°C and Alloy-282/900°C samples. As seen in the figure, Cr chemistries appeared similar between both samples. The peak centroid of 576.2 eV is indicative of the formation of Cr₂O₃. The difference in Ni chemistry between the two samples is shown in Figure 6.28. The figure indicates presence of NiO (and/or NiOOH) and Ni(OH)₂ on Alloy-22/800°C whereas, that of only Ni(OH)₂ on Alloy-282/900°C. The formation of hydroxides is highly unlikely unless there was deterioration of the NiO oxide due to absorption of atmospheric moisture. For our purposes, since the binding energies of the two Ni-oxides are similar we will consider the results to point to formation of NiO. The presence of Ti as TiO₂ was detected only on Alloy-282 which confirms with the chemistry of the base alloy and also is consistent with the results in section 6.3 where a thin layer of TiO₂ was proposed to form (Figure 6.20).

Depth profile analyses were performed on an Alloy-22/900°C sample. The thickness of the formed oxide proved to be too thick for sputtering down to the base metal for visually striking changes in the concentrations of the alloying elements. Figure 6.29 (a) and (b) show the as-received depth profile analyses as a plot of concentration versus depth of the elements. Up to the depth of sputtered oxide, Ni, Cr and O were simultaneously detected. At ~ 6700 Å Mo was detected with increasing concentration through to the end of the profile. W was detected at a depth of ~8800 Å.
Figure 6.30 gives the binding energies of oxides formed on the surface of Alloy-22/900°C as a function of increasing sputter depth.

Based on the above surface scans and depth profile analyses and in conjuncture with the optical microscopy and SEM-EDS results, a mechanism of oxide formation is put forth for the superalloys in this study. A schematic representation of the same is given in Figure 6.31 (a)-(c).

Figure 6.23. Surface scan of Alloy-22 oxidized at 800°C showing strong peak signals for Ni and O and weak signals of Cr.
Figure 6.24. XPS surface scan for Alloy-22 at 900°C showing strong Cr and O signals but weak Ni signals.
Figure 6.25. Binding energies of alloying elements found on Alloy-22.
Figure 6.26. XPS surface scan on Alloy-282 oxidized at 900°C indicating presence of a chromium oxide on the sample with some TiO₂.
Figure 6.27. Comparison between Alloy-282/900°C (red) and Alloy-22/800°C (blue) (normalized intensities).
Figure 6.28. Ni2p overlay: Alloy-282/900°C (red) and Alloy-22/800°C (blue) (normalized intensities) showing different Ni chemistries in the samples. Presence of NiO (and/or NiOOH) and Ni(OH)₂ are seen on Alloy-22/800°C whereas, that of only Ni(OH)₂ is seen on Alloy-282/900°C.
Figure 6.29 (a) and (b). Depth profile analyses for Alloy-22/900°C. The oxide was too thick for the XPS sputter depth profile to show variation in the concentrations. Up to the depth sputtered, presence of Ni, O and Cr were simultaneously detected. Even though XPS did give the expected changes in concentration of elements, SEM, EDS supporting results help in proposing a mechanism for oxidation.
Figure 6.30. Binding energies for O, Cr, Ni, Mo, W and C on Alloy-22/900°C sample.
Figure 6.31 (a)-(c). Proposed oxidation mechanism for Ni-base superalloys Alloy-22, Alloy-263 and Alloy-282, respectively, at elevated temperatures.
PART TWO – HIGH-STRENGTH LOW-ALLOY (HSLA) STEELS – RESULTS AND DISCUSSION

VII. ELECTROCHEMICAL CORROSION RESULTS ON FRICTION-TYPE ROCK BOLTS

7.1. Summary of Electrochemical Corrosion Results of Friction-Type & Split-Set Rock Bolts

In this study, the corrosion behavior of friction-type and split-set rock bolts were investigated as a function of temperature and concentration in simulated Yucca Mountain solutions. In deaerated electrolyte, the corrosion rate ranges from 34 to 211 μm/yr between 25° to 75°C encompassing all concentrations (1X, 10X and 100X). In aerated electrolyte, the rate ranges from 150 to 1600 μm/yr for 1X & 10X concentrations. For 100X concentration, the corrosion rate increased from ~210 to 2400 μm/yr between 25°C to 65°C, but decreased to 750 μm/yr from 65°C to 75°C. In addition, corrosion rates at 60°C and 90°C in 1X YM solution under aerated (compressed air) conditions were found to be 80.3 and 142 μm/yr, respectively.

7.2. Introduction

Rock bolts made of different steels are used in mines, road tunnels, nuclear repositories, anchor support of large electrical towers and others applications. In the past, criterion for selection of rock bolts was mainly based on empirical design and by comparing the strength 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 25°C to 90°C. In the future there may be temperature increases to 200°C 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 the mining industry, as well as underground nuclear repositories, the steels investigated in this study have broader applications than the rock bolts themselves. 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 7.1, 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 kinds of rock bolts that have been used for underground support materials. In the late 1970’s, Friction Rock Stabilizers (FRS) were introduced and have been widely used in mines and other underground support systems. Since then this type of bolt 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.

Figure 7.1. Underground support system for the proposed US nuclear repository [2]
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. 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 [56] 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 [57]. 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. [52] 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. [51] 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 1144) has been studied by Yilmaz et al. under simulated YM water [6, 48, 63]. 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 [211].

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 7.1.

<table>
<thead>
<tr>
<th>Type</th>
<th>SS33</th>
<th>SS39</th>
<th>SS46</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Diameter, in (mm)</td>
<td>1.30 (33)</td>
<td>1.54 (39)</td>
<td>1.81 (46)</td>
</tr>
<tr>
<td>Length, ft (mm)</td>
<td>8 (2438)</td>
<td>10 (3048)</td>
<td>12 (3658)</td>
</tr>
<tr>
<td>Load Capacity, tons (kN)</td>
<td>10 (88.96)</td>
<td>10 (88.96)</td>
<td>15 (133.45)</td>
</tr>
</tbody>
</table>

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.

7.3. Electrochemical Polarization Studies on Friction-Type Rock Bolts in Simulated YM Solutions

7.3.1. Effect of Temperature on Passivation of Friction-Type Rock Bolts in Deaerated YM water
Potentiodynamic polarization tests were carried out on A607 steel at different temperatures for three different concentrations of waters (1X, 10X and 100X). Figure 7.2 shows the potentiodynamic scan of A607 steel in 1X concentration of water at different temperatures. Since the corrosion potential (E_cor) at all temperatures is similar, only two temperatures are shown to maintain clarity. From this figure, it’s clear that the corrosion current density increases as the temperature increases, suggesting a higher corrosion rate at 90°C. Also, the corrosion potential is lower at 90°C than at 25°C, suggesting a more active material at 90°C. This kind of behavior is common for steel and is reported by Yilmaz et al.[63]. Figure 7.2 shows the same kind of behavior for 10X and 100X water concentration. For 1X solution, the corrosion potential range is from -0.74V to -0.76V, -0.725V to -0.742V for 10X
and -0.705V to -0.709V for 100X at all temperatures. It is 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, the protective passive film starts to break down and the breakdown potential is higher at higher temperatures. 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 for 10X and 100X waters due to a higher number of Cl ions present in the electrolyte.

Table 7.2 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 7.3. 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.[63]. When the temperature was raised above 65°C, the rate of increase in the corrosion rate 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 O₂ 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 [63] in 1X YM water for medium carbon steel rock bolts which is 160 μm/year at 85°C. Jolly et al.[51] determined the corrosion rate of slotted & tapered steel tube rock bolts (EX-TEN-H60 and KAI-WELL-55) in different deaerated mine waters at 17°C to be 10 to 48 μm/year for all mine waters. In another study, Tilmann et al.[52] reported the corrosion rate to be around 40 to 71 μm/year in 4 different lead and iron mines.

### Table 7.2. Corrosion Rates of ASTM A607 Steel in Deaerated Conditions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Environment</th>
<th>Concentration (X)</th>
<th>R_p (ohm·cm²)</th>
<th>I_corr (μA/cm²)</th>
<th>Corrosion Rate (μm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>N₂</td>
<td>1</td>
<td>8927</td>
<td>2.92 x 10⁻⁶</td>
<td>34</td>
</tr>
<tr>
<td>45</td>
<td>N₂</td>
<td>1</td>
<td>4626</td>
<td>5.63 x 10⁻⁶</td>
<td>57</td>
</tr>
<tr>
<td>65</td>
<td>N₂</td>
<td>1</td>
<td>3263</td>
<td>7.98 x 10⁻⁶</td>
<td>93</td>
</tr>
<tr>
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<td>N₂</td>
<td>1</td>
<td>2932</td>
<td>8.89 x 10⁻⁶</td>
<td>103</td>
</tr>
<tr>
<td>25</td>
<td>N₂</td>
<td>10</td>
<td>5312</td>
<td>4.90 x 10⁻⁶</td>
<td>57</td>
</tr>
<tr>
<td>45</td>
<td>N₂</td>
<td>10</td>
<td>2350</td>
<td>1.11 x 10⁻⁵</td>
<td>129</td>
</tr>
<tr>
<td>65</td>
<td>N₂</td>
<td>10</td>
<td>1587</td>
<td>1.64 x 10⁻⁵</td>
<td>191</td>
</tr>
<tr>
<td>90</td>
<td>N₂</td>
<td>10</td>
<td>1413</td>
<td>1.84 x 10⁻⁵</td>
<td>214</td>
</tr>
<tr>
<td>25</td>
<td>N₂</td>
<td>100</td>
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<td>8.04 x 10⁻⁵</td>
<td>93</td>
</tr>
<tr>
<td>45</td>
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<td>1780</td>
<td>1.46 x 10⁻⁵</td>
<td>170</td>
</tr>
<tr>
<td>65</td>
<td>N₂</td>
<td>100</td>
<td>1607</td>
<td>1.62 x 10⁻⁵</td>
<td>188</td>
</tr>
<tr>
<td>90</td>
<td>N₂</td>
<td>100</td>
<td>1437</td>
<td>1.81 x 10⁻⁵</td>
<td>211</td>
</tr>
</tbody>
</table>

The corrosion rate of any material depend on time and on the environment, so the results reported in this study are different than the others [51, 52]. 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. An optical micrograph presented in Figure 7.4 shows 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. [59] 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 reploting the corrosion rate data as a function of temperature and shown in Figure 7.5. The calculated activation energies were 10.77 kJ/mol for 1X, 18.29 kJ/mol for 10X and 15.46 kJ/mol for 100X solution.
Figure 7.2. Potentiodynamic polarization curves for A607 steel in deaerated water at different temperatures: (top) 1X, (middle) 10X, and (bottom) 100X, concentration of electrolyte.
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 7.6 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.
7.3.2. Effect of Concentration on Passivation of Friction-Type Rock Bolts in Deaerated YM water

Potentiodynamic scans for A607 rock bolts in different concentrations of electrolyte are presented in Figure 7.7 (a) and 7.7 (b). Figure 7.7 (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. At higher temperatures, this behavior was also observed, and is shown in Figure 7.7 (b). The cathodic portion of the potentiodynamic scan overlapped in case of 10X and 100X water and the $E_{corr}$ was close to each other. This suggests an insignificant increase in corrosion rate for both 25°C and 90°C between 10X and 100X. The calculated corrosion rates are shown in Table 7.3. 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.

7.3.3. Effect of Temperature on Passivation of Friction-Type Rock Bolts in Aerated YM 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 Figure 7.8 (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 Figure 7.8 (a-c). The cathodic portion of the potentiodynamic scan shows linear behavior for all concentrations at all temperatures.
Figure 7.7. Potentiodynamic Polarization curves of A607 steel in different concentrations of deaerated water (a) 25°C – left and (b) 90°C – right.

Figure 7.8. Potentiodynamic Polarization curve for A607 steel at different temperatures under aerated (oxygenated) conditions: (top) 1X, (middle) 10X and (bottom) 100X concentration.
Corrosion rates of A607 steel at different temperatures and concentrations are shown in Table 7.3. A corresponding plot of corrosion rate as a function of temperature for different concentrations is shown in Figure 7.9. 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 7.10. 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 higher 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 corrosion rates increase to a maximum value at intermediate temperatures for carbon steel [211, 212]. Similar kinds of behavior was observed by Yilmaz et al. [63] and Arjunan et al. [10] 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.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Environment</th>
<th>Concentration (X)</th>
<th>$R_p$ (ohm·cm²)</th>
<th>$I_{corr}$ (μA/cm²)</th>
<th>Corrosion Rate (μm/yr)</th>
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</table>

Figure 7.9. Corrosion rate of A607 steel as a function of temperature under aerated (oxygenated) conditions in different concentration of electrolyte.
7.3.4. Effect of Concentration on Passivation of Friction-Type Rock Bolts in Aerated YM Water

Potentiodynamic scans for A607 steel rock bolts in different concentrations of YM water are presented in Figure 7.11 (a) and (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, the corrosion potential was -360 mV in 1X water, -423 mV in 10X water and -493 mV in 100X water. The same trend was also observed at 90°C. 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 7.12. 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.

![Figure 7.10. Optical micrograph taken after the Potentiodynamic tests in 100X YM water at different temperatures: (a) top left, 25°C; (b) top right, 45°C; (c) bottom left, 65°C; (d) bottom right, 90°C.](image)

![Figure 7.11. Potentiodynamic polarization curve of A607 steel in different electrolyte concentration under aerated (oxygenated) conditions: (a) top left, 25°C and (b) bottom left, 90°C](image)
7.3.5. Effect of Environmental Conditions on Friction-Type Rock Bolts

The corrosion behavior was evaluated in aerated and deaerated conditions for the three different concentrations of water. Figure 7.7 (a) shows the potentiodynamic scans for three different concentrations in the deaerated condition. Figure 7.8 shows the potentiodynamic scan for three different concentrations in an aerated (oxygenated) environment. According to Figure 7.8, as the concentration increases, the corrosion potential, \( E_{\text{corr}} \), decreases. At room temperature, in 1X water, \( E_{\text{corr}} \) was measured as \(-0.35\)V and in 100X water as \(-0.48\)V. The calculated corrosion rate was also higher in 100X compared to 1X water, which is shown in Table 7.4. Overall, the corrosion rate is higher in the aerated condition than in deaerated condition. Under an oxygenated environment, in 1X water, the corrosion rate was \(158\)\(\mu\)m/year. This increased to \(197\)\(\mu\)m/year in 10X water and to \(211\)\(\mu\)m/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 \(\text{Ca}^{2+}, \text{Mg}^{2+}\) and \(\text{CO}_3^{2-}\), there is a possibility of forming thin \(\text{CaCO}_3\) 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. [63].

Table 7.4. Comparison of Corrosion Rates of ASTM A607 Steel

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Environment</th>
<th>Concentration (X)</th>
<th>( R_p ) (ohm·cm²)</th>
<th>( I_{\text{corr}} ) (µA/cm²)</th>
<th>Corrosion Rate (µm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>( \text{N}_2 )</td>
<td>1</td>
<td>8927</td>
<td>( 2.92 \times 10^{-6} )</td>
<td>34</td>
</tr>
<tr>
<td>25</td>
<td>( \text{N}_2 )</td>
<td>10</td>
<td>5312</td>
<td>( 4.90 \times 10^{-6} )</td>
<td>57</td>
</tr>
<tr>
<td>25</td>
<td>( \text{N}_2 )</td>
<td>100</td>
<td>3210</td>
<td>( 8.04 \times 10^{-6} )</td>
<td>93</td>
</tr>
<tr>
<td>25</td>
<td>( \text{O}_2 )</td>
<td>1</td>
<td>13095</td>
<td>( 1.99 \times 10^{-6} )</td>
<td>158</td>
</tr>
<tr>
<td>25</td>
<td>( \text{O}_2 )</td>
<td>10</td>
<td>1537</td>
<td>( 1.69 \times 10^{-5} )</td>
<td>197</td>
</tr>
<tr>
<td>25</td>
<td>( \text{O}_2 )</td>
<td>100</td>
<td>1436</td>
<td>( 1.81 \times 10^{-5} )</td>
<td>211</td>
</tr>
</tbody>
</table>

Two potentiodynamic scans, one aerated and other deaerated, are presented in Figure 7.13, 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 \( E_{\text{corr}} \). Observations showed that a passive layer began to form at around \(-0.62\)V, and that there was no increase in current density up to \(-0.55\)V, where the passive film began to break down. 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 7.13. Two potentiodynamic scans, under aerated and deaerated conditions in 100X YM water at 65°C along with micrographs taken after the experiment.

7.4. Corrosion Behavior of A607 Steel under Deaerated Conditions using the 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. Also, the pit starts 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. It was suggested that by using this method the pitting potential ($E_{pit}$), as well as critical potentials for stable and unstable pits, could be measured [212]. The current transients of A607 steel under different applied potentials are shown in Figure 7.14. 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, which shows the passive layer formation at this potential. Optical micrographs, which were taken after the potentiostatic scans, are shown in Figure 7.15 (a-d). At -700mV, the micrograph didn’t show any pitting. Pitting started to initiate at -600mV, which is shown in Figure 7.15 (b). Alonso-Falleiros et. al. [213] studied the potentiodynamic and potentiostatic tests for measuring the pitting potential of duplex stainless steels. They 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. Cheng and Liu [214] studied the metastable pitting of carbon steel by potentiostatic measurement at different applied potential. They concluded that the current fluctuation of the potentiostatic measurements is due to the formation of metastable pits.
Figure 7.14. Current transient of A607 steel at different applied potential in 1X electrolyte at room temperature.

Figure 7.15. 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 – (a) top left, -700mV; (b) top right, -600mV; (c) bottom left, -400mV; (c) bottom right, -200mV.

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 7.16. 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 7.16. Current transients in A607 steel taken at –600 mV as a function of temperature in 1X YM water.

7.5. **Effect of Individual Salts on the Corrosion Rate of Friction-Type Rock Bolts**

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 7.17, 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 (CaSO₄ and MgSO₄) are shown in Figure 7.18.

Figure 7.17. Potentiodynamic polarization curves for A607 steel in MgCl₂ and CaCl₂ obtained at room temperature.

Figure 7.18. Potentiodynamic polarization curves for A607 steel in MgSO₄ and CaSO₄ obtained at room temperature.
The corrosion potential is a little higher for the calcium sulfate, which suggest a similar trend, as in chloride salts. Figure 7.19 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 7.20. Another study was carried out on similar ions of different salts, which is shown in Figure 7.21. 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 7.22. The lowest corrosion rate was observed for sodium silicate and the highest corrosion rate was observed for sodium bicarbonate.
It is very difficult to understand the mechanism of corrosion in a multi-ionic environment, so a systematic study was performed to understand the effect of individual salts on the corrosion of A607 steel under deaerated conditions at room temperature. The highest corrosion rate was observed for NaHCO₃ (350 μm/yr) and KHCO₃ (150 μm/yr) salts, and lowest for NaSiO₃ (4 μm/yr). The HCO₃⁻ salts generally yield a lower corrosion rate because of formation of a thin protective layer on the steel sample. J. A. Alhajji et al. [215] worked on the effect of the bicarbonate ion concentration on uniform and localized corrosion of copper. In their study, they found that adding bicarbonate increases the corrosion resistance by forming a protective layer. In our study, we found that A607 steel shows some passivity in all bicarbonate salts. J. Dong et al. [216] observed the corrosion behavior of carbon steel in bicarbonate solutions. They concluded that the corrosion process accelerated at a higher concentration of bicarbonate, by dissolving the outer protective layer, whereas at lower concentration it inhibited this process. In our electrolyte, there are abundant bicarbonate ions (20,000ppm). Therefore, the observed corrosion rate is high for A607. The observed corrosion rate in chloride and sulfate salts varied from 25 to 55μm/year. It is well established that the corrosion rate in chloride and sulfate ions increases the corrosion rate for carbon steel. The observed corrosion rate in sodium silicate (4μm/year) was lowest among all the salts. The formation of protective silicate layers was observed as early as 1920 by Speller, suggesting natural silica precipitates onto pipe surfaces and promotes the formation of corrosion.
inhibiting films. Texter [217] reported that a "self-healing" protective film formed in hot water systems upon additions of soluble sodium silicates. In 1945, Stericker [218] suggested the utilization of sodium silicates as a corrosion inhibitor. There are two different opinions about the mechanism of sodium silicate as a corrosion inhibitor. One opinion is that sodium silicate inhibits corrosion by raising the pH of the water. However, others believe that silicates form a protective layer against corrosion. Wehle [219] showed that a dose of 7 ppm SiO₂ reduced the corrosion rate of galvanized steel significantly more than a NaOH treatment at the same pH. Duffek and McKinney [220] compared the effects of silicate treatment with NaOH treatment adjusted to the same pH. In our current study, we observed a wide passive region, which suggests a passive layer is formed. As a result, the observed corrosion rate was lower.

VIII. ELECTROCHEMICAL CORROSION RESULTS OF SWELLEX ROCK BOLTS

8.1. Summary of Electrochemical Corrosion of Swellex Rock Bolts

In this study, the electrochemical corrosion behavior of Swellex rock bolts was investigated in six different parts. The first part deals with the corrosion behavior of Double-Folded Water-Expanded (DFWE) Swellex Mn-24 Rock Bolts in YM solutions as a function of temperature, concentration, percentage of cold work and effects of different anions on both the anodic behavior and corrosion resistance, under aerated and deaerated conditions. The second part deals with the electrochemical corrosion behavior of Mn-24 rock bolts in YM solutions at 30°C and 90°C, along with associated surface characterization. The third part deals with the electrochemical corrosion behavior of Swellex rock bolts in simulated seawater (3.5% NaCl). The fourth part involves the passive corrosion behavior of Mn-24 rock bolt steel in J-13 & YM solutions. The last two parts deal with the electrochemical corrosion of Swellex rock bolts in YM solutions at 60°C and 90°C, as well as additional tests involving dry & deliquescent salt tests. Results indicate that the corrosion rate of Swellex DFWE rock bolt steel under aerated (oxygenated) conditions of YM solution at all temperatures and concentrations is much higher than in deaerated (nitrogen) conditions. The highest (at 90°C) and lowest (at 25°C) corrosion rates in 1X YM solution under deaerated conditions are 227 µm/yr and 30 µm/yr, respectively, whereas in aerated conditions, the highest (at 90°C) and lowest (at 25°C) corrosion rates are 2269 µm/yr and 243 µm/yr, respectively. Mn-24 rock bolt steel showed the highest CR of 429 µm/yr in BSW electrolyte at 60°C, and 561.7 µm/yr in SCW at 90°C under aerated (air) conditions. Also, under aerated conditions, pitting corrosion is observed in SDW at 90°C. The presence of silicate ions in the YM electrolyte inhibited the corrosion of rock bolt steel under deaerated conditions due to the formation of a passive film. However, the dissolution rate of the steel is higher in YM solution than in J-13 solution, due to the lack of nitrates in the YM solution. This indicates that nitrates have better inhibiting properties than silicates in solution. The Swellex rock bolt steel corroded badly in the dry and deliquescent salt tests due to galvanic corrosion.

8.2. Electrochemical Corrosion of DFWE Mn-24 Rock Bolt in YM Solution

8.2.1. Corrosion behavior in Deaerated (Nitrogen) YM water

8.2.1.1. Corrosion Behavior in Deaerated YM Solution – Effect of Concentration

Corrosion rates of Mn 24 rock bolt at 25°C in three different concentrations (1X, 10X and 100X) of YM water were calculated from potentiodynamic plots by using the polarization resistance method. Corrosion rates are given in Table 8.1. and shown graphically in Figure 8.1. From the plot it can be seen that the corrosion rate increased with an increase in concentration of the YM water, the highest corrosion rate of 110 µm/yr being observed in 100X water.

Table 8.1. Corrosion rates of Mn24 Rock bolt at 25°C in different concentrations under deaerated conditions.

<table>
<thead>
<tr>
<th>Water Concentrations (Times)</th>
<th>Rp (ohm.cm²)</th>
<th>Icorr (µA/cm²)</th>
<th>Corrosion rate (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deaerated (Nitrogen)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1X</td>
<td>9981.4</td>
<td>2.605</td>
<td>30</td>
</tr>
<tr>
<td>10X</td>
<td>4260.5</td>
<td>6.1026</td>
<td>69</td>
</tr>
<tr>
<td>100X</td>
<td>2676.4</td>
<td>9.7145</td>
<td>110</td>
</tr>
</tbody>
</table>
Potentiodynamic plots of three concentrations are given in Figure 8.2. From the Figure, it can be observed that the linear nature of the passivation in the anodic region decreased as the concentration of the electrolyte increased. At higher concentrations the critical current density increased. Primary passive potentials of 100X and 10X are much higher than the 1X water. For 1X, the passive current density is stable for about 0.3V, where as for the 10X and 100X the passive current density is meta-stable; this may be attributed to the presence of mixture of ions of high concentrations. Due to the increase in ionic concentration of chlorides and sulfates in the electrolyte at higher concentrations, corrosion inhibition is affected. Corrosion potentials for all the concentrations is in between -0.6 to -0.8V.

Figure 8.1. Corrosion rates of Mn 24 as a function of concentration under deaerated (nitrogenated) conditions of YM water.

Figure 8.2. Potentiodynamic polarization plots of Mn 24 rock bolt at 25°C in different concentration of deaerated (nitrogenated) YM water.
8.2.1.2. Corrosion Behavior in Deaerated YM Solution – Effect of Temperature

Similar to the effect of concentration, corrosion rates with respect to temperature linearly increased with an increase in temperature from 25°C to 90°C in 1X YM water. Corrosion rates, along with corrosion current and polarization resistance, are given in Table 8.2. Corrosion rates are plotted in Figure 8.3. From the plot we can see that effect of temperature is much more severe than the effect of concentration. A corrosion rate of 227 $\mu$m/yr at 90°C is observed in 1X water, which is much higher than the corrosion rate in 100X solution at 25°C. The higher corrosion rates at 90°C were confirmed by chemical analysis of the solution after the experiment to contain 0.16mg/L of iron (in the form of iron oxide), with small amounts of manganese and sulfur (in the form of manganese sulfate).

Potentiodynamic polarization scans in de-aerated (nitrogen) at different temperatures are plotted in Figure 8.4. Similar to the plots at different concentrations, corrosion potential for all the temperatures are in between -0.6V to -0.8V.

Table 8.2. Corrosion rates of Mn24 Rock bolt at different temperatures under deaerated (nitrogenated) conditions.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$R_p$ (ohm.cm$^2$)</th>
<th>$I_{corr}$ ($\mu$A/cm$^2$)</th>
<th>Corrosion rate ($\mu$m/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>9981.4</td>
<td>2.605</td>
<td>30</td>
</tr>
<tr>
<td>45°C</td>
<td>4874</td>
<td>5.334</td>
<td>61</td>
</tr>
<tr>
<td>65°C</td>
<td>2035</td>
<td>12.77</td>
<td>145</td>
</tr>
<tr>
<td>90°C</td>
<td>1300</td>
<td>20</td>
<td>227</td>
</tr>
</tbody>
</table>

Figure 8.3. Corrosion rates of Mn 24 as a function of temperature under deaerated (nitrogenated) conditions of YM water.

Corrosion behavior (corrosive, immune, passive) of a metal in an environment can be explained by Pourbaix’s Eh-pH diagrams, [95] based on corrosion potential and pH of the solution. From the Eh-pH diagram of iron in water, the potential range from -0.6V to -0.8V at a pH of 7.2 falls just near the start of oxidation of Fe to Fe$^{2+}$. However, it is in the Eh-pH of Fe-H$_2$O system, and YM water is a dilute salt solution. Therefore, it is very difficult to judge whether the Fe falls in an active or passive region. At all temperatures there is passivation in the anodic region. However, as the temperature increases, the pitting (break down) potential decreases; pitting potential at 25°C is around -0.4V and at 90°C it is around -0.62V. Observing both polarization graphs at 25°C and 90°C, the passive range is relatively less at 90°C. This may be due to the combined effect of oxidizers in the solutions and the temperature.
Figure 8.4. Potentiodynamic polarization plots of Mn 24 rock bolt at different temperatures of deaerated (nitrogenated) 1X YM water.

8.2.1.3. Corrosion Behavior in Deaerated YM Solution – Comparisons with Literature
Corrosion rates of different rock bolts along with I-beam low carbon steel are compared with the corrosion rates of Mn 24 rock bolt under similar conditions of 1X YM water [44, 46, 62, 221]. Corrosion rates with respect to concentrations are given in Table 8.3. Corrosion rates as a function of temperature are given in Table 8.4. The corrosion rate for Mn 24 in 1X and 100X solution is considered to be the highest after 4340 Steel [221]. At 100X concentration, steel set (LCS) showed the lowest corrosion rate. This can be attributed to the low carbon content of the steel [44].

Table 8.3. Corrosion rates comparison of rock bolts and I-beam as a function of concentrations at 25°C under deaerated (nitrogenated) conditions [44, 46, 62, 221].

<table>
<thead>
<tr>
<th>Water Concentration</th>
<th>4340 Steel (μm/year)</th>
<th>Mn-24 (μm/year)</th>
<th>Split Set SS46 (μm/year)</th>
<th>Williams MCS (μm/year)</th>
<th>LCS (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deaerated (Nitrogen)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1X</td>
<td>29</td>
<td>30</td>
<td>34</td>
<td>45</td>
<td>43</td>
</tr>
<tr>
<td>10 X</td>
<td>71</td>
<td>69</td>
<td>88</td>
<td>35</td>
<td>66</td>
</tr>
<tr>
<td>100 X</td>
<td>153</td>
<td>110</td>
<td>93</td>
<td>51</td>
<td>16</td>
</tr>
</tbody>
</table>
Table 8.4. Corrosion rates comparison of rock bolts and I-beam as a function of temperature under deaerated (nitrogenated) 1X YM water[44, 46, 62, 221].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>4340 Steel YM 1X (μm/year)</th>
<th>Mn-24 YM 1X (μm/year)</th>
<th>Split Set SS46 YM 1X (μm/year)</th>
<th>Williams MCS YM 1X (μm/year)</th>
<th>Steel set-LCS YM 1X (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>29</td>
<td>30</td>
<td>34</td>
<td>45</td>
<td>43</td>
</tr>
<tr>
<td>45°C</td>
<td>39</td>
<td>61</td>
<td>65</td>
<td>70</td>
<td>45</td>
</tr>
<tr>
<td>65°C</td>
<td>53</td>
<td>145</td>
<td>93</td>
<td>120</td>
<td>53</td>
</tr>
<tr>
<td>75°C</td>
<td>65</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>85°C</td>
<td>82</td>
<td>N/A</td>
<td>N/A</td>
<td>160</td>
<td>64</td>
</tr>
<tr>
<td>90°C</td>
<td>101</td>
<td>227</td>
<td>103</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Corrosion rates of all the materials mentioned in Table 8.4 are plotted in Figure 8.5 from 25°C to 90°C. The trend of increase in corrosion rate is identical in all the materials. Low Carbon Steel showed the lowest corrosion rate at higher temperatures as compared to all rock bolts. Mn24 showed the highest corrosion rate. Since the solution and the environment for all the materials are same, the change in corrosion rate can be attributed to the nature of the metal surface. For Mn 24, due to the expansion mechanism with high-pressure hydraulic force, there would have been some change in the nature of the material, such as residual stress or work hardening at the surface. This is due to a pile up of dislocations at the grain boundaries. These regions may have become sites of high energy, ready to react with the aqueous solutions and corrode away.

Figure 8.5. Corrosion rate comparison of rock bolts and I-beam as a function of temperature under deaerated (nitrogenated) conditions of 1X YM water.
8.2.1.4. Corrosion Behavior in Deaerated YM Solution – Activation Energy & Corrosion Resistance Strength

A plot of the logarithmic corrosion rate versus (1/T) is plotted in Figure 8.6. Activation energy of the corrosion reaction was determined to be 22.38 kJ/mol. The Corrosion Resistance Strength (CRS) is a new derived unit which is introduced in this research. Even though real units for the strength are N/m², usually in the mining industry or in underground rock reinforcement, the ultimate strength or loading capacity of the rock bolt is given in terms of kN. This CRS is useful to estimate the strength loss due to variation in corrosion rate with respect to temperature. CRS is the ultimate bearing load divided by the corrosion rate. As the denominator (corrosion rate) increases with an increase in temperature, the CRS decreases. In this case, the ultimate bearing load for Mn 24 rock bolt is 240kN. CRS of Mn 24 rock bolt is plotted as a function of temperature in Figure 8.7. From the plot it can be observed that the CRS drastically decreased until 65°C. From there, the change in magnitude is not significant. From this information, we can conclude that even though the corrosion rate is increased with temperature, the magnitude of bearing load has not changed at higher temperatures.

Figure 8.6. Activation Energy of Mn 24 rock bolt under deaerated (nitrogenated) conditions of YM water.

Figure 8.7. Corrosion Resistance Strength (CRS) of Mn 24 rock bolt under deaerated (nitrogenated) conditions of YM water.
8.2.2. Corrosion Behavior in Aerated (Oxygen) YM water

8.2.2.1. Corrosion Behavior in Aerated YM Solution – Effect of Concentration

In the aerated conditions, the corrosion rate increased with an increase in the electrolyte concentration. Corrosion rates, along with corrosion currents and polarization resistance, are given in Table 8.5. Corrosion rates are plotted in Figure 8.8.

In the aerated conditions, the type of corrosion was observed to be uniform. Yilmaz[62, 67], Lian[45] and Ranasooriya[53] also observed higher corrosion rates in aerated conditions as compared to deaerated conditions. Lian [45] observed lower corrosion rates for low carbon steels in J-13 1X[45] water due to presence of nitrates which inhibit corrosion. Corrosion rates of Medium Carbon Steel[62] were higher, and the maximum corrosion rate for 100X electrolyte is 226 μm/yr. However, for the 100X electrolyte, the corrosion rate for Mn 24 was observed to be around 240 μm/yr and for 1X YM solution, the corrosion rate was 145 μm/yr.

Potentiodynamic polarization scans for 1X, 10X and 100X are shown in Figure 8.9. Passivation in the anodic region was not exhibited for any of the three concentrations studied. Due to the mixed potential theory, the cathodic curve intersected the anodic curve well above the passive region due to the reduction of oxygen. Hence, there is a new high corrosion potential.

Table 8.5. Corrosion rates of Mn24 Rock bolt at 25°C in different concentrations under aerated (oxygenated) conditions.

<table>
<thead>
<tr>
<th>Water Concentrations</th>
<th>( R_p ) (ohm.cm(^2))</th>
<th>( I_{corr} ) (( \mu A/cm^2 ))</th>
<th>Corrosion rate (( \mu m/year ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerated (Oxygen)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1X</td>
<td>2032.9</td>
<td>12.7816</td>
<td>145</td>
</tr>
<tr>
<td>10X</td>
<td>1322.8</td>
<td>19.6553</td>
<td>223</td>
</tr>
<tr>
<td>100X</td>
<td>1231</td>
<td>21.121</td>
<td>240</td>
</tr>
</tbody>
</table>

Figure 8.8. Corrosion rates of Mn 24 as a function of concentration under aerated (oxygenated) conditions of YM water.

Figure 8.9. Potentiodynamic polarization plots of Mn 24 rock bolt at 25°C in different concentrations of aerated YM water.
8.2.2.2. Corrosion Behavior in Aerated YM Solution – Effect of Temperature

Corrosion rates and corrosion current at different temperatures are given in Table 8.6. Corrosion rates are plotted in Figure 8.10. Corrosion rates linearly increase with increasing temperature, showing that the corrosion rate is a first-order function with respect to temperature. The highest corrosion rate at 90°C is 2269 μm/yr.

Anodic and cathodic potentiodynamic polarization scans for expanded Mn24 in 1X YM-UNR water at 25°C and 90°C are shown in Figure 8.11. From Figure 8.11, it can be observed that there is no passivation in the anodic region at all temperatures. These kinds of anodic-cathodic regions were observed in all concentrations and at all temperatures. Due to the increase in oxygen concentration the corrosion potential is well above the passive range; the cathodic reduction kinetics curve intersected the anodic oxidation curve at higher potential. Due to the absence of a passive peak, there is no critical current density. This is evident from the linear increase in the current density in the anodic region with increasing applied potential. The corrosion rate of the metal was uniformly increased at higher potential.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>R_p (ohm.cm²)</th>
<th>I_corr (μA/cm²)</th>
<th>Corrosion rate (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>2032.9</td>
<td>12.7816</td>
<td>145</td>
</tr>
<tr>
<td>45°C</td>
<td>307.43</td>
<td>84.57</td>
<td>959</td>
</tr>
<tr>
<td>65°C</td>
<td>165.83</td>
<td>166.82</td>
<td>1778</td>
</tr>
<tr>
<td>90°C</td>
<td>130.0</td>
<td>200</td>
<td>2269</td>
</tr>
</tbody>
</table>

Table 8.6. Corrosion rates of Mn24 Rock bolt at different temperatures in 1X aerated YM water.

Figure 8.10. Corrosion rates of Mn 24 as a function of temperature under aerated conditions in YM water.  
Figure 8.11. Potentiodynamic polarization plots of Mn 24 rock bolt at different temperatures of aerated 1X YM water.
After the experiment at 90°C, it is observed that the color of the solution changed from clear to reddish. Yellowish brown colored water and thick-corroded iron-oxide layer on the sample after the experiments are shown in Figure 8.12 (a) and 8.12 (b) respectively. After chemical analysis of the solution, it was observed that there is 4.7mg/liter of iron in the solution and 0.057mg/L of manganese. The severity of the solution can be explained by the concentration of chlorides in oxidizing conditions. Higher concentrations of chlorides contribute to higher corrosion rates. In aerated 1X solution at 90°C, the chloride concentration was observed at ~1000mg/liter. However, at the same concentration and temperature in deaerated conditions, the chloride concentration was ~380mg/liter. Hence, from the quantity of metal dissolved in the solution, the corrosion rate in aerated solution is higher than in deaerated solution. Also, from the analysis, there is no increase in bicarbonate and silicate ions in solution, which are good indicators for corrosion inhibition. Yilmaz[62] observed deep pits on the sample surface at 85°C in 1X YM water. In our study, after the experiment at 90°C, the sample was characterized by using optical microscopy to examine surface morphology. It was observed there is lot of pits on the surface. The optical micrograph is shown in Figure 8.13. Shreir explained about pitting corrosion in his book[222]. According to him, the pitting corrosion usually occurs in near-neutral solutions of halides or hydrogen anions of halides, and chloride is one of the aggressive ions causing pitting in steels. In general, mine waters contain very high concentrations of chlorides and sulfates in near-neutral pH solutions. Similar results are observed in our case, resulting with both uniform and pitting corrosion.

Figure 8.12. Pits formed over a small region on Mn24 sample in aerated 1X YM water at 90°C.

Figure 8.13. Pits formed over a small region on Mn24 sample in 1X concentration aerated electrolyte at 90°C. Magnification at 400X.
8.2.2.3. Corrosion Behavior in Aerated YM Solution – Comparisons with Literature

Corrosion rates of all rock bolts as a function of concentration and temperature are given in Tables 8.7 and 8.8. Corrosion rates for all the rock bolts and I-beam are plotted in Figure 8.14. The highest corrosion rate is observed for SS-46 rock bolt at 90°C, followed by the Mn 24 rock bolt.

Table 8.7. Corrosion rate comparison of rock bolts and I-beam as a function of concentration at 25°C under aerated conditions [44, 46, 62, 221].

<table>
<thead>
<tr>
<th>Water Concentration</th>
<th>4340 Steel (μm/year)</th>
<th>Mn-24 (μm/year)</th>
<th>Split Set SS46 (μm/year)</th>
<th>Williams MCS (μm/year)</th>
<th>Steel set-LCS (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerated (Oxygen)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 X</td>
<td>244</td>
<td>145</td>
<td>23</td>
<td>124</td>
<td>216</td>
</tr>
<tr>
<td>10 X</td>
<td>142</td>
<td>223</td>
<td>197</td>
<td>136</td>
<td>370</td>
</tr>
<tr>
<td>100 X</td>
<td>616</td>
<td>240</td>
<td>211</td>
<td>226</td>
<td>794</td>
</tr>
</tbody>
</table>

Table 8.8. Corrosion rates comparison of rock bolts and I-beam as a function of temperature under aerated 1X YM water [44, 46, 62, 221].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>4340 Steel YM 1X (μm/year)</th>
<th>Mn-24 YM 1X (μm/year)</th>
<th>Split Set SS46 YM 1X (μm/year)</th>
<th>Williams MCS YM 1X (μm/year)</th>
<th>Steel set-LCS YM 1X (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>244</td>
<td>145</td>
<td>23</td>
<td>124</td>
<td>216</td>
</tr>
<tr>
<td>45°C</td>
<td>799</td>
<td>959</td>
<td>858</td>
<td>320</td>
<td>1104</td>
</tr>
<tr>
<td>65°C</td>
<td>1053</td>
<td>1778</td>
<td>1280</td>
<td>630</td>
<td>934</td>
</tr>
<tr>
<td>75°C</td>
<td>1446</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>85°C</td>
<td>1303</td>
<td>N/A</td>
<td>N/A</td>
<td>1134</td>
<td>351</td>
</tr>
<tr>
<td>90°C</td>
<td>1296</td>
<td>2269</td>
<td>5015</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 8.14. Corrosion rate comparison of rock bolts and I-beam as a function of temperature under aerated conditions of 1X Yucca Mountain solution.
With the exception of LCS, corrosion rates for all other rock bolts increased with increasing temperature. Yilmaz[62] and Lian[45] observed increases in corrosion rates with an increase in temperature for MCS and LCS in 1X YM water and J-13 water, respectively. Since, the water chemistry is similar, corrosion rates obtained in this study are important to compare with those of Yilmaz[62]. McCright[130] determined corrosion rates for 1020 carbon steel from potentiodynamic polarization scans at higher temperatures (80°C-90°C) in aerated J-13 water and reported around 800 microns per year. Ranasooriya[53] also observed 16% mass loss in split sets and standard expanded in electrochemical experiments in various mine water chemistries.

8.2.2.4. Corrosion Behavior in Aerated YM Solution – Activation Energy & Corrosion Resistance Strength
A plot of the logarithm of the corrosion rate versus (1/T) is shown in Figure 8.15. The activation energy calculated for Mn-24 in aerated, 1X YM water is 16.45 kJ/mol. CRS of Mn 24 rock bolt under aerated conditions of 1X YM water is given in Figure 8.16. Initially, the CRS decreases drastically until 45°C, where it begins to flatten out. The CRS is very low (~1.66) at 25°C, and decreases to ~0.11 at 90°C, which is considered very week and may result in failure of the rock bolt. However, in practical circumstances, these kinds of high oxidizing conditions would not exist. One should consider these experiments as the upper bound of the oxidation conditions.

8.2.3. Passive Layer – Three Potentials in Anodic Region
To study the passive behavior of Mn-24 rock bolt three different potentials were chosen in the passive current density region \(-0.593\text{V}, -0.510\text{V} \text{ and } -0.402\text{V}\). The first one, at \(-0.593\text{ V}\), is just above the critical current density. The second one (-0.510V) is in the middle of passive region, and the third is at the end of passive region (breakdown potential, E_{bp}). A potentiodynamic plot with these three potentials is shown in Figure 8.17. The E_{corr} was observed to be -0.662V. To study the nature of the corrosion in the anodic region, three different samples were electrochemically etched at different potentials under similar conditions during the experiment. First, at the starting point of passive film formation (-0.593V); second point is at the center of the film formation zone (-0.510V) and third at the breakdown potential (0.402V). After etching, the samples were characterized by using optical microscope at different potentials and shown in Figure 8.18. From the figure, at -0.593V it can be seen that there are few pitting sites initiated. At -0.510V, interestingly we can see only few pitting sites already formed and the rest being thin transparent film formed on the metal surface. At the E_{bp}, as expected, there are a lot of deep pits formed due to the breakdown of the passive film and the surface is nearly degraded, which can be seen in Figure 8.18 (c). To see the depth of pits formed, one of the pits was magnified further, as shown in Figure 8.18 (d).
Figure 8.17. Polarization curve for expanded Mn 24 Rock Bolt at 25°C in 1X YM water.

Figure 8.18. Expanded Mn24 specimen at RT in 1X concentrated electrolyte, etched at different potentials showing the formation of pits: ((a) – upper left): at -0.593V applied potential (E_{app}); ((b) – upper right): few pits with transparent film formed at -0.510V; ((c) – lower left): at the breakdown potential (E_{bp}) -0.402V, showing lots of pits on the surface; ((d) – lower right): magnified pit formed at -0.402V.
8.2.4. Effect of Anions on Anodic Behavior

One hundred times (100X) the concentrations of MgCl$_2$·6H$_2$O, MgSO$_4$·7H$_2$O, NaSiO$_3$·9H$_2$O and NaHCO$_3$ salts in distilled water were used to study the anodic behavior of Mn-24 rock bolt. A family of potentiodynamic polarization plots of Mn-24 rock bolt in 100X concentrations of these anions used in this study is shown in Figure 8.19. As expected from the literature[131], among all the anions, chloride and sulfate are the most aggressive anions for the corrosion of steels. No passivation is observed in chlorides and sulfates. Good passivation is observed in silicate solutions for a wide range of potentials. Bicarbonates also showed some passivation, but the corrosion potential is higher, which may lead to higher rates of general corrosion than silicates alone. Overall, silicates act as good corrosion inhibitors in the solution. This type of corrosion inhibition mechanism is observed in YM water for medium carbon steel (MCS) through Deodeshmukh’s XPS study.[43] Also, Sarc et al.[223] observed huge passive regions up to one volt in different concentrations of silicate.

![Figure 8.19. Effect of anions on the corrosion behavior of Mn 24 rock bolt in 100X concentration.](image)

8.2.5. Sodium Silicate as a Corrosion Inhibitor

To study the passive behavior of the silicate layer on the surface of the steel, a sample of Mn-24 steel was potentiostatically run for two hours at a passive potential of -0.53V at 25°C in 1X YM water. The potentiostatic scan is shown in Figure 8.20. From the figure, it can be observed that the current decreased drastically, and eventually the current transient flattened out. This indicates a thick barrier in between the metal surface and the solution. After the experiment, the sample’s surface was analyzed using SEM and area mapping. From the SEM analysis, it is observed that there is a thick layer of SiO$_2$ on the surface of the metal sample. A SEM picture of thick layers of SiO$_2$ is shown in Figure 8.21(a). At higher magnification, SiO$_2$ chains with an average diameter of ~100nm are observed, shown in Figure 8.21(b). The SEM mapping is shown in Figure 8.22. This type of chain-like SiO$_2$ was observed by Lehrman [224] in 1952 on water piping. Silicates are used as one of the corrosion inhibitors to control corrosion in industrial processes; especially where there are corrosion problems due to different water chemistries [225-235].
Figure 8.20. Potentiostatic scan of Mn 24 rock bolt in 1X YM water at 25°C.

Figure 8.21(a). Thick passive layer of SiO$_2$ on the metal surface.

Figure 8.21(b). Thick SiO$_2$ chains, with average pore size of around 100nm.
8.2.6. Effect of Cold Working on Anodic Behavior
Due to the movement of rock in the tunnel, the rock bolt is constantly under some form of stress or cold working. However, there is a certain amount of cold working experienced by rock bolts. Therefore, it is useful to see how the amount of cold work affects the corrosion behavior of the rock bolt. In an attempt to understand the effect of cold working, Inflated Mn 24 rock bolt was cold worked by a 29, 60 and 78 % reduction in area. Potentiodynamic plots for all cold-worked Mn 24 along with inflated (in the picture it is abbreviated as A-I: As Inflated) rock bolt experiments in 1X YM water is shown in Figure 8.23. From the plots it can be observed that the passive layer in anodic region for AI is stable, and the passive current density ranges for about 300 mV. Also, the breakdown potential is quite high. For 29CW, the passive layer is meta-stable; also the critical current density is much higher than AI, whereas for 60CW and 78CW, there is no passive layer. This type of corrosion behavior for cold-worked metals is not uncommon. With the increase in cold working, dislocation density at the grain boundaries increases. Because the atomic layers at the grain boundaries are uneven, the bonding is poor and this region becomes a high energy region. In terms of corrosion phenomena, the grain boundaries become anodes and the grains become cathodes. Therefore, as the amount of cold working is increased, the grain boundaries corrode and it is very hard to form a stable passive film. The same phenomenon was observed for 78CW sample.
8.3. Electrochemical Corrosion of Swellex Mn-24 Rock Bolt in YM Solution

In the first part of this section, general corrosion rates in YM ground and simulated waters at 30°C (Temperature in period V) and surface analysis of a highly-corroded sample by XPS, SEM–EDS and thin film X-ray diffraction are presented. Similar to the first part, in the second part, general corrosion rates at 90°C (Temperature in period IV) and surface analysis using the above-mentioned techniques in different YM ground and simulated waters are presented. In the final part, pitting and repassivation behavior of Mn 24 rock bolt in Acidic Concentrated Solution (SAW) and Basic Dilute Solution (BSW) are presented by using cyclic polarization.

8.3.1. Lower Temperature (30°C)

8.3.1.1. Corrosion Rates

General corrosion rates of Mn 24 rock bolt at 30°C in different YM waters under aerated (compressed air) conditions are given in Table 8.9. Average corrosion rates from three repeatable experiments are plotted in Figure 8.24. From the figure, it can be observed that the lowest corrosion rate of 5.5 μm/yr is observed in SCW water. The highest corrosion rate of 429 μm/yr is observed in BSW. Even though YM water does not have inhibitors like nitrates, the corrosion rate in this solution is ~270 μm/yr. The corrosion rate in J-13 is obviously lower than in YM water.

Table 8.9. Corrosion rates in YM waters at 30°C

<table>
<thead>
<tr>
<th>YM Waters</th>
<th>Corrosion Rates (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCW</td>
<td>5.54</td>
</tr>
<tr>
<td>SAW</td>
<td>128.8</td>
</tr>
<tr>
<td>J-13</td>
<td>204.6</td>
</tr>
<tr>
<td>YM 1X</td>
<td>270.9</td>
</tr>
<tr>
<td>SDW</td>
<td>346</td>
</tr>
<tr>
<td>BSW</td>
<td>429</td>
</tr>
</tbody>
</table>
8.3.1.2. Surface Characterization (BSW)

From the corrosion results, it is very interesting to see that the corrosion rate in BSW is much higher than in all of the other YM waters. After the experiment, a black layer was observed on the sample surface and is shown in Figure 8.25. Surface analysis of the sample was done by using thick-film glancing X-ray diffraction, SEM-EDX and X-ray Photoelectron Spectroscopy (XPS). Thin-film X-ray diffraction showed NaCl salt and Fe$_3$O$_4$ on the sample surface. Similar to X-ray diffraction, EDS also showed O, Na, Cl and Fe on top of the sample. SEM results and SEM-EDS results are shown in Figures 8.26 and 8.27, respectively.

Figure 8.25. Black layer on the surface of the sample after the experiment at 30°C.
To support the results from X-ray diffraction and EDS, XPS was done on the sample to a depth of 50 to 100 Å. XPS survey results showed Fe, O, Na and C at different binding energies. The XPS survey is shown in Figure 8.28. Binding energies of O and Fe are shown in Figures 8.29(a) and 8.29(b), respectively and binding energies of Na and Cl are shown in Figures 8.30(a) and 8.30(b). Interestingly, from the XPS results, along with Fe3O4, Fe2O3 is on the surface of the sample. Percentages of Fe2O3 and Fe3O4 are shown in Table 8.10.
Figure 8.28. XPS survey of black layer on the surface of the sample after the experiment at 30°C.

Figure 8.29. Binding energy of (a) oxygen, and (b) iron peaks in BSW water.
Figure 8.30. Binding energy of (a) Na, and (b) Cl peaks in BSW water.

<table>
<thead>
<tr>
<th>YM water</th>
<th>Fe₃O₄, FeO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSW</td>
<td>28</td>
<td>72</td>
</tr>
</tbody>
</table>
8.3.2. High Temperature (90°C)

8.3.2.1. Corrosion Rates
Similar to the low temperature experiments for Mn 24 rock bolt, three polarization resistance experiments were done under air at 90°C. Average corrosion rates are given in Table 8.11. Corrosion rates are plotted in Figure 8.31.

<table>
<thead>
<tr>
<th>YM Waters</th>
<th>Corrosion Rates (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDW</td>
<td>43.77</td>
</tr>
<tr>
<td>J-13</td>
<td>252.4</td>
</tr>
<tr>
<td>SAW</td>
<td>325</td>
</tr>
<tr>
<td>BSW</td>
<td>523.3</td>
</tr>
<tr>
<td>YM-UNR</td>
<td>546.2</td>
</tr>
<tr>
<td>SCW</td>
<td>561.7</td>
</tr>
</tbody>
</table>

From the table, it can be observed that the lowest corrosion rate of ~44 μm/yr is observed for SDW water. The highest corrosion rate of 562 μm/yr is observed in SCW, followed by 546 μm/yr in YM 1X water. Other concentrated waters, like BSW and SAW, show slightly lower corrosion rates than YM 1X solution. In BSW solution at 30°C and 90°C, the corrosion rate difference is slight. This is due to the salt saturation limit of the solution at higher temperatures. After the experiment, salt precipitants were observed on the surface of the sample, as well as in the solution. Salt deposits on the working electrode (sample) and precipitated salts in the solution are shown in Figures 8.32(a) and 8.32(b). This kind of precipitation is also observed for 100X YM water and other waters at very high concentrations [62].
8.3.2.2. Surface Characterization (1X YM)

Even though the corrosion rate of SCW is high, the difference between SCW and simulated YM solution is very minimal. Throughout this research, the solution of interest has been simulated 1X YM solution, and it is much more interesting to see the corrosion products formed on the sample in this solution. XPS analysis is shown in Figure 8.33.

Figure 8.33. XPS survey of the sample surface after the experiment at 90°C.
In the XPS survey, Fe and O peaks were observed between 500 to 800eV of binding energy. Unlike in BSW, in 1X YM water 100% hematite (Fe₂O₃) is observed. Fe and O peaks are shown in Figure 8.34(a) and 8.34(b). Similar to BSW, iron chemical states are shown in Table 8.12.

Table 8.12. XPS Analysis-Iron chemical states (in % Fe)

<table>
<thead>
<tr>
<th>YM Water</th>
<th>Fe₂O₄, FeO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

8.3.3. Cyclic Polarization

8.3.3.1. Cyclic Polarization of Mn24 in SAW and SDW

In high chloride solutions with high pH, such as SAW, there is a potential of pitting corrosion. Cyclic polarization experiments help to see the pitting and repassivation behavior of metal in such environments. To study the localized corrosion (pitting) behavior of Mn 24 in acidic solutions, two experiments in SAW at 30°C and 90°C were done under aerated (compressed air) conditions. Also, to study the localized behavior in basic solutions at high temperature, cyclic polarization experiment in SDW was done at 90°C. Cyclic polarization plots of Mn 24 in SCW at 30°C and 90°C are shown in Figures 8.35(a) and 8.35(b), respectively, and the cyclic polarization plot for SDW is shown in Figure 8.36. The pitting potential and repassivation potentials are given in Table 8.13.

Table 8.13. Pitting and repassivation potentials of SAW and SDW Waters

<table>
<thead>
<tr>
<th></th>
<th>SAW (90°C)</th>
<th>SAW(30°C)</th>
<th>SDW (90°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentials (V)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pitting Potential (Eₚₚ)</td>
<td>-0.5</td>
<td>N/A</td>
<td>-0.176</td>
</tr>
<tr>
<td>Passivation Potential (Eₚᵦᵦ)</td>
<td>-0.4/0.465</td>
<td>-0.366</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 8.35(a). Cyclic polarization of Mn 24 in SAW water at 30°C

Figure 8.35(b). Cyclic polarization of Mn 24 in SAW water at 90°C
From the figures, it can be observed that the pitting potential in SAW is -0.5V and the repassivation potential is either -0.4V or -0.465 based on reverse scan crossing at two different potentials. Even by considering the lowest potential -0.465V, the repassivation potential is higher than the pitting potential. A more positive protection and small difference in between pitting potential and protection potential is an indication of greater resistance to localized corrosion. In the experiment at 30°C in SAW, along with presence of high concentrations of chlorides and sulfates, there is a very high concentration of nitrates. Due to the presence of nitrates, during the reverse scan the passive film is reforming quick enough to prevent localized corrosion, whereas, in the case of 90°C this is quite different. First, at this high temperature there is no passive layer observed in the forward scan and also there is a big hysteresis. The corrosion rate is high and due to the big loop after the formation of a pit, pit growth is more likely. Due to the high temperature factor, sometimes anions like chlorides and sulfates are more dominant than the corrosion inhibiting anions like nitrates or silicates. The worst case is in SDW at 90°C. The cyclic polarization plot is entirely different for the SDW than other two. Even though the pH conditions are not as severe in this case, the repassivation loop was never completed. There is extensive pitting on the surface of the sample; also the pits formed are huge. In this case, these pits will further grow, which can be detrimental to the metal.
8.4. Electrochemical Corrosion Behavior of Swellex Rock Bolts in 3.5% NaCl

In this section, uniform corrosion rates and anodic corrosion behavior of different existing Double-Folded Water-Expanded (DFWE) rock bolts in seawater are determined. The salts within seawater, notably sodium chloride, mean that this type of corrosion is different and more damaging than the type of iron rust that is commonly seen in everyday life. Seawater is a very harsh environment for iron and steel. Iron will corrode 5 times faster in seawater than in freshwater, and some 10 times faster than in air of normal humidity[236]. Even for stainless steel, due to chlorides in the sea water, localized corrosion such as pitting is a big problem. Seawater contains ~3.5 wt% of NaCl, whereas YM water contains lots of inhibiting ions, such as silicates. This study is a baseline study to see the corrosion behavior of DFWE rock bolts (with different bearing load capacities) and Alloy 22 in sea water under deaerated (nitrogen) conditions at 25°C. Also, the effect of temperature on the anodic behavior of Mn 24 at different temperatures is presented.

8.4.1. Corrosion Rates of Rock Bolts
Corrosion rates of Swellex rock bolts (Mn 24, Std., Pm 24) and Alloy 22 in de-aerated conditions of seawater are given in Table 8.14. The highest corrosion rate of 42 μm/yr is observed for both Pm 24 and Std. rock bolts; the lowest corrosion rate of 8.7 μm/yr was observed for Alloy 22. The corrosion rate of Mn 24 is around 39.7 μm/yr. In terms of corrosion rate differences, all the rock bolts showed nearly the same rates. However, Mn 24 has the lowest rate of the three Swellex steels. Potentiodynamic polarization plots are shown in Figure 8.38. From the figure, it can be observed that Alloy 22 shows passivation for a wide range of potentials in the anodic region. However, all the rock bolt materials show no passivation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Corrosion Rate(μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 22</td>
<td>8.72</td>
</tr>
<tr>
<td>Mn 24</td>
<td>39.7</td>
</tr>
<tr>
<td>Pm 24</td>
<td>42.2</td>
</tr>
<tr>
<td>Std.</td>
<td>42.1</td>
</tr>
</tbody>
</table>

Table 8.14. Corrosion rates of rock bolts and Alloy 22 in sea water at 25°C

Figure 8.38. Polarization plots of double folded water expanded rock bolts (Mn 24, Std., Pm 24) and Alloy 22 in sea water at 25°C under de-aerated conditions.
8.4.2. Anodic Corrosion Behavior of Mn 24 Rock Bolt in 3.5% NaCl

Potentiodynamic plots of Mn 24 under deaerated seawater at different temperatures are shown in Figure 8.39. Contrary to the results discussed in section 8.1, no passivation is observed at all temperatures. Also, at higher potentials, current increased as the temperature reached 65°C. Based on the results from Figure 8.39, it can be concluded that seawater is more aggressive than the YM water, due to the chloride content in solution.

![Figure 8.39. Polarization plots of Mn 24 rock bolt at different temperatures in sea water at 25°C under de-aerated conditions.](image)

8.5. Passive Corrosion Behavior of Swellex Mn 24 Rock Bolt in J-13 and YM waters

In the above sections the passive behavior of Mn 24 rock bolt in YM waters is presented, especially in 1X YM water due to presence of silicate ions, the passivity at 25°C is steady for a certain rate of potential in the anodic region. Similarly, due to presence of nitrates in J-13 well water, passivation is observed at higher potentials of the anodic region. Potentiodynamic polarization graphs of Mn 24 in both J-13 and 1X YM water are shown in Figure 8.40. However, the passive corrosion behavior of such a layer or the change in current density as a function of time cannot be extracted from only the potentiodynamic polarization experiments. At the same time it is very difficult to do longer potentiostatic electrochemical experiments at these high potentials. To see the passive current density of Mn 24 in J-13 and 1X YM water two passive potentials, -0.50V from the J-13 plot and -0.53V from the YM-UNR plot were selected for a two-hour potentiostatic experiment. Selected potentials are shown in Figure 8.40. Potentiostatic experiments in both J-13 and 1X YM solutions are shown in Figures 8.41 and 8.42, respectively. In both solutions, due to the increase in the passive layer, the current density drastically decreased and flattened out by the end of two hours. After the end of the experiment, the passive current density in J-13 water was much lower than in 1X YM water. Since both curves were exponential, a power function was used to fit both the equations[237]. Fitted functions are showed in Figures 8.41 and 8.42. From the fitted functions, the passive current density at any time can be estimated. Using ASTM G 59 [238] and ASTM G 102 [239], corrosion rates were estimated by using the passive current density from the power equation. Extrapolated corrosion rates in both waters are given in Table 8.15. These graphs indicate that the passive layer is growing as a function of time in both solutions. From the extrapolated corrosion rate values shown in Table 8.15, it seems that both nitrates and silicates in J-13 and YM-UNR (1X YM water) are contributing to very thick layers. Among silicates and nitrates, nitrates seem to be a much stronger and more effective inhibitor. This kind of passive behavior and reduced corrosion rates was also observed in similar research related to YM corrosion, as well as other studies [240-243].

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Figure 8.40. Polarization plots of Mn 24 rock bolt in J-13 and 1X YM water at 25°C under deaerated conditions.

Figure 8.41. Potentiostatic scan of Mn 24 at -0.50V in J-13 well water at 25°C under deaerated conditions.
Table 8.15. Extrapolated passive dissolution rates

| Time  | YM -UNR | J-13
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Corrosion rates (μm/year)</td>
<td></td>
</tr>
<tr>
<td>1 hour</td>
<td>7.26E+00</td>
<td>2.41E+00</td>
</tr>
<tr>
<td>1 day</td>
<td>1.02E+00</td>
<td>1.45E-01</td>
</tr>
<tr>
<td>1 year</td>
<td>2.69E-02</td>
<td>7.79E-04</td>
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<tr>
<td>2 years</td>
<td>1.75E-02</td>
<td>4.22E-04</td>
</tr>
<tr>
<td>5 years</td>
<td>7.08E-03</td>
<td>1.87E-04</td>
</tr>
<tr>
<td>10 years</td>
<td>6.49E-03</td>
<td>1.01E-04</td>
</tr>
</tbody>
</table>

Figure 8.42. Potentiostatic scan of Mn 24 at -0.50V in J-13 well water at 25°C under deaerated conditions.
8.6. Electrochemical Corrosion of Potential Rock Bolts in YM water

8.6.1. Low Temperature (60°C)
This is a qualitative electrochemical study of all existing rock bolts in 1X YM water under aerated (compressed air) conditions at two temperatures, 90°C and 60°C, to represent temperature periods IV and V, respectively. Among the studied materials, a wide variety of mechanically-anchored rock bolts are used, such as Williams®, which is a Medium Carbon Steel (MCS), and Friction Rock Stabilizers (FRS) such as Split-Set® (SS 46) and Swellex® rock bolts (Mn 24, Pm 24 and Std.). Along with these rock bolt materials, the corrosion behavior of Low Carbon Steel (LCS) was also studied. Since the rock bolt names are copyrighted, these are represented by the type of steel or by abbreviations. All other electrochemical experiments presented in Section 8.1 were tested in oxygen, whereas these were tested in compressed air.

In this study, only the general corrosion rates are determined by using the polarization resistance technique. No anodic corrosion mechanism was studied by potentiodynamic polarization. The calculated corrosion rates at 60°C are given in Table 8.16. A corrosion rate comparison plot is shown in Figure 8.43. Among all the materials, SS-46 showed the highest corrosion rate of 80.3 microns per year and Std. Swellex rock bolt showed the lowest corrosion rate of 43 microns per year. All other materials showed relatively-close corrosion rates.

<table>
<thead>
<tr>
<th>Rock Bolts</th>
<th>Corrosion Rate (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 46</td>
<td>80.3</td>
</tr>
<tr>
<td>LCS</td>
<td>66.6</td>
</tr>
<tr>
<td>MCS</td>
<td>54.5</td>
</tr>
<tr>
<td>Pm 24</td>
<td>51.4</td>
</tr>
<tr>
<td>Mn 24</td>
<td>46.5</td>
</tr>
<tr>
<td>Std.</td>
<td>43</td>
</tr>
</tbody>
</table>

Figure 8.43. Corrosion rates of potential rock bolts in aerated (compressed air) 1X YM water at 60°C.
8.6.2. High Temperature (90°C)
Corrosion rates determined at 90°C are given in Table 8.17 and a corrosion rate comparison plot is given in Figure 8.44. Unlike at 60°C, at 90°C MCS severely corroded. The highest corrosion rate for MCS is ~447 microns per year and the lowest corrosion rate was observed for Mn 24 at 62 microns per year. As expected, corrosion rates at higher temperatures in aerated (compressed air) conditions are due to high oxygen dissolution rates.

<table>
<thead>
<tr>
<th>Rock Bolts</th>
<th>Corrosion Rate (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCS</td>
<td>447</td>
</tr>
<tr>
<td>Std.</td>
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<tr>
<td>LCS</td>
<td>258.8</td>
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<td>Pm 24</td>
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<tr>
<td>SS 46</td>
<td>142</td>
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<tr>
<td>Mn 24</td>
<td>62</td>
</tr>
</tbody>
</table>

Figure 8.44. Corrosion rates of potential rock bolts in aerated (compressed air) 1X YM water at 90°C

8.7. Dry & Deliquescent Salt Corrosion on Swellex Rock Bolts

8.7.1. Effect of Dry Salts on the Corrosion of Swellex Rock Bolt Steels
With the exception of a couple of Swellex steels (Mn 24 and Std.), all other alloys were not affected by dry salts. These steels showed some micro-sized pits on the surface. SEM pictures of Mn 24 before and after the experiment are shown in Figures 8.45 and 8.46. From these pictures, it can be observed that there are a lot of micro-pits on the surface of Mn 24 after the experiment. SEM-EDS studies were done on one of the pits. From the EDS analysis, it is observed that there is NaCl and iron oxide present inside the pit. Chemical analysis results are shown in Figure 8.47. Therefore, chlorides in dry salts affect HSLA steels in the form of pitting corrosion.
8.7.1. Effect of Deliquescent Salts on the Corrosion of Swellex Rock Bolt Steels

In another set of experiments with a coupon of Mn-24 sitting on top of the sample with salt in between, it was observed that there is galvanic corrosion between Mn 24 coupons and all other alloys. A highly-corroded Mn 24 coupon is shown in Figure 8.48(a) and an unaffected sample of Alloy 22 is shown in Figure 8.48(b). In this test, all alloys behaved as cathodes; Mn 24 coupons on top of the salt became anodes and the deliquescent salt acted as the electrolyte. According to the galvanic series, the extent of corrosion in Mn 24 coupons was severe. This is due to large differences in the electrochemical potential between steel (Fe) and other Cr-rich alloys, as well as the constant supply of air (circulating air bubbled through hot water). Therefore, deliquescent salts are much more detrimental to HSLA steels but there is no effect on other alloys. Hence, Alloy 22 waste container is immune to both dry salt and deliquescent salt tests,[172] with and without weights on the salt.
IX. ELECTROCHEMICAL CORROSION OF AISI 4340 STEEL IN MULTI-IONIC SOLUTIONS

9.1. Summary of Electrochemical Corrosion of AISI 4340 Steel in Multi-Ionic Solutions

In this study, the electrochemical corrosion behavior and associated corrosion rates of AISI 4340 steel were determined in two different parts. In the first part, potentiodynamic polarization and electrochemical impedance spectroscopy using three different concentrations (1X, 10X, 100X) of simulated Yucca Mountain solution were used under aerated (oxygenated) and deaerated (nitrogenated) conditions to determine baseline corrosion rates from 25°C to 90°C. These rates show a maximum of ~300 \( \mu \text{m/yr} \) at 45°C (deaerated conditions), and a maximum of ~2200 \( \mu \text{m/yr} \) at 65°C (aerated conditions) in simulated YM solutions.

In the second part, potentiodynamic polarization under deaerated conditions was used to determine the corrosion rates and passivity behavior of 4340 steel using different combinations of sodium silicate (\( \text{Na}_2\text{SiO}_3 \)) and sodium bicarbonate (\( \text{NaHCO}_3 \)), in both pure water and simulated seawater (3.5% NaCl). These experiments were carried out to examine the potential inhibiting properties of the silicate and/or bicarbonate ions on the surface of the steel. For these experiments, results indicate that the steel corrodes < 70 \( \mu \text{m/yr} \) in solutions containing sodium silicate, but corrodes > 2,000 \( \mu \text{m/yr} \) in solutions containing sodium bicarbonate.

9.2. Polarization Studies in Simulated Yucca Mountain Solutions

AISI 4340 steel samples were potentiodynamically polarized in 1X, 10X and 100X simulated Yucca Mountain solutions at six different temperatures – 25°C, 45°C, 65°C, 75°C, 85°C and 90°C – under a continuous purging of either nitrogen or oxygen gas. A representative summary of these polarization curves is shown in Figure 9.1. In each case, the potentiodynamic scans for 75°C and 90°C were intentionally left out because these showed virtually the same electrochemical behavior as the curves at 85°C. They are shown in the appendix.

9.2.1. Polarization Studies under Deaerated Conditions

The polarization effects under deaerated conditions of AISI 4340 steel in simulated Yucca Mountain solutions are shown in Figure 9.1 (a-c) and Figure 9.2. These representative polarization curves indicate that as a function of solution concentration, the steel exhibits moderate passivity at lower temperatures, transforming to virtually no passivity at higher temperatures.

Average corrosion rates ranged from 29 \( \mu \text{m/yr} \) to 308 \( \mu \text{m/yr} \) overall. Figure 9.3 shows the average corrosion rates obtained from polarization in deaerated YM solutions. In general, rates increased linearly with temperature for 1X and 10X concentrations, and activation energies for these concentrations were consistent with these results. For the highest temperature tested (90°C), the average corrosion rate was calculated to be 174 \( \mu \text{m/yr} \) in 10X Yucca Mountain solution. In the 100X concentration, corrosion rates showed mixed behavior, peaking at 45°C and decreasing to minimum at 75°C. This type of behavior is similar to the corrosion rates for deaerated 100X YM solution published by Arjunan[10] using ASTM A-36 steel. However, it is also possible that this data is incorrect, as other researchers, such as Yilmaz[62] and Rahman[244], have published results that show the corrosion rates increasing in all deaerated YM concentrations as temperature is increased.
Figure 9.1. Potentiodynamic polarization plots of AISI 4340 steel in simulated Yucca Mountain solutions. Top to bottom – nitrogenated: (a) 1X, (b) 10X, (c) 100X; oxygenated: (d) 1X, (e) 10X, (f) 100X.
Figure 9.2. Potentiodynamic polarization plots of AISI 4340 steel in deaerated, simulated Yucca Mountain solutions. Left to right: (a) 25°C, (b) 45°C, (c) 65°C, (d) 85°C.

Figure 9.3. Corrosion rates of AISI 4340 steel obtained from potentiodynamic polarization in deaerated, simulated Yucca Mountain solutions.
9.2.2. Polarization Studies under Aerated (Oxygenated) Conditions

Figure 9.1 (d-f) shows the effects of aeration on AISI 4340 steel in simulated Yucca Mountain solutions. These polarization plots indicate that the steel exhibits no passivity in the anodic region, leading to active dissolution of iron in solution. This active dissolution raises the corrosion potential \(E_{corr}\) approximately 100 to 200 mV higher than in the deaerated conditions. This increase in corrosion potential increases the pitting potential \(E_{pit}\) of the steel accordingly.

Average corrosion rates obtained from these experiments are shown in Figure 9.4. For 1X & 10X concentrations, corrosion rates peaked at 75°C, whereas for the 100X concentration, the average corrosion rate peaked at 65°C. This high corrosion rate value of 2,193 μm/yr is similar to the values obtained by Rahman[244] for ASTM A607 steel – 2,182 μm/yr at 55°C in 100X YM water, and 2,393 μm/yr at 65°C. In all cases, the corrosion rates decreased as the temperature increased beyond the maximum rate. These decreased values could be due to the decreased solubility of oxygen in solution at higher temperatures;[110] other researchers[10, 62, 244] have shown similar behavior. Arjunan[10] reported lower average corrosion rates for I-beam steel (ASTM A-36 steel) in all aerated YM solution concentrations at 65°C and 85°C, and Yilmaz[63] reported lower corrosion rates at higher temperatures for Rock Bolt Carbon Steel (AISI 1144 steel) in 100X YM solution. Another reason could be due to the precipitation of CaCO₃ from solution onto the surface of the specimen. Jiang et al.[245] reported that when Ca²⁺ ions (in the form of CaCl₂) were added to solutions with the same Cl⁻ concentration, the corrosion rate of N80 steel actually decreased. Also, Yilmaz[62] and Lian[246] both reported that “precipitate layers” of calcium carbonate formed on the surface of the samples at higher temperatures, in both YM and J-13 solutions, suggesting that this salt is actually responsible for decreasing the corrosion rates of these carbon steels. Figure 9.5 shows a comparison of the corrosion rates between ASTM A-36 and AISI 4340 steels, and Table 9.1 shows a comparison of the average corrosion rates of AISI 4340 steel, Rock Bolt Carbon Steel[63] and I-beam Steel,[10] in all Yucca Mountain solutions. It’s interesting to note that the corrosion rate values for 4340 steel in 1X YM solution are higher than those in 10X solution. This behavior has already been reported by Arjunan[10], but only at temperatures above 25°C. One possible explanation may be the increase in Ca²⁺ species in solution, as described above. Table 9.2 shows the activation energies obtained in both aerated and deaerated conditions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Environment</th>
<th>Concentration (X)</th>
<th>AISI 4340 Steel CR (μm/yr)</th>
<th>Rock Bolt CS CR (μm/yr)</th>
<th>I-Beam Steel CR (μm/yr)</th>
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<tr>
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Table 9.2. Activation energies for 4340 steel run under potentiodynamic polarization in YM solutions.

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<tr>
<th>Yuca Mountain Solution Concentration (X)</th>
<th>Activation Energy (kJ/mol)</th>
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<td></td>
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<tr>
<td>10X</td>
<td>32.3</td>
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</table>
9.2.3. Electrochemical Corrosion Effects in Multi-Ionic Solutions

In solutions containing several different types of ions, such as simulated Yucca Mountain solutions, corrosion effects on the surface of the specimen showed varying amounts of pitting, depending on solution concentration, temperature and environmental conditions. In all cases, pits were uniformly distributed and round in shape, regardless of environment.

In aerated conditions, pitting developed soon after $E_{corr}$ due to a lack of passivity from the oxygen content in solution. The size of pits varied from small to large, depending on concentration. These pits developed soon after For 10X concentration, the sizes of most pits were small, with a few large ones; however, for 100X concentration, the reverse was true. This indicates that the size and amount of pitting is dependent on the concentration of chlorides in solution, since chlorides are required to initiate pitting in steels.[247] Figure 9.6 shows the effects of different sizes and amounts of pitting of 4340 steel in two different solution concentrations under aerated conditions.

![Figure 9.6. Micrographs of exposed surfaces of 4340 steel in aerated conditions: (a) 85°C in 100X Yucca Mountain solution; (b) 75°C in 100X Yucca Mountain solution.](image)

For deaerated conditions, passivity did develop beyond the anodic region, prior to pitting. To determine the composition of the products formed on the surface of the steel that gave passivity, a specimen was potentiostatically polarized in 100X YM solution at a passive potential of -525 mV for two hours. Results show that the products formed nodules of CaCO$_3$ in the form of calcite and aragonite, over the entire surface. Figure 9.7 shows a SEM micrograph of the morphology of the nodules, and Figure 9.8 shows the XRD spectra for the calcium carbonate nodules.

Although it has already been proven that the passivity is due to a “colorless, brittle, dielectric-type”[63] layer consisting of a thick network of SiO$_2$ molecules,[248] it has also been proven that calcium ions in the presence of chlorides decrease the corrosion rate of N80 steel.[245] This low-carbon steel was tested in the presence of chlorides (3% & 4.6%, respectively), and according to the authors,[245] “the corrosion rate decreased due to the addition of Ca$^{2+}$ ions in solution. Although Yucca Mountain water has a much lower chloride concentration, it also contains calcium cations from CaCl$_2$ and CaSO$_4$. Therefore, these salts have the potential in decreasing the corrosion rate of this (and other) type(s) of steel that will be used in the repository.
Figure 9.7. SEM micrograph showing the morphology of the CaCO₃ nodules on top of the steel’s surface during potentiostatic polarization for two hours in 100X YM solution under nitrogen at 45°C and -525 mV.

Figure 9.8. X-ray Diffraction spectra of calcium carbonate nodules formed on top of the steel’s surface during potentiostatic polarization for two hours in 100X YM solution under nitrogen at 45°C and -525 mV.
Electrochemical Impedance Spectroscopy (EIS) of AISI 4340 Steel in Simulated Yucca Mountain Solutions

Electrochemical Impedance Spectroscopy was performed in conjunction with potentiodynamic polarization to help correlate the effects of the polarization scans in section 4.2. Impedance spectra was measured and recorded in 100X YM solutions under both oxygenated and nitrogenated conditions. The results are shown as conventional Nyquist & Bode plots in Figures 9.9 and 9.10. The corrosion rate is a function of the diameter of the semicircles given in the plots – the smaller the diameter, the lower the resistance to corrosion, and hence, the higher the corrosion rate. For aerated conditions, this correlates well with Figures 17(a) and 17(c). At 65°C, the corrosion rate hits a maximum due to a minimum amount of ohmic resistance at the metal-solution interface. Above and below this temperature, the corrosion rates are lower; hence, a larger amount of resistance is observed at these temperatures. Additionally, all Bode plots show a single phase angle maxima. For deaerated conditions, a Warburg tail is seen at 45°C, and continues as the temperature increases. This correlates well with the 45°C potentiodynamic scan of Figure 18(c). At higher temperatures, the Warburg tail is much more pronounced, indicating a diffusion-controlled electrochemical reaction.[249] At lower temperatures, the Bode plots show a single phase angle maximum; at higher temperatures, they show a double phase angle maximum. This indicates that at higher temperatures, the electrode’s surface is porous, much like a coating. This type of behavior is consistent with some spectra of polymer-coated metals.[27]

Figure 9.9. Impedance spectra recorded on AISI 4340 steel in oxygenated 100X YM water. Top to bottom: (a) 25°C, (b) 45°C, (c) 65°C and (d) 85°C.
Figure 9.10. Impedance spectra recorded on AISI 4340 steel in nitrogenated 100X YM water. Top to bottom: (a) 25°C, (b) 45°C, (c) 75°C and (d) 85°C.
9.4. Electrochemical Corrosion in SiO\(_2\) \& HCO\(_3\) Solutions

Potentiodynamic polarization was used to determine the corrosion rates and electrochemical passivity behavior of AISI 4340 steel under deaerated (reducing) conditions. Deaeration was used as a baseline to determine the most stable passive regions for 4340 steel in silicate and/or bicarbonate solutions. Specimens or coupons would then be “pretreated,” or coated with silicate and/or bicarbonate ions under a constant potential within these passive regions potentiostatically, similar to anodization or galvanization, prior to testing for corrosion resistance.

Potentiodynamic tests were run at four different temperatures – 25°C, 45°C, 65°C and 80°C – in twenty-four (24) different solution concentrations containing sodium silicate, sodium bicarbonate and/or sodium chloride. Tables 9.3 and 9.4 show corrosion rate data for 4340 steel in silicate and bicarbonate solutions, in pure (deionized/distilled) water and simulated seawater (3.5% NaCl) solutions. Representative summaries of these corrosion rates and their corresponding activation energies are shown in Table 9.5 and Figure 9.11. It’s important to note that these graphs show the corrosion rate versus chemical composition. Therefore, at a constant temperature, the corrosion rate could be increasing or decreasing as the amount of chemical constituent in solution increases or decreases. In addition, experimental corrosion rates obtained for 4340 steel in deaerated 3.5% sodium chloride solution using potentiodynamic polarization are presented in Table 9.6, which was not reported in the literature. The activation energy was determined to be 28 kJ/mol. The corrosion rate for 4340 steel in pure, deaerated water was determined to be ~51 μm/yr at 25°C. However, values for temperatures above 25°C were not determined. Apparently, obtaining corrosion rates in low-conductivity water is a challenge,[250] and monitoring corrosion rates in low-conductivity water has only been done using sophisticated electrochemical techniques – LPR (linear polarization resistance), EIS and crevice corrosion current – as well as direct measurement techniques, such as weight loss and highly-sensitive electrical resistance galvanic probes. Currently, these are the only known techniques for measuring corrosion rates and associated behavior of carbon steels in low-conductivity water.

Table 9.3. Corrosion rate data for 4340 steel in deaerated, silicate and bicarbonate solutions in pure water.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration (M = moles/liter)</th>
<th>(E_{corr}) (V_SSC(^{-1}))</th>
<th>(I_{corr}) (μA/cm(^2))</th>
<th>Corrosion Rate(^2) (μm/yr)</th>
<th>Corrosion Rate(^2) (mpy)</th>
</tr>
</thead>
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156
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<th>Temperature (°C)</th>
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<th>$E_{corr}$ (V SSC$^1$)</th>
<th>$I_{corr}$ (μA/cm$^2$)</th>
<th>Corrosion Rate$^2$ (μm/yr)</th>
<th>Corrosion Rate$^2$ (mpy)</th>
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$^1$ SCC = Silver-Silver Chloride Reference Electrode  
$^2$ average value
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<th>SiO$_3^{2-}$ (M)</th>
<th>pH</th>
<th>Conductivity (μS/cm)</th>
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$^1$ SCC = Silver-Silver Chloride Reference Electrode  
$^2$ average value
Figure 9.11. Overall corrosion rates of 4340 steel in silicate-bicarbonate solutions. Top (a): pure water; bottom (b): simulated seawater. The corrosion rates for 0.5M sodium bicarbonate at higher temperatures are not shown.
Table 9.5. Test solutions used and the corresponding index for Figure 9.11, showing selective activation energy values.

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<th>Solution Concentration M (moles/liter)</th>
<th>Composition #</th>
<th>Activation Energy (kJ/mol)</th>
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</tbody>
</table>

Table 9.6. Corrosion rate data for AISI 4340 steel in deaerated, 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$E_{\text{corr}}$ (V$_{\text{SSC}}$)</th>
<th>$I_{\text{corr}}$ (μA/cm$^2$)</th>
<th>CR (μm/yr)</th>
<th>CR (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-0.743</td>
<td>2.0</td>
<td>24</td>
<td>1.0</td>
</tr>
<tr>
<td>45</td>
<td>-0.717</td>
<td>4.6</td>
<td>51</td>
<td>2.0</td>
</tr>
<tr>
<td>65</td>
<td>-0.704</td>
<td>8.0</td>
<td>92</td>
<td>3.6</td>
</tr>
<tr>
<td>80</td>
<td>-0.694</td>
<td>12.0</td>
<td>139</td>
<td>5.5</td>
</tr>
</tbody>
</table>

9.4.1. Effects of Temperature

Temperature is an important variable in controlling the rate of corrosion. As the temperature is increased in the system, less activation energy is required to produce an electrochemical reaction. Results show that in general, the corrosion rates increased with increasing temperature. Critical current density ($I_{\text{crit}}$) increased as temperature increased for most of the solutions, with the exceptions of the silicates in saltwater, the solution of [0.005M SiO$_3^{2-}$ + 0.1M HCO$_3^-$] in pure water, and the [silicates + 0.5M HCO$_3^-$], both in pure water and seawater. Likewise, the passive current density ($I_{\text{pass}}$), increased for most of the solutions tested. Only the bicarbonates in pure water, the silicates in simulated seawater and 0.1M HCO$_3^-$ in seawater showed a decrease in the passive current density. The 1M HCO$_3^-$ solutions showed neither an increase nor decrease in $I_{\text{pass}}$. However, most of the solutions tested showed a decreasing breakdown potential ($E_{\text{bp}}$). The exceptions were the bicarbonates, [silicates + 0.5M HCO$_3^-$] and [silicates + 0.1M HCO$_3^-$], all in simulated seawater. Additionally, some scans showed the formation of secondary oxygen peaks with secondary passive regions, such as the bicarbonates in pure water, as well as the [silicates + 0.1M HCO$_3^-$] in simulated seawater. Figures 9.12 and 9.13 show representative potentiodynamic scans of these observations. Additional representative scans are shown in the appendix.

A near-textbook example of the “effect of increasing acid concentration and temperature on passivity,” as stated in Principles and Prevention of Corrosion, by D.A. Jones,[110] is shown in Figure 9.14. This effect shows that $I_{\text{crit}}$. 

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$E_{\text{pp}}$ and $I_{\text{pass}}$ all increase as temperature increases. According to Jones,[110] this phenomenon occurs under “severe conditions of higher acidity and temperature,” which “decrease the passive potential range and increase current densities and corrosion rates at all potentials.” Although this effect is discussed in the context of stainless steels, it was observed for 4340 steel in only one concentration: [0.025M Na$_2$SiO$_3$ + 0.1M NaHCO$_3$] in pure water. This could be due to a combination of FeCO$_3$ and silicic acid, H$_2$SiO$_3$, during the active to passive transformation. Silicic acid is itself a weak acid,[251] and the formation of FeCO$_3$ is thermodynamically favorable.[252] Therefore, because FeCO$_3$ forms in the presence of HCO$_3^-$ “at potentials more anodic than the active to passive transition,”[58] a possible chemical reaction between sodium silicate and the iron substrate, as detailed by Fujita et al., may be taking place which would increase the activation energy required to transition from active to passive, creating a primary passivation potential ($E_{\text{pp}}$) that increases with temperature. Thus, less energy is required for the formation of the passive layer, and of FeCO$_3$ from the previous chemical reaction. This, in turn, requires less energy for the thin film(s) to break down at high potentials, which show a decreasing $E_{\text{pp}}$ as temperature is increased.

![Figure 9.12](image_url). Representative potentiodynamic scans showing the effects of temperature: 0.5M NaHCO$_3$ in pure water.
Figure 9.13. Representative potentiodynamic scans showing the effects of temperature: 0.025M Na₂SiO₃ + 0.1M NaHCO₃ in simulated seawater.

Figure 9.14. Representative potentiodynamic scans of [0.025M SiO₃²⁻ + 0.1M HCO₃⁻] in pure water showing the “near-textbook” effect of increasing acid concentration and temperature on passivity.
9.4.2. Effects of Silicate Ions

The effects of increasing silicate concentrations on the polarization and passivity behavior of 4340 steel in pure water at 45°C are shown in Figure 9.15. It can be seen from these scans that the passivity of 4340 steel in sodium silicate is very high, as is the breakdown potentials (E_{bp}) and pitting potentials (E_{pil}). This passivity is due to a “self-healing” thin-film of silica, that has an amorphous, “honeycomb-like” structure.[253] When compared to Rock Bolt Carbon Steel,[58] as in Figure 9.16, the breakdown potential is approximately 1100 mV higher. Also, for most of the temperature tested, the corrosion rate decreases as the silicate concentration is increased. However, at higher temperatures and low silicate concentrations, the electrochemical passivation becomes unstable, generating electrochemical noise and/or an incomplete curve. This is due to precipitation of the silicate ions out of solution at these high temperatures.

Figure 9.15. Effect of silicate ions on the passivity of 4340 steel at 45°C.
The polarization behavior of 4340 steel in simulated seawater (3.5% NaCl solution) with three different silicate concentrations (0.005M, 0.01M & 0.025M) at two different temperatures is shown in Figures 9.17 and 9.18. It can be seen from these figures that both sets of curves show similar characteristics. All curves show an overall reduction in both passivity and potential, compared to their counterparts in pure water. They also show an increasing passive current density prior to their breakdown potentials. This is due to the increased conductivity and electronegativity of the chloride ions in solutions. At 25°C, the 0.01M $\text{SiO}_3^{2-}$ curve shows a lower $E_{corr}$ and $I_{corr}$ than both the 0.005M & 0.025M $\text{SiO}_3^{2-}$ curves, which coincides with the average corrosion rates stated in Table 9.4. The curves at 80°C show similar behavior.
9.4.3. Effects of Bicarbonate Ions
The molar effects of bicarbonate ions on 4340 steel in pure water were also examined for potential corrosion inhibition. A representation of these electrochemical effects is shown in Figures 9.19 and 9.20. From the figure, it can be seen that one oxygen peak is created in 0.1M HCO$_3^-$, whereas two distinct oxygen peaks form in 0.5M & 1M HCO$_3^-$. This indicates that there are two different passive regions in 0.1M HCO$_3^-$, and three regions in 0.5M & 1M HCO$_3^-$, prior to film breakdown. Also, the breakdown and pitting potential values are nearly the same as the potentials for silicates in pure water. However, for bicarbonates, both $I_{corr}$ and $I_{pass}$ increase with an increase in molar concentrations. These increases are more pronounced at lower temperatures than at higher temperatures.
The polarization behavior of 4340 steel in 3.5% NaCl solution with different concentrations of HCO$_3^-$ ions is shown in Figures 9.21 – 9.23. It was observed that $I_{\text{corr}}$ increased with increasing bicarbonate concentration, regardless of temperature. Pitting potential ($E_{\text{pit}}$) also increased as concentration increased for each temperature tested. However, there was no passivity observed for 0.1M HCO$_3^-$ until 65°C. For 0.5M HCO$_3^-$, passivity did not occur until 45°C. Also, this passive region produced an oxidation peak at a potential of approximately -300 mV at 65°C. Passivity was apparent in all 1M HCO$_3^-$ solutions for all temperatures tested. Higher temperatures produced unstable passive films for 0.5M HCO$_3^-$ and 1M HCO$_3^-$ solutions.
Figure 9.22. Effect of addition of bicarbonate ions on passivity in 3.5% NaCl solution at 65°C.

Figure 9.23. Effect of addition of bicarbonate ions on passivity in 3.5% NaCl solution at 80°C.
9.4.4. Effects of Silicate & Bicarbonate Ions on Passivation

Potentiodynamic polarization scans for 4340 steel in pure water showing the effects of different concentrations of silicate and bicarbonate ions at 25°C and 80°C are shown in Figures 9.24 and 9.25. These curves show that the amount of passivity obtained for 4340 steel is significant when various concentrations of silicates and/or bicarbonates are added in solution. However, when no amount of ions is present in solution, no passivity is obtained. When in the presence of bicarbonates, passivity is due to the formation of FeCO₃ by a dissolution-precipitation mechanism originally proposed by Ogundele and White,[252] using the following reactions:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]  \hspace{1cm} (2.1)
\[ \text{Fe} + \text{HCO}_3^- \rightarrow \text{FeCO}_3 + \text{H}^+ + 2e^- \]  \hspace{1cm} (9.1)

However, a passive film may also be created using a combination of (9.1) and the reaction:[247]

\[ \text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + 2e^- \]  \hspace{1cm} (9.2)

According to Cheng et al.[247] Equation (4.1) is “dependent on HCO₃⁻ concentration and pH, and is favored by high HCO₃⁻ concentrations.” Therefore, for high concentrations of bicarbonate above approximately -0.2V, Fe²⁺ oxidizes to ferric oxide according to the following reaction:

\[ 4\text{Fe}^{2+} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \]  \hspace{1cm} (9.3)

These metallurgical reactions result in the passivation of the steel.[247]

It is clear from Figures 9.26 and 9.27 that I₉corr and I₉pass are higher in both bicarbonate and bicarbonate-silicate concentrations than silicate concentrations in pure water. As temperature is increased for pure silicate solutions, more current is required to sustain a corrosion-resistant film on the steel’s surface. At 25°C, the passive behavior for 0.1M HCO₃⁻ shows a large oxidation peak before minimal current density resumes, compared to 0.5M HCO₃⁻, which shows a smaller oxidation peak prior to resuming passivity. This type of behavior isn’t shown at higher temperatures, indicating that if bicarbonates are used solely to create a passive film on the surface of the steel at room temperature, passivation will require much higher current densities and/or a very limited potential range to apply a corrosion-resistant film. If done industrially, this would require much higher costs to perform the work. These problems can be alleviated if higher temperatures are used, as there is only one oxidation peak beyond the active-to-passive transition. Also, the passive-potential range is increased to more than 1000 mV, an observation made by Cheng and Luo[254] with ASTM A516-70 carbon steel. However, if sodium silicate is added, the passive current density (I₉pass) is further minimized and the applied potential increased, due to suppression of any additional oxidation peaks by the silicate ions. At 25°C, a solution of [0.01M Na₂SiO₃ + 0.1M NaHCO₃] produced a passive current density of ~1.4 to 1.5 μA/cm² over a potential range of ~80 to 870 mV. At 80°C, the current density is increased to ~4.1 to 4.4 μA/cm² over a smaller potential range of ~90 to 459 mV. However, because it was observed that silicates precipitate out of solution at higher temperatures, increasing the silicate content from 0.01M to 0.025M improved the stability of the solution substantially. The amount of passive current density was reduced slightly, but the potential range did not vary significantly.
The effects of silicate and bicarbonate ions on the polarization of 4340 steel in simulated seawater (3.5% NaCl) solution are shown in Figures 9.26 and 9.27. Like the two previous sections, the addition of sodium chloride into the solution decreases the passivity and the overall potential range of the electrochemical potentiodynamic scans. Also, the pitting potential ($E_{\text{pit}}$) decreased as well. However, unlike the potentiodynamic scans without 3.5% NaCl,
the $E_{corr}$ for 0.01M SiO$_3^{2-}$ in 3.5% NaCl was lower than the rest of the curves, including the 3.5% NaCl curve, at 25°C. This was true for higher temperatures as well. On the other hand, the potentiodynamic scans using simulated seawater only (i.e. – no additional ions) showed that the $E_{corr}$ value migrated to a more positive value as temperature was increased, while the $E_{corr}$’s of the bicarbonate-based solutions stayed near the same potential. Figure 9.28 shows the differences in corrosion rates of silicate and/or bicarbonate solutions in simulated seawater. It can be seen that high concentrations of bicarbonates, even when mixed with silicates, give relatively high corrosion rates as opposed to solutions that only contain silicates. A solution of simulated seawater gives a surprisingly higher corrosion rate at 80°C than does 0.01M SiO$_3^{2-}$ or [0.01M SiO$_3^{2-}$ + 0.1M HCO$_3^-$], indicating that the addition of silicates and/or low concentrations of bicarbonates are competing with chloride ions for electrons during the cathodic-to-anodic transition, limiting the amount of current that can be impressed on the surface of the sample and reducing the rate of oxidation with the base metal.

Figure 9.26. Potentiodynamic polarization curves of 4340 steel at 25°C in 3.5% NaCl solution with: (A) No additional ions, (B) 0.1M HCO$_3^-$, (C) 0.5M HCO$_3^-$, (D) 0.01M SiO$_3^{2-}$, (E) 0.01M SiO$_3^{2-}$ + 0.1M HCO$_3^-$, (F) 0.01M SiO$_3^{2-}$ + 0.5M HCO$_3^-$. 
Figure 9.27. Potentiodynamic polarization curves of 4340 steel at 65°C in 3.5% NaCl solution with: (A) No additional ions, (B) 0.1M HCO$_3^-$, (C) 0.5M HCO$_3^-$, (D) 0.01M SiO$_3^{2-}$, (E) 0.01M SiO$_3^{2-}$ + 0.1M HCO$_3^-$, (F) 0.01M SiO$_3^{2-}$ + 0.5M HCO$_3^-$. 

Figure 9.28. Corrosion rates of 4340 steel in 3.5% NaCl solution with: (A) 0.5M HCO$_3^-$, (B) 0.01M SiO$_3^{2-}$ + 0.5M HCO$_3^-$, (C) 0.1M HCO$_3^-$, (D) 0.01M SiO$_3^{2-}$ + 0.1M HCO$_3^-$, (E) No additional ions, (F) 0.01M SiO$_3^{2-}$. 

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9.4.5. Electrochemical Corrosion Effects in \( \text{SiO}_3^{2-} \) & \( \text{HCO}_3^- \) Solutions

In solutions containing bicarbonate ions, such as 0.5M & 1M \( \text{HCO}_3^- \), corrosion products on the surface of the specimen show a white, porous coating, regardless of chloride content. After the specimen is removed from solution, the coating turns golden yellow upon reaction with air, and when dry, turns a deep red/maroon color, similar to rusted steel. Figures 9.29 and 9.30 shows photographs of the corrosion products of two different specimens immersed in concentrated bicarbonate solutions.

This material has been identified in the literature\[255, 256\] as iron carbonate, \( \text{FeCO}_3 \), a porous, non-adherent structure that comes off easily in the presence of water or solution, as well as iron hydroxide, \( \text{Fe(OH)}_3 \), which gives it the reddish color. The material below this is a dull-gray, very-adherent layer identified as iron hydrogen carbonate (iron bicarbonate), \( \text{Fe(HCO}_3)_2 \).\[256\] This structure can be seen in Figure 9.30 (a), in between the reddish areas. These reaction products are most likely due to the formation of dissolved carbon dioxide (CO\(_2\)) gas in solution,\[252, 256, 257\] and subsequent formation of \( \text{FeCO}_3 \) and \( \text{Fe(HCO}_3)_2 \). This dissolved carbon dioxide pits the steel by attaching to the steel surface as small gas bubbles, which then induce a crevice around themselves, developing into a pit.\[256\] The pits on the surface are small near the center, but become very large near the edges of the sample. This is due to edge effects, caused by increased current density at these sites.\[258\] Figure 9.30 (b) shows a micrograph of a pit in the center of the sample. This type of pitting is not limited to just carbon steels, but has been known to occur in stainless steels as well.\[259\]

Figure 9.29. (a) Corrosion products on the surface of 4340 steel in 0.5M \( \text{HCO}_3^- \) in simulated seawater at +100 mV and 25°C; (b) micrograph of pit on exposed surface after removal of corrosion products from solution.

Figure 9.30. (a) Corrosion products on the surface of 4340 steel in 1M \( \text{HCO}_3^- \) in pure water at -110 mV; (b) micrograph of pit on exposed surface.

In solutions containing silicate and bicarbonate ions, pitting occurred in two different forms, depending on temperature. For a solution containing \([0.01\text{M SiO}_3^{2-} + 0.5\text{M HCO}_3^-]\) in 3.5% sodium chloride at 25°C, surface pits appeared round and randomly distributed. However, at 80°C in a seawater solution containing \([0.005\text{M SiO}_3^{2-} + \text{HCO}_3^-]\)
0.5M HCO$_3^-$], the pits appeared longitudinal and stringy, like “rows of very small pits.”[256] Figure 9.31 shows examples of these two observations. These types of pitting have been observed in the literature[256] using line pipe (carbon) steel in CO$_2$-containing brine solutions. Although the solutions used in this study were deaerated with nitrogen gas, the observation of this type of pitting suggests that bicarbonate ions were reduced to hydroxides and carbon dioxide gas as stated above, even in the presence of silicates. However, because the silicate concentration is low, and the temperature is high, the SiO$_3^{2-}$ ions reduce to silica gel (SiO$_2$) and precipitate from solution, allowing the steel surface to be attacked by the chloride ions and the dissolved CO$_2$ gas. This type of attack produces pitting, which can be disastrous in an industrial environment. This is the main reason why pipeline steels fail in the oil and gas industries.

Figure 9.31. Micrographs of exposed surfaces of 4340 steel specimens: (a) [0.01M SiO$_3^{2-}$ + 0.5M HCO$_3^-$] in simulated seawater at 25°C and +1.10 V; (b) [0.005M SiO$_3^{2-}$ + 0.5M HCO$_3^-$] in simulated seawater at 85°C and +44.7 mV.

X. IMMERSION CORROSION OF HIGH-STRENGTH STEELS

10.1. Summary of Immersion Corrosion of High-Strength Steels

The results of immersion corrosion tests in simulated 1X Yucca Mountain solution for Swellex Mn-24 Rock Bolt steel and AISI 4340 steel are presented below. For AISI 4340 steel, immersion corrosion rates in simulated 1X YM solution show that the steel corrodes at a rate > 2500 μm/yr at 75°C in aerated conditions when partially-immersed in solution, but corrodes < 0.5 μm/yr at 25°C in deaerated conditions when fully-immersed in solution. In nearly all cases, corrosion rates were higher at the partially-immersed positions than at the fully-immersed or vapor-immersed positions. For the ambient (static-air) conditions, rates stabilized at near-constant values of ~15 μm/yr when the coupons were suspended above the solution, and ~150 μm/yr for when the coupons were partially- and fully-immersed in the electrolyte. Pre-treatment of 4340 steel coupons using sodium silicate increased the corrosion resistance by a factor of 1.2 to 4.7 when immersed in 1X YM solutions. For Mn-24 steel, coupons at the half-immersed position corroded at the highest rate under both aerated and deaerated conditions in 1X YM solution. For deaerated conditions, Mn-24 steel corroded at a rate of 50.78 microns/yr at room temperature (25°C). For aerated conditions, the highest corrosion rate was 2598 microns/yr at 75°C.

10.2. Immersion Corrosion of AISI 4340 Steel in Simulated Yucca Mountain Solutions

Weight loss tests were conducted in simulated 1X Yucca Mountain solution at 25°C, 45°C and 75°C by bubbling compressed air or nitrogen gas into solution for a period of 10 days and 7 days, respectively. Additionally, weight loss tests were conducted at 20°C under a static air environment (i.e. – no purging of gas) in 1X Yucca Mountain solution for a period of 240 days. All solutions were clear and colorless prior to specimen immersion.

10.2.1. Immersion Corrosion under Aerated (Oxygenated) Conditions

In general, corrosion rates for the partially-immersed specimens were greater than both the vapor-immersed and fully-immersed specimens, at all temperatures under aerated conditions. This is due to concentration effects at the
vapor-solution interface caused by the reduction-oxidation (redox) reaction between the oxygen gas and the iron substrate. This redox reaction creates preferential anodes and cathodes above and below the water line, giving rise to higher corrosion rates than samples that are fully-immersed in solution or not immersed in solution.[62] These rates were generally lower than those obtained from the potentiodynamic experiments.

10.2.2. Immersion Corrosion under Deaerated (Nitrogenated) Conditions
Deaerated conditions produced corrosion rates much lower than those reported from electrochemical polarization at the same temperatures and solution concentration. However, it is well known that corrosion rates due to polarization always result in higher values than from weight loss tests.[62] Therefore, values obtained from electrochemical polarization can be considered to be conservative upper values. Table 10.1 shows the average immersion corrosion rates for AISI 4340 steel in simulated Yucca Mountain solution.

10.2.3. Immersion Corrosion under a Static Air Environment
For the 240-day experiment, weight loss measurements showed remarkably different values compared to the aerated and deaerated experiments. Because of the ambient conditions and lack of continuous gas purging, there were virtually no redox reactions taking place at the vapor-solution interface of the partially-immersed coupon. This produced corrosion rates of 148.6 μm/yr and 154.4 μm/yr at the fully-immersed and partially-immersed positions, which are very close to each other. However, a corrosion rate of 14.1 μm/yr was measured at the vapor-immersed position. This value is comparable to the average corrosion rate obtained at the vapor-immersed position at 25°C under deaerated conditions. These results indicate that under static conditions, the steel will corrode minimally without a steady supply of oxygen. Figure 10.1 shows the corrosion rate profile at different immersion positions in YM 1X solution at 20°C. Figure 10.2 shows a normalized mass loss profile under ambient conditions in simulated YM solution.

### Table 10.1. Average Immersion Corrosion Rates for AISI 4340 Steel in Simulated 1X Yucca Mountain Solution.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Environment (purging gas)</th>
<th>Position</th>
<th>Corrosion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Air</td>
<td>full immersion</td>
<td>340 μm/yr (13.4 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>Air</td>
<td>partial immersion</td>
<td>528 μm/yr (20.8 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>Air</td>
<td>vapor immersion</td>
<td>343 μm/yr (13.5 mpy)</td>
</tr>
<tr>
<td>45</td>
<td>Air</td>
<td>full immersion</td>
<td>532 μm/yr (20.9 mpy)</td>
</tr>
<tr>
<td>45</td>
<td>Air</td>
<td>partial immersion</td>
<td>1466 μm/yr (57.7 mpy)</td>
</tr>
<tr>
<td>45</td>
<td>Air</td>
<td>vapor immersion</td>
<td>524 μm/yr (20.6 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>Air</td>
<td>full immersion</td>
<td>685 μm/yr (27.0 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>Air</td>
<td>partial immersion</td>
<td>2567 μm/yr (101.1 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>Air</td>
<td>vapor immersion</td>
<td>927 μm/yr (36.5 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>N₂</td>
<td>full immersion</td>
<td>0.5 μm/yr (0.02 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>N₂</td>
<td>partial immersion</td>
<td>25.6 μm/yr (1.01 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>N₂</td>
<td>vapor immersion</td>
<td>16.7 μm/yr (0.66 mpy)</td>
</tr>
<tr>
<td>45</td>
<td>N₂</td>
<td>full immersion</td>
<td>4.4 μm/yr (0.17 mpy)</td>
</tr>
<tr>
<td>45</td>
<td>N₂</td>
<td>partial immersion</td>
<td>32.9 μm/yr (1.30 mpy)</td>
</tr>
<tr>
<td>45</td>
<td>N₂</td>
<td>vapor immersion</td>
<td>25.6 μm/yr (1.01 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>N₂</td>
<td>full immersion</td>
<td>20.6 μm/yr (0.81 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>N₂</td>
<td>partial immersion</td>
<td>80.1 μm/yr (3.15 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>N₂</td>
<td>vapor immersion</td>
<td>117.0 μm/yr (4.6 mpy)</td>
</tr>
<tr>
<td>20</td>
<td>None</td>
<td>full immersion</td>
<td>148.6 μm/yr (5.85 mpy)</td>
</tr>
<tr>
<td>20</td>
<td>None</td>
<td>partial immersion</td>
<td>154.4 μm/yr (6.08 mpy)</td>
</tr>
<tr>
<td>20</td>
<td>None</td>
<td>vapor immersion</td>
<td>14.1 μm/yr (0.56 mpy)</td>
</tr>
</tbody>
</table>
Corrosion rates of 4340 steel were also compared to the corrosion rates of Rock Bolt Carbon Steel. Yilmaz[62, 63] reported an average corrosion rate of ~45 μm/yr over a time period of 107 days for RBCS fully-immersed in 1X Yucca Mountain solution. For virtually the same amount of time – 110.5 days – the corrosion rate for 4340 steel was ~180 μm/yr, indicating that 4340 steel corrodes about four times as fast as ordinary medium carbon steels. Figure 10.3 shows a comparison of RBCS and 4340 steel fully-immersed in 1X YM solution over a period of ~110 days.
10.2.4. Immersion Corrosion Effects in Multi-Ionic Solutions

The corrosion products formed on the surface of the steel in ambient and aerated conditions were characterized using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) techniques. The different layers formed on the steel coupons consisted of a protective, thin film of Mg(OH)$_2$ with an outer layer consisting of two types of iron oxides – magnetite, Fe$_3$O$_4$, and lepidocrocite, FeO(OH). Figures 10.4 and 10.5 show SEM micrographs of the morphologies of the Mg(OH)$_2$ layer and the rust layers, respectively. Figure 10.6 shows the XRD spectra of the rust films formed on the substrate of the steel.

![Figure 10.3. Normalized mass loss profile of Rock Bolt Carbon Steel[62, 63] and AISI 4340 Steel, fully-immersed in 1X YM solution at 20°C.](image)

Figure 10.3. Normalized mass loss profile of Rock Bolt Carbon Steel[62, 63] and AISI 4340 Steel, fully-immersed in 1X YM solution at 20°C.

**Figure 10.4.** SEM micrograph showing the morphology of the Mg(OH)$_2$ layer formed on top of the steel sample after immersion experiments at 20°C.

**Figure 10.5.** SEM micrograph showing the morphology of the corrosion products formed on top of the steel sample after immersion experiments at 20°C.
10.3. Immersion Corrosion of “Pre-Treated” AISI 4340 Steel in Simulated Yucca Mountain Solutions

Weight loss tests were conducted using coupons of “pre-treated” 4340 steel at 25°C and 75°C under aerated conditions for a continuous period of 10 days. These coupons were soaked in 0.01M Na₂SiO₃ solution for 24 hours, and dried in an oven overnight. They were then immersed and tested in two different solutions – 3.5% NaCl solution and 1X Yucca Mountain solution. The results of these tests are presented below.

10.3.1. Effects of Temperature on Corrosion Rate
Table 10.2 shows the corrosion rates for AISI 4340 steel pre-treated with 0.01M Na₂SiO₃ and immersed in 3.5% NaCl and YM 1X solutions over a continuous period of 10 days. In each case, weight loss rates at 75°C were much higher than 25°C at all positions, with the exception of the fully-immersed position at 25°C in 3.5% NaCl solution, and the vapor-immersed position at 25°C in Yucca Mountain 1X solution. Both of these positions showed higher corrosion rates over 10 days of exposure than their counterparts at 75°C. However, the corrosion rates of the fully-immersed coupons differed by only 32.4 µm/yr, whereas the vapor-immersed coupons differed by 82.6 µm/yr, roughly 2.5 times higher. This is most likely due to concentration cell effects[62] from interaction with the rising oxygen in the air from the solution[258].
Table 10.2. Corrosion rates for AISI 4340 steel pre-treated with 0.01M Na₂SiO₃ under aerated (air) conditions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Environment (solution)</th>
<th>Position</th>
<th>Corrosion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3.5% NaCl</td>
<td>full immersion</td>
<td>517 μm/yr (20.4 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>3.5% NaCl</td>
<td>partial immersion</td>
<td>943 μm/yr (37.1 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>3.5% NaCl</td>
<td>vapor immersion</td>
<td>566 μm/yr (22.3 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>3.5% NaCl</td>
<td>full immersion</td>
<td>549 μm/yr (21.6 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>3.5% NaCl</td>
<td>partial immersion</td>
<td>1231 μm/yr (48.5 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>3.5% NaCl</td>
<td>vapor immersion</td>
<td>1145 μm/yr (45.1 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>YM 1X</td>
<td>full immersion</td>
<td>176 μm/yr (6.9 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>YM 1X</td>
<td>partial immersion</td>
<td>257 μm/yr (10.1 mpy)</td>
</tr>
<tr>
<td>25</td>
<td>YM 1X</td>
<td>vapor immersion</td>
<td>281 μm/yr (11.1 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>YM 1X</td>
<td>full immersion</td>
<td>236 μm/yr (9.3 mpy)</td>
</tr>
<tr>
<td>75</td>
<td>YM 1X</td>
<td>partial immersion</td>
<td>717 μm/yr (28.2 mpy)</td>
</tr>
</tbody>
</table>

10.3.2. Effects of Chloride Content on Corrosion Rate
The corrosion rates of pre-treated 4340 steel immersed in 3.5% NaCl and YM 1X solutions were presented in the previous section. It is clear from Table 10.2 that an increase in chlorides in solution increases the corrosion rate during immersion. This is evident from the photographs taken after the coupons were removed from the solutions. Figures 10.7 and 10.8 show the photographs.

Figure 10.7. Photographs of coupons after removal from 3.5% NaCl solution: (a) 25°C; (b) 75°C.

Figure 10.8. Photographs of coupons after removal from YM 1X solution: (a) 25°C; (b) 75°C.
As can be seen from the figures, the simulated seawater solution is much more aggressive than the Yucca Mountain solution, due to the increased chloride concentration. Yucca Mountain solution has approximately a 0.02 wt.% Cl\(^{-}\) concentration, whereas simulated seawater (3.5% NaCl) has a 2.2 wt.% Cl\(^{-}\) concentration – 110\% higher. Therefore, corrosion rates in simulated seawater should be at least 110\% greater than in Yucca Mountain solution. For all positions (at constant temperature) this is the case. Corrosion rates range from 172\% to 578\% higher in 3.5% NaCl than YM 1X solution. In Figure 10.7 (b), the coupon nearly severed in two during partial-immersion in 3.5% NaCl solution at 75°C due to this effect, and the vapor-immersed coupon at this same temperature is heavily damaged due to a combination of pitting and generalized corrosion.

10.3.3. Effects of Pre-treatment with 0.01M Na\(_2\)SiO\(_3\)

The effect of pre-treating 4340 steel coupons in 0.01M Na\(_2\)SiO\(_3\) solution prior to immersing them in YM 1X solution provided a significant decrease in the corrosion rate, as compared to no pre-treatment. For YM 1X solution only, corrosion rates decreased by a factor of 1.2 to 2.1 at 25°C, and 2.9 to 4.7 at 75°C. However, the coupons that were not pre-treated in 0.01M Na\(_2\)SiO\(_3\) solution were cleaned approximately every 48 hours, whereas the pre-treated coupons were left in solution for the full 10 days continuously. If the pre-treated coupons had been removed after 48 hours for cleaning, a better comparison could have been made for that exposure time. Therefore, one-to-one comparison of corrosion rate values from immersion in YM 1X waters should be taken as a conservative estimate.

10.4. Immersion Corrosion of Swellex Mn-24 Rock Bolt Steel in Simulated Yucca Mountain Solutions

In this section, standard laboratory immersion[260] mass loss results are presented for Mn-24 rock bolt steel under deaerated 1X YM solution at 25°C. Also, mass loss results are presented for Mn-24 in aerated (air) YM solution at 25°C and 75°C.

10.4.1. Immersion Corrosion in Deaerated 1X YM Solution

Standard immersion tests of Mn 24 rock bolt steel was done at 25°C for 353 hours. Corrosion rates for all the samples (fully-immersed, partially-immersed and non-immersed) in 1X YM solution at 25°C are given in Table 10.3. Normalized mass loss results are shown in Figure 10.9. Calculated corrosion rates are shown in Figure 10.10. Corrosion rates for half-immersed sample showed highest corrosion rate of 50.78 microns per year. Non-immersed sample showed corrosion rate of around 40 microns per year. Fully-immersed sample showed the lowest corrosion rate of 16.27 microns per year.
Table 10.3. Corrosion rates of Mn 24 under deaerated 1X YM water at 25°C

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Full</th>
<th>Half</th>
<th>None</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CR</td>
<td>CR</td>
<td>CR</td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>222</td>
<td>24.10</td>
<td>30.8</td>
<td>25.56</td>
</tr>
<tr>
<td>353</td>
<td>16.27</td>
<td>50.78</td>
<td>39.9</td>
</tr>
</tbody>
</table>

10.4.2. Immersion Corrosion in Aerated 1X YM Solution at 25°C

Corrosion rates of Mn24 in aerated (air) 1X YM water at 25°C for all the three specimens are given in Table 10.4. Normalized mass loss in grams is plotted in Figure 10.11. Normalized mass loss is shown to compare relative mass loss among three specimens. Corrosion rates are plotted in Figure 10.12. Similar to the deaerated, in aerated half-immersed showed the highest corrosion rate of around 634 microns per year. The corrosion rate for half-immersed is more than twelve times higher than that in de-aerated. Even the lowest corrosion rate of 265 microns per year observed for fully-immersed in aerated is more than sixteen times of de-aerated fully-immersed samples. Similar to the de-aerated conditions, in aerated conditions the corrosion rate for fully-immersed sample is increased and then decreased and then again increased. Lowest corrosion rate for the fully-immersed and highest corrosion rate for half-immersed is explained in next section.

![Figure 10.11. Normalized mass loss of Mn 24 at 25°C in aerated 1X YM-UNR water at 25°C.](image)

![Figure 10.12. Corrosion rates of Immersion tests samples in aerated 1X YM-UNR water at 25°C.](image)

Table 10.4. Corrosion rates of Mn 24 under aerated 1X YM water at 25°C

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Full</th>
<th>Half</th>
<th>None</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CR</td>
<td>CR</td>
<td>CR</td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>48</td>
<td>135.3</td>
<td>169.2</td>
<td>82.2</td>
</tr>
<tr>
<td>96</td>
<td>176.4</td>
<td>276.3</td>
<td>215.1</td>
</tr>
<tr>
<td>144</td>
<td>213.8</td>
<td>428.1</td>
<td>315.8</td>
</tr>
<tr>
<td>192</td>
<td>219.9</td>
<td>455.2</td>
<td>305.7</td>
</tr>
<tr>
<td>240</td>
<td>233.6</td>
<td>523.0</td>
<td>372.5</td>
</tr>
<tr>
<td>288</td>
<td>232.6</td>
<td>510.0</td>
<td>401.7</td>
</tr>
<tr>
<td>336</td>
<td>261.3</td>
<td>606.3</td>
<td>429.7</td>
</tr>
<tr>
<td>384</td>
<td>255.4</td>
<td>599.8</td>
<td>427.8</td>
</tr>
<tr>
<td>432</td>
<td>259.8</td>
<td>631.2</td>
<td>466.0</td>
</tr>
<tr>
<td>480</td>
<td>265.0</td>
<td>623.7</td>
<td>468.2</td>
</tr>
</tbody>
</table>
10.4.2. Immersion Corrosion in Aerated 1X YM Solution at 75°C

Aerated immersion corrosion experiments were done for 480 hours at 75°C. Similar to 25°C, at 75°C the highest corroded sample is also at the half-immersed position. Corrosion rates of Mn 24 under aerated (air) at 75°C are given in Table 10.5. Normalized mass loss is plotted in Figure 10.13. Corrosion rates are plotted in Figure 10.14. Analogous to the electrochemical corrosion experiments, corrosion rates in aerated (air) conditions are much higher than in the deaerated conditions.

The highest corrosion rate of 2598.4 microns per year was observed for the half-immersed sample, and the lowest corrosion rate was observed for fully-immersed sample of 885.3 microns per year. In the experiments, both in aerated and deaerated conditions at different temperatures, the half-immersed sample showed the highest corrosion rate due to the concentration cell effects. In aerated conditions, it is due to the oxygen concentration difference in and above the solution. In deaerated conditions, since all the oxygen is removed by purging nitrogen gas all the time, this concentration cell effect is due to the difference in temperature. Also, it may be due to the ionic concentration in and above the solution. Especially in aerated (air) conditions, due to oxygen concentration difference, areas with more oxygen became cathodic with respect to the other areas with less oxygen. Less oxygenated areas (below water line) became anodes. Hence, there is continuous corrosion in the half-immersed sample.

In the non-immersed sample, the corrosion rate was higher than the fully-immersed sample. This is due to water drops on the surface of metal in the vapor phase. Areas under the water drops act as anodes, due to less oxygen under the water at the iron surface, whereas the rest of the sample has abundant oxygen. Hence, this acts as the cathode, resulting in the reduction of oxygen to hydroxide. This kind of corrosion results in pitting on the surface of the sample. Three cleaned samples after the experiment at 75°C are shown in Figure 10.15. From the figure, it can be observed that the non-immersed sample underwent significant pitting corrosion, as well as the half-immersed sample. Pitting corrosion of iron under water droplets is shown in Figure 10.16. In the fully-immersed sample, the corrosion rate is lower than the other two samples, mostly due to the formation of un-soluble corrosion products like Fe₂O₃ on the surface of the metal, interrupting the corrosion process between metal and solution. Corrosion mechanisms for all three samples are shown in Figure 10.17.
Table 10.5. Corrosion rates of Mn 24 under aerated 1X YM water at 75°C

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Full</th>
<th>Half</th>
<th>None</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corrosion rate (μm/year)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>48</td>
<td>470.9</td>
<td>1934.3</td>
<td>828.7</td>
</tr>
<tr>
<td>96</td>
<td>475.1</td>
<td>2078.6</td>
<td>797.5</td>
</tr>
<tr>
<td>144</td>
<td>491.7</td>
<td>2060.3</td>
<td>858.6</td>
</tr>
<tr>
<td>192</td>
<td>688.6</td>
<td>2279.9</td>
<td>858.3</td>
</tr>
<tr>
<td>240</td>
<td>758.2</td>
<td>2472.7</td>
<td>980.0</td>
</tr>
<tr>
<td>288</td>
<td>828.5</td>
<td>2632.2</td>
<td>1140.7</td>
</tr>
<tr>
<td>336</td>
<td>845.9</td>
<td>2874.6</td>
<td>1271.9</td>
</tr>
<tr>
<td>384</td>
<td>856.2</td>
<td>2707.3</td>
<td>1194.8</td>
</tr>
<tr>
<td>432</td>
<td>899.8</td>
<td>2714.2</td>
<td>1179.2</td>
</tr>
<tr>
<td>480</td>
<td>885.3</td>
<td>2598.4</td>
<td>1134.6</td>
</tr>
</tbody>
</table>

Figure 10.15. Specimens after 480 hours at 75°C in aerated 1X YM water.

Figure 10.16. Corrosion mechanism of non-immersed samples in aerated 1X YM water [261].

Figure 10.17. Corrosion mechanism of immersion test samples in aerated 1X YM water.
10.4.3. Comparisons with Other Rock Bolt Materials

Among all the immersion corrosion experiments, the experiment at 75°C is most significant. Primarily, this test was done to compare the corrosion rate of Mn 24 with existing corrosion results under similar conditions for other rock bolt materials. Corrosion rates of Mn 24 along with corrosion rates of medium carbon steel [48] and AISI-SAE 4340 steel[83] are given in Table 10.6. Corrosion rates are plotted in Figure 10.18. From the Figure, it can be seen that for all the experiments irrespective of the metal, the corrosion mechanism is similar. In terms of the difference in oxygen concentration, the half-immersed sample showed the highest corrosion rate. The lowest corrosion rate of 200 microns per year is observed for medium carbon steel for the fully-immersed position. However, among all the alloys, Mn 24 showed the highest corrosion rate in all samples – full-, half- and non-immersed. This may be due to surface stresses in the Mn 24 steel, relative to the other alloys.

Table 10.6. Corrosion rate comparison in aerated 1X YM water at 75°C. [63, 262]

<table>
<thead>
<tr>
<th>Sample Position</th>
<th>MCS</th>
<th>Mn 24</th>
<th>4340</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μm/year</td>
<td>μm/year</td>
<td>μm/year</td>
</tr>
<tr>
<td>None</td>
<td>510</td>
<td>1135</td>
<td>927</td>
</tr>
<tr>
<td>Half</td>
<td>1000</td>
<td>2598</td>
<td>2567</td>
</tr>
<tr>
<td>Full</td>
<td>200</td>
<td>885</td>
<td>685</td>
</tr>
</tbody>
</table>

Figure 10.18. Corrosion rates of different rock bolt materials in aerated 1X YM water at 75°C.
XI. OXIDATION KINETICS AND CHARACTERIZATION OF HIGH-STRENGTH LOW-ALLOY STEELS

11.1. Summary of Oxidation Kinetics and Characterization Analyses of HSLA Steels

The high temperature oxidation kinetics of HSLA steels (Split Set Friction Rock Stabilizers (SS-46) and folded-tube Mn-24 steels were determined at 600°C, 675°C, 750°C, 775°C, 800°C, 825°C, and 900°C for a period of 100 hr. oxidation. Analysis of the oxidation weight gain curves of both SS-46 and Mn-24 shows that there are three distinct oxidation regions of the weight gain curves observed for both the rock bolt steels (SS-46 and Mn-24): (1) an incubation period, (2) a first oxidation region, where the steels follow a rate law given by \( y(\text{kg} \cdot m^{-2}) = k_0^{0.43} - k_0^{0.62} \) and (3) a parabolic oxidation regime thereafter. The rate constants determined for the first oxidation region for the steels show that the activation energies of both the HSLA steels is comparable at 82 kJ/mol for Mn-24 and 102 kJ/mol for SS-46. Parabolic oxidation rate constants for both the steels show considerable scatter on an Arrhenius plot. Activation energies of ~82 kJ/mol for Swellex Mn-24, and ~83 kJ/mol for SS-46, were determined based on calculated parabolic rate constants. The scatter on the rate constants is attributed to the observed blistering of oxide scales and breakaway oxidation. Similar discrepancies have been observed by Jha et.al [118] during oxidation studies in low alloy steels oxidized under high pressure oxidative environment from 700 to 1000°C for oxidation times between 10 to 250 hours. The oxidation mechanisms for these rock bolt materials showed the presence of a noticeable fraction of wustite (FeO), along with hematite (Fe₂O₃) and magnetite (Fe₃O₄) phases, which were confirmed by in-situ synchrotron micro-diffraction studies on SS-46 and Mn-24 at 800°C.

11.2. Weight Gain Kinetics and Microstructural Analyses of HSLA Steels

Long term oxidation studies were carried out on the two HSLA steels under pure oxygen atmospheres and at different holding temperatures for 100 hrs. The isothermal temperatures selected were 600°C, 675°C, 750°C, 775°C, 800°C, 825°C and 900°C. The weight gain versus time plots for Mn-24 and SS-46 are given in Figures 11.1 and 10.2, respectively. Although data were collected every 30 seconds, the figures show data for every 2 hours for clarity. As seen from Figure 11.1, oxidation rates are seen to increase with temperature. Oxidation kinetics at all temperatures (except at 600°C) show a period of fast and linear oxidation followed by a sluggish phase. At 750°C, the kinetics is slower than those at 675°C after about 22 hours. Oxidation kinetics at 775°C initially follows the 750°C kinetics closely, and then become higher than the low temperature kinetics, as expected. At 825 and 900°C, the oxidation kinetics are very fast right from the starting as compared to those observed at other temperatures and undergo breakaway oxidation after only a few hours of oxidation. At 900°C, breakaway oxidation is observed after about 30 hours and at 825°C it is observed after about 32 hours. Although Figure 11.1 suggests that the oxidation kinetics at 600°C looks constantly increasing, there is definite spalling of the oxide layer observed after about 37 hours on an expanded scale. A strong change in slope is observed at points where a break in the protective oxide film is encountered on a square of weight gain data per unit area vs. square root of time plot.

For SS-46 (Figure 11.2) oxidation rates show a consistent increase with increasing temperature. Oxidation rates at 600 and 675°C are slow initially up to about 22 hours as compared to the oxidation rates at temperatures from 750 to 900°C. Breakaway oxidation is observed for 900°C after only about 5.5 hours. Changes in slopes indicating oxide spalling are observed for 775°C at ~ 83.19 hours, for 800°C at ~ 50.56 hours and for 825°C at about 39 hours.

The experiments in this study were carried out by superposing a known irregularity in the temperature regime to create an isothermal temperature profile with a sinusoidal time varying perturbation. Such a perturbation can also be interpreted as a structured uncertainty in the desired temperature. A typical modulated temperature superimposed with the average isothermal temperature and weight percent gain for the SS46 sample (T = 750°C) is shown in the inset in Figure 11.2. Model-free calculation of activation energies based on modulated weight gains observed are found in references [263-265]. It is seen though, that activation energy calculation using the model free technique is quite dependent on the localized weight changes occurring in the small time period of modulations. The period of modulations chosen in all the experiments in this study was only 200 seconds whereas the total duration of each experiment was 100 hours. It is expected that temperature modulated thermogravimetry will be more relevant when conducting non-isothermal ramping experiments since the weight gain curves (depending upon the material) would display noticeable changes even with short time periods. Such an effect will be more pronounced depending upon
the heating rate of the experiment as well. For example, the oxidation curves of pure iron reported by Roy et al. [266] in their non-isothermal experiments reveal a steep slope of the weight gain per unit area. Therefore, in this study, the calculation of activation energy as well as oxidation kinetic parameters based only on the traditional analysis is emphasized.

For the oxidation kinetics experiments conducted for SS46 and Mn24 in this study, the oxidation regimes were typically divided into three parts: (1) initial stage oxidation region (that can be considered as incubation period for
lower temperature but is linear-type for higher temperature) (2) a first oxidation regime (time exponent of rate law varying from 0.40 to 0.63, depending upon material and temperature), and (3) a second oxidation regime following parabolic-type oxidation for longer oxidation time. A transient portion is observed between each of the regimes where the kinetics undergoes transition from one regime to another. A plot of log \((y/\text{kg.m}^2\cdot\text{s}^{-1})\) versus log \((t/\text{s})\) is shown in Figure 11.3 for Mn24 at 800°C. It is visually clear that during the initial stages of oxidation, the slope of \(\frac{\text{d}(\log y)}{\text{d}(\log t)}\) is relatively small. For SS46 it is 0.009 (600°C), 0.014 (675°C), 0.017 (750°C), 0.074 (775°C), 0.041 (800°C), 0.045 (825°C), and 0.015 (900°C) whereas for Mn24 it is 0.007 (600°C), 0.023 (675°C), 0.03 (750°C), 0.071 (775°C), 0.053 (800°C), 0.026 (825°C), and 0.033 (900°C). For the first oxidation regime, a rate law was determined for SS46 and Mn24 which conformed to the general form of equation 2.17. For SS46, the index of rate law varies from ~0.40 to ~0.65.

Figure 11.3. Log-Log plot of weight gain per unit surface area versus time for Mn-24 at 800°C showing the different oxidation regimes.

Figure 11.4. Kinetic parameters for Mn-24 at 800°C for the first oxidation regime \((t = 0.083 \text{ to 29.4 hr})\).

For Mn24, it varies from ~0.43 to ~0.63. A plot of \(\log y\) versus \(\log t\) for determining kinetic parameters based on the regression data is shown in Figure 11.4 for Mn24 at 800°C and the values for rate constant and index of rate law for
Longer oxidation periods (up to 100 hrs) showed the oxidation kinetics to follow parabolic oxidation for SS46 as well as Mn24. For SS46, parabolic regimes started at: ~52.36 hrs (600°C), ~65.7 hrs (675°C), ~22 hrs (750°C), ~13 hrs (775°C), ~65 hrs (800°C), ~68 hrs (825°C), and ~66.5 hrs (900°C); whereas for Mn24 the regimes started at: ~20.5 hrs (600°C), ~61 hrs (675°C), 19.5 hrs (750°C), ~34.5 hrs (775°C), ~45.8 hrs (800°C), ~50.6 hrs (825°C), and ~50 hrs (900°C). Parabolic rate constants for SS-46 and Mn-24 were calculated by plotting weight gain per unit surface area (y) versus root t as directed by Pieraggi et al. [189] and as discussed above. It has been shown by numerous researchers [116, 118-120, 267] that metals and alloys demonstrate oxidation rate laws that deviate from the classic Linear, Parabolic or Logarithmic rate equations. Sometimes a combination of these rate laws is also observed for a material over a period of oxidation times. Most of the times a period of transient faster kinetics is initially observed, succeeded by the steady state parabolic law. When the initial weight gain m does not contribute to steady state rate control because of initial growth of poorly protective oxide scale, Pieraggi [189] suggests using a plot of m versus t^{1/2} for evaluation. Pieraggi [189] clearly demonstrated that the use of a m^{1/2} versus t plot for analyses does not allow for the determination of the true parabolic constant kp nor the transient weight m. A combined plot of m versus t^{1/2} for SS-46 and Mn-24 is shown in Figure 11.7 for comparison and shows the value of kp = 9.99 x 10^{-9} kg^2.m^{-4}.s^{-1} for SS-46 at 750°C is an order of magnitude higher than that for Mn-24 which is kp = 1.717 x 10^{-10} kg^2.m^{-4}.s^{-1} suggesting that the long term oxidation resistance of Mn-24 at 750°C is better than that of SS-46. Although a higher kp value implies a higher activation energy and thus better oxidation resistance, overall comparison of kp values for the steels under study at different temperatures shows no definite suggestion of a better oxidation resistance of one material over the other since there is considerable scatter in the values (Figure 11.8). Although the linear regression fit to the parabolic rate constants is extremely low, based on calculated values, activation energy of Swellex Mn-24 was ~82 kJ/mol and that for SS-46 was found to be ~83 kJ/mol.

Oxidation studies carried out on carbon steels (compositions of 0.2 to 0.8%C) by Runk and Kim [268] in 100 Torr of dry oxygen gave activation energies of about 25.08 kJ/mol and 30.9 kJ/mol for the observed initial two-stage logarithmic oxidation kinetics and 104.2 kJ/mol the following parabolic kinetics respectively. These studies performed by Runk and Kim [268] were carried out at low temperatures in the range of 200-330°C. Malik and Whittle [269] also studied the oxidation behavior of Fe-C alloys, in the temperature range of 600-850°C in dry oxygen for about 24 hours. The parabolic rate constant for their Fe-0.1%C alloy at 850°C was calculated as 1.2 x 10^{-11} kg^2.m^{-4}.s^{-1} whereas the parabolic rate constant for the Swellex Mn-24 HSLA in this study with a comparable carbon content of 0.16%C was found to be 1.62 x 10^{-7} kg^2.m^{-4}.s^{-1} at 825°C. But it should be noted that the isothermal oxidation times for the two alloys vary considerably. The parabolic rate constants of Mn-24 (8.0 x 10^{-7} kg^2.m^{-4}.s^{-1}) and SS-46 (3.29 x 10^{-11} kg^2.m^{-4}.s^{-1}) at 900°C reported in this study are lower than those reported for a low carbon steel (containing Fe-0.04C-0.2Mn-0.02Si) (4.9 x 10^{-5} kg^2.m^{-4}.s^{-1}) at 1000°C oxidized in a 15% oxygen atmosphere by Abuluwefa et al.[270]. It has been reported previously that the formation of an oxide layer at between 600 to 850°C for carbon steels [269] follows parabolic kinetics for oxidation up to 24 hrs. However, in this study, the oxidation kinetics is divided into three parts as described above. It has been found that a rate law y = k' t^{1/2} holds for the first stage of oxidation followed by parabolic kinetics. The corresponding parabolic rate constant at 900°C for pure iron in air or oxygen atmosphere as reported by Chen and Yuen [271] is 2.94 x 10^{-5} kg^2.m^{-4}.s^{-1}; but it has to be noted that the experiments in this study to determine the parabolic oxidation constants were carried out for 100 hrs while typical oxidation experiments for pure iron do not exceed a few hours. Both the steels in this study are low carbon, low alloy steels. The carbon content of the steels ~0.1 wt% is well below the carbon contents that steels undergo decarburization[271].
Table 11.1. Rate constant (k) and order of reaction (n) for the first oxidation regime for HSLA steels.

<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)a</th>
<th>Activation energy (kJ/mol)b</th>
<th>k⁰ (kg² m⁻⁴ s⁻⁰.⁵²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn24</td>
<td>600</td>
<td>0.4257 0.52</td>
<td>2.675 x 10⁻⁴ 9.23 x 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>675</td>
<td>0.6272 0.52</td>
<td>9.097 x 10⁻⁵ 3.46 x 10⁻⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.5022 0.52</td>
<td>6.039 x 10⁻⁴ 4.85 x 10⁻⁴</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>775</td>
<td>0.573 0.52</td>
<td>3.375 x 10⁻⁴ 6.46 x 10⁻⁴</td>
<td></td>
<td>82.27 9.1</td>
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<tr>
<td></td>
<td>800</td>
<td>0.4343 0.52</td>
<td>2.011 x 10⁻³ 6.82 x 10⁻⁴</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>825</td>
<td>0.5734 0.52</td>
<td>8.235 x 10⁻⁴ 1.54 x 10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.4736 0.52</td>
<td>3.214 x 10⁻³ 1.75 x 10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS46</td>
<td>600</td>
<td>0.4568 0.52</td>
<td>9.328 x 10⁻⁵ 4.46 x 10⁻⁵</td>
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<td></td>
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<tr>
<td></td>
<td>675</td>
<td>0.6234 0.52</td>
<td>5.401 x 10⁻⁵ 2.05 x 10⁻⁴</td>
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</tr>
<tr>
<td></td>
<td>750</td>
<td>0.6342 0.52</td>
<td>1.405 x 10⁻⁴ 4.91 x 10⁻⁴</td>
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<tr>
<td></td>
<td>775</td>
<td>0.5679 0.52</td>
<td>3.856 x 10⁻⁴ 6.47 x 10⁻⁴</td>
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<td>101.58 65.91</td>
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<tr>
<td></td>
<td>825</td>
<td>0.4808 0.52</td>
<td>1.572 x 10⁻³ 7.58 x 10⁻⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.4046 0.52</td>
<td>7.236 x 10⁻³ 1.84 x 10⁻³</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 is actually different for the two temperatures (hence different units of k), to determine activation energy the index was assumed to be n = 0.52 for consistent units while plotting ln(k) versus 1/T.
Figures 11.5 and 11.6. Plot of ln \( k \) (kg m\(^{-2}\) s\(^{-0.52}\)) versus 1/T (K) for calculation of activation energy for Mn-24 and SS-46 for the first oxidation regime. The time exponent of rate law has been assumed to be 0.52 to maintain consistency of units.

Morphology of the oxides formed on the SS-46 and Mn-24 steels was studied under Scanning Electron Microscope. Figures 11.9 to 11.15 show the micrographs for Mn-24 at different temperatures. At 600\(^\circ\)C, both steels showed uniform grains all over the surface.

At 600\(^\circ\)C (Figure 11.9) a single layered smooth oxide scale was observed on the Mn-24, varying in thickness from \(~95.7\) m at its thinnest and \(~145\) m at its thickest after 100 hours of isothermal oxic holding. This oxide layer on
Mn24 showed greater porosity as compared to that seen in the SS46 oxide. The oxide layer on Mn24 seemed to have pores at the alloy-oxide interface and at 675°C there seemed to be partial detachment of the oxide from the base alloy as also cracks running inside the layer itself, as seen in Figure 11.10. Larger grains were observed in the interior of the alloy as compared to the ones found near the oxide layer at this temperature. The nominal composition of the oxide layer on Mn24 at 600°C was found to be Fe (75.73 wt%, 47.60 at%) and O (23.73 wt%, 52.05 at%) showing that the oxide is primarily composed of hematite and some retained wustite. The nominal composition of the oxide layer on Mn24 oxidized at 675°C is Fe (72.76 wt%, 44.06 at%) and O (26.14 wt%, 55.26 at%) also suggesting a mixture of hematite and wustite.

For Mn24 oxidized at 800°C three distinct layers are observed: an innermost layer of wustite (FeO), an intermediate layer of magnetite (Fe3O4) mixed with some amounts of Fe2O3 and the outermost layer rich in oxygen of hematite (Fe2O3). A smooth seam-like layer is also observed between the magnetite and hematite which is believed to be a transition layer composed mostly of hematite with some amount of magnetite giving it a distinct look. Details are given in Figure 11.11 (a). The approximate thickness of the layers measured on Mn-24 oxidized at 800°C was: FeO—30.4μm, Fe3O4—106μm, Fe2O3—varied between 160 to 167μm.

Figure 11.12 shows the single layer oxide layer formed on SS-46 at 600°C. A thickness of 33μm to ~45μm was observed at this temperature. Superimposed EDS results show the presence of single-layered hematite (Fe2O3). The oxide layer on SS46 oxidized at 675°C disintegrated when the sample was taken out of the sample pan after the experiment. The base alloy seemed to be intact but the oxide broke. EDS results on this broken oxide suggest the presence of a mixture of hematite and magnetite, as shown in Figure 11.13. For the alloy oxidized at 750°C, EDS line scan is shown in Figure 11.14. The nominal compositions of the metal oxide interface for SS46 oxidized at 750°C is Fe (78.99 wt%, 52.3 at%), O (20.49 wt%, 47.35 at%), and Mn (0.52 wt%, 0.35 at%). The oxide thickness varied between 0.871 μm to 1.5 μm. The 100-hour SS46 sample seemed to stick to the sample pan and when it was pulled out the oxide layer broke from the substrate but did not disintegrate.

Figure 11.7. A plot of y versus t^{0.5} for SS46 and Mn24 to show the long term parabolic oxidation behavior at 750°C. The parabolic rate constant of Swellex Mn-24 is an order of magnitude lower than SS46.
Figure 11.8. A plot of $\ln k_p (\text{kg.m}^{-2}.\text{s}^{-1})$ versus $1/T$ (K) to determine the activation energy for (a) Mn-24 and (b) SS-46 for the second oxidation regime. Scatter in temperature dependence of the parabolic constants on the Arrhenius plot is attributed to oxide-scale failure and the formation of different oxides[271].

For SS-46 oxidized at 800°C, the micrograph in Figure 11.15 shows the presence of double layers of hematite. Wustite is found in the cracks of the oxide layer. The separated layer is rich in hematite and has some magnetite. As the oxide layer cracks and separates, oxygen enters through the cracks and oxidation to hematite is favored. The inner hematite layer on SS46 was ~35.2 μm and the outer layer was ~133 to 143.2 μm in thickness.
Figure 11.9. SEM micrograph of Mn-24 at 600°C. Porosity at the scale-alloy interface is observed.

Figure 11.10. SEM micrograph of Mn-24 at 675°C shows partial detachment of the oxide from alloy either purely because of internal stresses or as a result of epoxy shrinkage during mounting.

Figure 11.11. (a) Three distinct layers in the oxide scale observed on Mn-24 after 100 hr oxidation at 800°C. (b) Synchrotron x-ray micro-diffraction confirmed the presence of hematite, magnetite and wustite layers from L to R. The scale formed on this alloy is thicker than SS46.
Figure 11.12. SEM micrograph of SS-46 oxidized at 600°C showing a porosity free, adherent oxide scale of Fe₂O₃.

Figure 11.13. SEM micrograph and EDS spot analyses on SS-46 at 675°C showing hematite formation.
The presence of the aforesaid oxide layers on Mn-24 and SS-46 samples oxidized at 800°C was confirmed with Synchrotron white beam x-ray micro-diffraction, the results for which are shown in Figures 11.11 and 11.15 respectively. The samples were scanned under a 1 μm size polychromatic beam with a 2.5 μm step size and a Laue diffraction pattern was collected at each step and indexed for phase identification. No diffraction pattern was observed for magnetite since it is believed to be extremely fine grained. It is believed to be formed with a very fine nanometer-size grain structure compared to the micrometric size of the wustite and hematite grains. The distribution of magnetite is probably in the dark region where no Bragg peak is observed between the iron and the hematite. Presence of magnetite can be confirmed only after performing a depth-profile analysis of the oxidized sample.

Scale structures found on steels vary considerably from the well established scale structures that form on pure iron [272-275]. Although pure iron sports a three layered oxide structure with wustite being the thickest innermost layer, under normal pressure Fe$_{1-x}$O is metastable below 570°C (~843 K) and decomposes to metallic iron and magnetite[276]. It has not been reported to be a predominant oxide layer during long term oxidation[277]. Chen and Yuen [271] have described the formation of blisters and different layered scale structures very well. Stresses due to different diffusion coefficients of iron and oxygen, different thermal expansion coefficients of the oxide scale and the substrate and the plasticity of the oxide scale are factors causing blistering of the scale. Once the scale detaches from the base alloy, the iron rich wustite formed near the substrate is oxidized to higher oxides after long term oxidation [271, 273, 274]. The pseudomorphic conversion of wustite to hematite is also thermodynamically favored involving internal atomic arrangements in the dry state [277]. The process usually takes place at higher temperatures. The presence of a thin layer of wustite is also a result of the very slow cooling rate of the samples [278].

Also, powder x-ray diffraction of the oxide layer at 900°C (9 hr oxidation times) showed the presence of wustite in noticeable fraction although the pattern was predominantly hematite and magnetite (Figure 11.16). In-situ low angle x-ray diffraction on the oxidized samples would yield a better understanding of the different oxide phases as they form.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt. %</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>79</td>
<td>52</td>
</tr>
<tr>
<td>O</td>
<td>20</td>
<td>47</td>
</tr>
<tr>
<td>Mn</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 11.14. EDS line scan on SS-46 oxidized at 750°C. The micrograph also shows the globular morphology of the oxide.
Figure 11.15. Oxide layers on SS46 at 800°C. (a) Three distinct layers in the oxide scale observed after 100 hr oxidation; (b) L to R: Wustite, possibly magnetite and hematite layers are identified based on the EDAX results and validated by synchrotron x-ray micro-diffraction.

Figure 11.16. X-ray Diffraction Pattern of as-received SS-46 sample and after oxidation at 900°C. The oxidized sample shows predominantly hematite and magnetite with noticeable amounts of wustite.
XII. SUMMARY & CONCLUSIONS

The corrosion rates of different steels and Alloy 22 proposed for use in the Yucca Mountain Nuclear Waste Repository have been determined by various methods. These include electrochemical potentiodynamic polarization, dry/deliquescent salt tests and weight loss methods in various solutions, such as simulated YM waters, different concentrations of silicates and bicarbonates (with and without 3.5% NaCl), solutions with high concentrations of corrosion products and dry salt mixtures. In addition, high-temperature oxidation kinetics were performed on Alloy 22, Ni-base superalloys and HSLA steels using thermogravimetric analysis (TGA) to determine the kinetics parameters and activation energies of these materials. Important findings for the YM project are presented below:

CORROSION BEHAVIOR OF ALLOY 22

The corrosion rates of Alloy 22 using potentiodynamic polarization at different temperatures and concentrations of YM waters increased as the temperature increased for both aerated and deaerated conditions. For 100X YM solution, the corrosion rate increased 1.55 times (76 to 118 μm/yr) from 25°C to 45°C, whereas it increased 1.19 times (from 141 to 168μm/yr) in the temperature ranges of 65°C to 90°C. Corrosion rates in aerated electrolyte were less than those of the deaerated due to the formation of a more protective, passive oxide film. As the electrolyte concentration increased the corrosion rate of Alloy 22 increased more significantly in the deaerated condition. For welded Alloy 22, results show that the overall corrosion rate of the weld specimen is higher than that of the base metal for the as-welded condition. However, the heat-treated condition revealed that the corrosion rate between base and welded specimens was comparable. 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. The microstructure of the corroded, welded sample showed attacks on the dendritic region for the as-weld and also for the heat treated specimens. In simulated seawater (3.5% NaCl) at 25°C under deaerated conditions, Alloy 22 showed a wide range of passivation, as well as a low corrosion rate of 8.7 microns per year. This corrosion rate was slightly higher than in solutions containing “corrosion products” that could come in contact with the waste containment structure. Of the eight different solutions that were tested, Fe³⁺ solution showed the highest corrosion rate at ~5 μm/yr at 90°C. However, a mixture of all the corrosion products in solution showed a corrosion rate 9X higher, at ~54 μm/yr at 60°C. XPS depth profile analysis of Alloy 22 in mixed solution at 60°C showed thin layers of Ni-, Cr- and Mo-oxides. XPS analysis after cyclic polarization in ferric solution at 90°C also showed a multi-oxide layer. This could be due to availability of ions in solution and oxygen from the purging gas. Approximately 340nm of iron oxide was formed as the top oxide layer. Other oxide layers were produced underneath with thicknesses of 40nm (Ni) and 60nm (Cr, Mo), respectively. Alloy 22 was not affected by either dry or deliquescent salts.

CORROSION BEHAVIOR OF HSLA STEELS

The corrosion behavior of different High-Strength Low-Alloy (HSLA) steels – Swellex Premium, Swellex Standard, Swellex Manganese and Friction-type Rock Bolt steel – was investigated as a function of temperature and concentration from 25°C to 90°C in simulated YM electrolyte and simulated seawater (3.5% NaCl) under aerated and deaerated conditions, as well as in various “corroded solutions” and dry/deliquescent salt situations. The corrosion rates of FRS steel in 1X and 10X YM solution ranged from ~30 to 200 μm/yr under deaeration, and from 150 to 1600 μm/yr under aeration. For 100X YM solution, corrosion rates peaked at ~2400 μm/yr under aerated conditions.

The electrochemical corrosion behavior of Swellex Mn 24 rock bolt in YM water was much higher under aeration than deaeration. Corrosion rates from 25°C to 90°C in dilute (1X) YM water under deaerated conditions ranged from 30 μm/yr to 227 μm/yr, and in aerated conditions ranged from 243 μm/yr to 2269 μm/yr. Among all types of YM solutions, the highest corrosion rate of 429 μm/yr was observed in BSW water at 30°C. At 90°C, the highest corrosion rate of 562 μm/yr was observed in SCW water and the second highest corrosion rate was observed in 1X YM water. The calculated passive dissolution rate in YM water after 10,000 years is 9 x 10^5 μm/yr, whereas in J-13 well water, the dissolution rate is 2.2 x 10^7 μm/yr. It seems that nitrates present in J-13 water are much better at inhibiting corrosion than silicates in YM water. However, in simulated seawater, DFWE Swellex rock bolt steel showed high corrosion rates of ~40 μm/yr, as well as no passivation, due to the presence of chlorides in the solution. At both 60°C and 90°C, Mn 24 steel showed the lowest corrosion rate in 1X YM water under aerated conditions using compressed air. Additionally, it was observed that the passive layer formed on the surface at a potential of -
0.5V under de-aerated 1X YM water from potentiostatic polarization is a thick, porous SiO2-layer. Due to the effect of cold working, this passive layer slowly disappears with an increase in the percentage of cold working the material prior to testing.

In dry salt conditions at 200°C, Mn 24 rock bolt showed significant pitting corrosion, due to presence of chlorides. All other alloys (304L SS, 316L SS, and Inconel 825) including Alloy 22 showed no corrosion. In deliquescent salt test at 200°C with Mn 24 metal coupon on top of salt, the Mn 24 metal coupon corroded badly due to galvanic corrosion.

Stellite steels were also tested using traditional weight loss methods by immersion in YM electrolyte. For all de-aerated and aerated immersion tests, the half-immersed sample under aerated conditions showed the highest corrosion rates: 624 μm/yr at 25°C & 2598 μm/yr at 75°C. These high rates were due to the oxygen concentration cell effects at the vapor-solution interface.

CORROSION BEHAVIOR OF AISI-SAE 4340 STEEL

The average corrosion rates of AISI 4340 steel in simulated Yucca Mountain solutions under deaerated conditions using potentiodynamic polarization increased as temperature increased from 25°C to 90°C for 1X and 10X concentrations. In 100X solution, average values peaked at 45°C with a maximum of ~300 μm/yr. For aerated conditions, corrosion rates peaked at 75°C in 1X and 10X concentrations, with a maximum of ~2200 μm/yr at 65°C in 100X solution. This high corrosion rate is similar to the values obtained by Rahman[244] for ASTM A607 steel – 2,182 μm/yr at 55°C in 100X YM water, and 2,393 μm/yr at 65°C. In all cases, the corrosion rates decreased as the temperature increased beyond the maximum value in simulated YM solutions.

Potentiodynamic polarization was also used under deaerated conditions to determine the corrosion rates and passivity behavior of 4340 steel using different combinations of sodium silicate (Na2SiO3) and sodium bicarbonate (NaHCO3), in both pure water and simulated seawater (3.5% NaCl). These experiments were carried out to examine the potential inhibiting properties of the silicate and/or bicarbonate ions on the surface of the steel. For the silicate/bicarbonate experiments, results indicate that the steel corrodes less than 70 μm/yr in solutions containing only sodium silicate, but corrodes more than 2,000 μm/yr in solutions containing only sodium bicarbonate. Rate values containing various mixtures of each constituent were in between. The addition of 3.5% NaCl decreased the average corrosion rate values, as well as the overall passive behavior, when compared to silicate/bicarbonate solutions without a significant chloride presence.

Immersion corrosion under simulated 1X YM solution showed that the steel corrodes at a rate greater than 2500 μm/yr at 75°C in aerated conditions when partially-immersed in solution, but corrodes less than 0.5 μm/yr at 25°C in deaerated conditions when fully-immersed in solution. In nearly all cases, corrosion rates were higher for samples at the partially-immersed positions than at the fully-immersed or vapor-immersed positions. For conditions involving a static-air environment, rates stabilized at near-constant values of ~15 μm/yr when the coupons were suspended above the solution, and ~150 μm/yr when the coupons were partially- and fully-immersed in the electrolyte. Also, 4340 steel corrodes 4X as fast (~180 μm/yr) as Rock Bolt Carbon Steel in the same environment.[48, 63] Pre-treatment by immersion in sodium silicate prior to testing increased the corrosion resistance of the steel coupons by a factor of 1.2 to 4.7 when immersed in aerated 1X YM solution.

HIGH-TEMPERATURE OXIDATION KINETICS

High-temperature oxidation kinetics and associated characterization of three Ni-base superalloys showed two distinct regimes, namely the initial transient period of extremely fast kinetics and the parabolic oxidation regime. HSLA rock bolt steels on the other hand showed three distinct regions, namely the initial incubation period, the first oxidation regime (time exponent of rate law varying from 0.40 to 0.63, depending upon material and temperature), and the second oxidation regime following parabolic-type oxidation for longer oxidation times. For the Ni-base superalloys, parabolic rate constant values increased from ~10^-13 to 10^-9 with increasing temperature, and activation energies increased from 232 kJ/mol for Alloy-282 to 289 kJ/mol for Alloy-263. Alloy 22 showed an activation energy near the middle at 263 kJ/mol. A plot of $k_p$ as a function of (1/T) shows Alloy-282 to have better oxidation resistance up to 980°C, but when activation energies over the whole temperature range are calculated, Alloy-263 shows the best average oxidation resistance. This is due to high amounts of Cr, Co and Ti in the alloy matrix.
Cobalt and titanium are known to improve the oxidation resistance marginally, and titanium is known to promote the formation of Cr$_2$O$_3$. This is suggested to be the reason for the highest oxidation resistance of Alloy-263 amongst the three superalloys. For the HSLA steels, rate constants determined for the first oxidation region show that the activation energies of both steels is comparable at 82 kJ/mol for Mn24 and 102 kJ/mol for SS46. For the parabolic oxidation regime, activation energies of \( \sim 82 \) kJ/mol for Swellex Mn-24 and \( \sim 83 \) kJ/mol for SS-46 were determined based on calculated parabolic rate constants. The scatter on the rate constants is attributed to the observed blistering of oxide scales and breakaway oxidation. Similar discrepancies have been observed by Jha et al. [118] during oxidation studies in low alloy steels oxidized under high pressure oxidative environment from 700 to 1000°C for oxidation times between 10 to 250 hours. The oxidation mechanisms for these rock bolt materials showed the presence of a noticeable fraction of wüstite (FeO), along with hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) phases, which was confirmed by in-situ synchrotron micro-diffraction studies at 800°C. Tables 12.1 and 12.2, as well as Figure 12.1, show the parabolic rate constants and activation energies for the Ni-base superalloys and HSLA steels, respectively. Table 12.3 shows the amount of material converted to oxide after exposure at different times for these materials.
Table 12.1. Parabolic rate constants for Ni-base superalloys at different temperatures\(^5\).

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Rate constant (k) (kg m(^{-2})s(^{-1}))</th>
<th>Activation energy (kJ/mol)</th>
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</thead>
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<td>(5.04 \times 10^{-36})</td>
<td></td>
</tr>
<tr>
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</tr>
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<td>900</td>
<td>(1.30 \times 10^{-11})</td>
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</tr>
<tr>
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<td>980</td>
<td>(5.83 \times 10^{-10})</td>
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</tr>
<tr>
<td></td>
<td>1100</td>
<td>(7.13 \times 10^{-9})</td>
<td></td>
</tr>
<tr>
<td>Alloy-22</td>
<td>100</td>
<td>(4.41 \times 10^{-38})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>(1.53 \times 10^{-29})</td>
<td></td>
</tr>
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<td></td>
<td>300</td>
<td>(5.55 \times 10^{-24})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>(3.55 \times 10^{-17})</td>
<td>288.65</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>(1.7 \times 10^{-13})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>(2.35 \times 10^{-11})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>(1.06 \times 10^{-10})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>(7.86 \times 10^{-10})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>(7.97 \times 10^{-9})</td>
<td></td>
</tr>
<tr>
<td>Alloy-263</td>
<td>100</td>
<td>(1.63 \times 10^{-36})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>(8.22 \times 10^{-29})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>(8.50 \times 10^{-24})</td>
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<td></td>
<td>700</td>
<td>(2.54 \times 10^{-12})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>(1.37 \times 10^{-11})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>(1.86 \times 10^{-10})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>(8.28 \times 10^{-10})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>(9.94 \times 10^{-9})</td>
<td></td>
</tr>
</tbody>
</table>

\(^5\) Calculations for low temperatures (100, 200, 300 and 500°C) done by assuming that the same oxidation rate laws exist at these temperatures as those at higher temperatures.
Table 12.2. Parabolic rate constants for HSLA steels at different temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Rate constant (k) (kg m(^{-2})s(^{-1}))</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-24</td>
<td>900</td>
<td>8.0 x 10(^{-7})</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>825</td>
<td>1.62 x 10(^{-7})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.4 x 10(^{-9})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>775</td>
<td>6.01 x 10(^{-9})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>1.72 x 10(^{-10})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>675</td>
<td>1.23 x 10(^{-9})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>4.01 x 10(^{-8})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
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</tr>
<tr>
<td></td>
<td>300</td>
<td>3.60 x 10(^{-12})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>9.59 x 10(^{-14})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3.67 x 10(^{-16})</td>
<td></td>
</tr>
<tr>
<td>SS-46</td>
<td>900</td>
<td>3.29 x 10(^{-7})</td>
<td>83</td>
</tr>
<tr>
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<td>825</td>
<td>7.52 x 10(^{-9})</td>
<td></td>
</tr>
<tr>
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<td>800</td>
<td>1.39 x 10(^{-8})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>775</td>
<td>4.22 x 10(^{-8})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>9.99 x 10(^{-9})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>675</td>
<td>4.32 x 10(^{-9})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>7.70 x 10(^{-9})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>7.60 x 10(^{-10})</td>
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<td>8.48 x 10(^{-12})</td>
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<tr>
<td></td>
<td>100</td>
<td>7.63 x 10(^{-16})</td>
<td></td>
</tr>
</tbody>
</table>

\(^6\) Calculations for low temperatures (100, 200, 300 and 500°C) done by assuming that the same oxidation rate laws exist at these temperatures as those at higher temperatures.
Table 12.3. Amount of material converted to oxide after exposure at different times.

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Rate constant ( (k_p) ) (kg(^2)m(^{-4})s(^{-1}))</th>
<th>Weight loss (kg/m(^2)) ( t = 1 ) year</th>
<th>Weight loss (kg/m(^2)) ( t = 10 ) years</th>
<th>Weight loss (kg/m(^2)) ( t = 100 ) years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy-22</td>
<td>900</td>
<td>1.30 x 10(^{-11})</td>
<td>0.02</td>
<td>0.06</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>5.63 x 10(^{-17})</td>
<td>4.21 x 10(^{-5})</td>
<td>1.33 x 10(^{-4})</td>
<td>4.21 x 10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.04 x 10(^{-28})</td>
<td>9.80 x 10(^{-11})</td>
<td>3.09 x 10(^{-10})</td>
<td>9.79 x 10(^{-10})</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5.04 x 10(^{-36})</td>
<td>1.26 x 10(^{-14})</td>
<td>3.99 x 10(^{-14})</td>
<td>1.26 x 10(^{-13})</td>
</tr>
<tr>
<td>Alloy-263</td>
<td>900</td>
<td>1.06 x 10(^{-10})</td>
<td>0.06</td>
<td>0.18</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3.55 x 10(^{-17})</td>
<td>3.35 x 10(^{-5})</td>
<td>1.06 x 10(^{-4})</td>
<td>3.35 x 10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.53 x 10(^{-29})</td>
<td>2.20 x 10(^{-11})</td>
<td>6.95 x 10(^{-11})</td>
<td>2.19 x 10(^{-10})</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>4.41 x 10(^{-38})</td>
<td>1.18 x 10(^{-15})</td>
<td>3.72 x 10(^{-15})</td>
<td>1.18 x 10(^{-14})</td>
</tr>
<tr>
<td>Alloy-282</td>
<td>900</td>
<td>1.86 x 10(^{-10})</td>
<td>0.07</td>
<td>0.24</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1.17 x 10(^{-17})</td>
<td>1.92 x 10(^{-5})</td>
<td>6.07 x 10(^{-5})</td>
<td>1.92 x 10(^{-4})</td>
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<tr>
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<td>200</td>
<td>8.22 x 10(^{-29})</td>
<td>5.09 x 10(^{-11})</td>
<td>1.61 x 10(^{-10})</td>
<td>5.09 x 10(^{-10})</td>
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<tr>
<td></td>
<td>100</td>
<td>1.63 x 10(^{-36})</td>
<td>7.16 x 10(^{-15})</td>
<td>2.27 x 10(^{-14})</td>
<td>7.17 x 10(^{-14})</td>
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<td>Mn-24</td>
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<td>8.00 x 10(^{-7})</td>
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<td>15.88</td>
<td>50.23</td>
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<td>0.23</td>
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<td>9.59 x 10(^{-14})</td>
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<td>1.08 x 10(^{-3})</td>
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<td>3.22</td>
<td>10.18</td>
<td>32.21</td>
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<td>1.77</td>
<td>5.61</td>
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<td>4.91 x 10(^{-4})</td>
<td>1.55 x 10(^{-3})</td>
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</table>
REFERENCES


5. Certificate of Tests-Republic Engineered Products: Massillon, OH.


106. Hladky, K., L.M. Callow, and J.L. Dowson, in Revised Manuscript. 1980: Corrosion and Protection Centre, UMIST, Manchester M60 1QD.
123. Wright, I.G. 1972, Metal and Ceramics information center.


APPENDIX

Polarization Plots and Immersion Corrosion Rates for AISI-SAE 4340 Steel in Simulated Yucca Mountain Solutions and Silicate/Bicarbonate Solutions
Figure A1. Potentiodynamic polarization plot of 4340 steel as a function of concentration at 75°C in aerated, simulated Yucca Mountain solution.

Figure A2. Potentiodynamic polarization plot of 4340 steel as a function of concentration at 90°C in aerated, simulated Yucca Mountain solution.
Figure A3. Potentiodynamic polarization plot of 4340 steel as a function of concentration at 75°C in deaerated, simulated Yucca Mountain solution.

Figure A4. Potentiodynamic polarization plot of 4340 steel as a function of concentration at 90°C in deaerated, simulated Yucca Mountain solution.
Figure A5. Corrosion rate profiles of AISI 4340 steel at different immersion positions in 1X YM solution at 25°C.

Figure A6. Corrosion rate profiles of AISI 4340 steel at different immersion positions in 1X YM solution at 45°C.
Figure A7. Corrosion rate profiles of AISI 4340 steel at different immersion positions in 1X YM solution at 75°C.

Figure A8. Effect of silicate ions on passivity at 25°C in pure water.
Figure A9. Effect of silicate ions on passivity at 80°C in pure water.

Figure A10. Effect of bicarbonate ions on passivity at 25°C in simulated seawater.
Figure A11. Potentiodynamic polarization curves of 4340 Steel at 45°C in simulated seawater: (A) No additional ions, (B) 0.1M HCO$_3^-$, (C) 0.5M HCO$_3^-$, (D) 0.01M SiO$_3^{2-}$, (E) 0.01M SiO$_3^{2-}$ + 0.1M HCO$_3^-$, (F) 0.01M SiO$_3^{2-}$ + 0.5M HCO$_3^-$. 

Figure A12. Potentiodynamic polarization curves of 4340 Steel at 80°C in simulated seawater: (A) No additional ions, (B) 0.1M HCO$_3^-$, (C) 0.5M HCO$_3^-$, (D) 0.01M SiO$_3^{2-}$, (E) 0.01M SiO$_3^{2-}$ + 0.1M HCO$_3^-$, (F) 0.01M SiO$_3^{2-}$ + 0.5M HCO$_3^-$. 

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Figure A13. Representative potentiodynamic scans showing the effects of temperature: 1M NaHCO$_3$ in pure water.

Figure A14. Representative potentiodynamic scans showing the effects of temperature: 1M NaHCO$_3$ in simulated seawater.
Figure A15. Representative potentiodynamic scans showing the effects of temperature: 0.5M NaHCO$_3$ in simulated seawater.

Figure A16. Representative potentiodynamic scans showing the effects of temperature: 0.1M NaHCO$_3$ in pure water.
Figure A17. Representative potentiodynamic scans showing the effects of temperature: 0.1M NaHCO₃ in simulated seawater.

Figure A18. Representative potentiodynamic scans showing the effects of temperature: 0.005M Na₂SiO₃ in pure water.
Figure A19. Representative potentiodynamic scans showing the effects of temperature: 0.005M Na₂SiO₃ in simulated seawater.

Figure A20. Representative potentiodynamic scans showing the effects of temperature: 0.01M Na₂SiO₃ in pure water.
Figure A21. Representative potentiodynamic scans showing the effects of temperature: 0.01M Na$_2$SiO$_3$ in simulated seawater.

Figure A22. Representative potentiodynamic scans showing the effects of temperature: 0.025M Na$_2$SiO$_3$ in pure water.
Figure A23. Representative potentiodynamic scans showing the effects of temperature: 0.025M Na$_2$SiO$_3$ in simulated seawater.

Figure A24. Representative potentiodynamic scans showing the effects of temperature: [0.005M Na$_2$SiO$_3$ + 0.5M NaHCO$_3$] in pure water.
Figure A25. Representative potentiodynamic scans showing the effects of temperature: [0.005M Na$_2$SiO$_3$ + 0.5M NaHCO$_3$] in simulated seawater.

Figure A26. Representative potentiodynamic scans showing the effects of temperature: [0.01M Na$_2$SiO$_3$ + 0.5M NaHCO$_3$] in pure water.
Figure A27. Representative potentiodynamic scans showing the effects of temperature: [0.01M Na₂SiO₃ + 0.5M NaHCO₃] in simulated seawater.

Figure A28. Representative potentiodynamic scans showing the effects of temperature: [0.025M Na₂SiO₃ + 0.5M NaHCO₃] in pure water.
Figure A29. Representative potentiodynamic scans showing the effects of temperature: [0.025M Na$_2$SiO$_3$ + 0.5M NaHCO$_3$] in simulated seawater.

Figure A30. Representative potentiodynamic scans showing the effects of temperature: [0.005M Na$_2$SiO$_3$ + 0.1M NaHCO$_3$] in pure water.
Figure A31. Representative potentiodynamic scans showing the effects of temperature: [0.005M Na$_2$SiO$_3$ + 0.1M NaHCO$_3$] in simulated seawater.

Figure A32. Representative potentiodynamic scans showing the effects of temperature: [0.01M Na$_2$SiO$_3$ + 0.1M NaHCO$_3$] in pure water.
Figure A33. Representative potentiodynamic scans showing the effects of temperature: [0.01 M Na₂SiO₃ + 0.1 M NaHCO₃] in simulated seawater.

Figure A34. Comparisons of average corrosion rates of 4340 steel – deaerated with NaHCO₃ in pure water.
Figure A35. Comparisons of average corrosion rates of 4340 steel – deaerated with NaHCO₃ in simulated seawater.

Figure A36. Comparisons of average corrosion rates of 4340 steel – deaerated with NaHCO₃ in pure water (PW) and simulated seawater (SW).
Figure A37. Comparisons of average corrosion rates of 4340 steel – deaerated with Na$_2$SiO$_3$ in pure water.

Figure A38. Comparisons of average corrosion rates of 4340 steel – deaerated with Na$_2$SiO$_3$ in simulated seawater.
Figure A39. Comparisons of average corrosion rates of 4340 steel – deaerated with Na₂SiO₃ in pure water (PW) and simulated seawater (SW).

Figure A40. Comparisons of average corrosion rates of 4340 steel – deaerated with Na₂SiO₃ + 0.5M NaHCO₃ in pure water.
Figure A41. Comparisons of average corrosion rates of 4340 steel – deaerated with Na$_2$SiO$_3$ + 0.5M NaHCO$_3$ in simulated seawater.

Figure A42. Comparisons of average corrosion rates of 4340 steel – deaerated with Na$_2$SiO$_3$ + 0.5M NaHCO$_3$ in pure water (PW) and simulated seawater (SW).
Figure A43. Comparisons of average corrosion rates of 4340 steel – deaerated with Na$_2$SiO$_3$ + 0.1M NaHCO$_3$ in pure water.

Figure A44. Comparisons of average corrosion rates of 4340 steel – deaerated with Na$_2$SiO$_3$ + 0.1M NaHCO$_3$ in simulated seawater.
Figure A45. Comparisons of average corrosion rates of 4340 steel – deaerated with Na₂SiO₃ + 0.1M NaHCO₃ in pure water (PW) and simulated seawater (SW).

Figure A46. Comparisons of average corrosion rates of 4340 steel – deaerated in simulated seawater with no additional ions, 0.005M Na₂SiO₃, and 0.1M NaHCO₃.