A natural analogue for long-term passivity

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A NATURAL ANALOGUE FOR LONG-TERM PASSIVITY

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering
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Date of Approval:
July 1, 2003

Keywords: corrosion, passive behavior, nuclear waste, josephinite

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A NATURAL ANALogue FOR LONG-TERM PASSIVITY

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ABSTRACT

The U.S. Department of Energy (DOE) has been engaged in a viability study for a potential underground geological repository in Yucca Mountain, Nevada. The repository is being designed for disposal of high level nuclear waste. A reference design for the repository has focused on the use of natural and manmade barriers to assure that radionuclide release will not be significant though an extended time period on the order of 10,000 years. The reference design utilizes manmade metallic components that are expected to last for this time period. The specified metallic materials depend on a phenomenon known as metallic passivity to achieve their expected service lives. It is difficult to demonstrate this type of service life for these metallic materials as they have only been in commercial use for less than 100 years. There have been metal artifacts and metallic materials that have survived for long time periods, however, little is known about whether these artifacts have been exposed to conditions where they have been immune to corrosion, exhibiting passive behavior, or actively corroding at an extremely low rate.

A demonstration of metallic passive behavior being maintained over many thousands of years would greatly increase confidence in the expectation that passive behavior could be maintained on the repository waste package materials. Long-lived metallic materials, such as iron, copper, nickel, and alloys based on these metals are materials that demonstrate passive behavior and have been identified in the literature as possible
analogues, potentially useful to provide additional confidence in making projections of such long-term passive behavior.\textsuperscript{1, 4, 28, 45}

This paper presents a study into some aspects of the corrosion behavior of Josephinite. Josephinite is a naturally occurring assemblage of a metallic alloy of nickel and iron in conjunction with a host rock. The typical metallic composition is approximately 70% nickel and 30% iron. The material has been reported in association with geologic features with age into the millions of years. The study used corrosion measurement techniques to assess the behavior of the mineral immersed in aqueous solutions of various pH. Corrosion measurement techniques utilized included potentiodynamic polarization, open circuit corrosion potential, and electrochemical impedance spectroscopy. Other techniques utilized in the study included visual and metallographic examinations with both optical and scanning electron microscopy.

Test results from this study indicate that passive behavior characterizes Josephinite specimens immersed in naturally aerated buffered aqueous solutions in a range of pH from 6 to 9. This range has been reported for the geographic area where Josephinite materials are found in southwest Oregon. This suggests that passive behavior may be responsible for the material longevity as opposed to the material being immune or undergoing slow but active corrosion.
1. NUCLEAR WASTE ISSUE

High level nuclear waste material has been accumulated by many countries that utilize nuclear materials. These nuclear materials have been used to produce electricity, provide propulsion for naval vessels, and for the manufacture of nuclear weapons. Some elements of the waste are radioactive isotopes that are hazardous for long periods of time. Safe containment of these radioactive isotopes requires their isolation until they no longer pose a significant risk to human health and the environment.

As of December, 1998, the United States had accumulated 38,500 metric tons of used, or spent nuclear fuel from commercial power plants. The commercial spent fuel is currently stored in 33 states at 72 power plants and one commercial storage facility. The amount of spent fuel is expected to double by the year 2035 if all of the currently operating nuclear plants complete their initial 40-year licensing period. By 2035, the United States is expected to accumulate an additional 2,500 metric tons of spent nuclear fuel from nuclear weapons and other defense related programs. Figure 1 shows the current location of nuclear waste needing long-term storage. Figure 2 illustrates the DOE projected flow of waste to the disposal site.

Geologic disposal of radioactive waste has been a focus of scientific research for more than 40 years. As early as 1957, a National Academy of Sciences' report to the Atomic Energy Commission recommended burial of radioactive waste in geologic formations with the objective of isolating waste long enough for the hazardous radioactive products to decay to low levels. \(^{26}\)
2. REFERENCE DESIGN FOR NUCLEAR WASTE CONTAINMENT

The U.S. Department of Energy (DOE) has been engaged in a viability study\(^*\) for disposal of high level nuclear waste using a reference design for a potential underground geological repository in Yucca Mountain, Nevada. The Yucca Mountain site is approximately 150 miles northwest of Las Vegas and is located in a currently semi-arid environment receiving about 7 inches of precipitation annually. The purpose of the repository is to protect people from harmful radionuclide releases for an extended period of time on the order of 10,000 years.\(^1,2\)

Reference design parameters for the repository call for a storage density of 80 to 100 metric tons of uranium (MTU) per acre. (One MTU is the amount of spent fuel that contained 1,000 kilograms of uranium before irradiation). The repository is designed to provide for a total loading of 70,000 MTU contained within the approximately 1,200-acre site. Most of the waste will consist of spent nuclear fuel from civilian reactors.

Recent reference designs published by the DOE\(^26\) for the repository have focused on the combined use of both natural and engineered barriers to provide multiple layers of defense against release of radioactive materials into the environment. A portion of the engineered barrier system calls for utilization of double-walled, all metal waste packages to hold the nuclear materials. A concept drawing of the waste packages is provided in Figure 3. The waste is to be isolated in approximately 10,000 individual containers, with

\(^*\) The viability study was conducted as part of a site characterization effort to assess whether the Yucca Mountain Site was suitable for long-term storage of nuclear waste. The site is currently (2003) in the license application preparation stage.
each package holding up to 21 pressurized water reactor or 44 boiling water reactor waste assemblies. The waste packages would be approximately 1-1/2 to 2 m diameter and 3-1/2 to 6 m long depending on the type of waste.

The reference design calls for the waste packages to be placed in single rows within stabilized horizontal tunnels, or drifts, which are to be excavated in the unsaturated rock zone of Yucca Mountain, Nevada. The tunnels are to be placed approximately 300 meters below the surface of the mountain and 300 meters above the existing water table. The placement is part of the natural barrier system in the reference design, which is depicted in Figure 4. After the waste packages are placed into the drifts, the drifts are to be sealed and the repository placed in a monitored status for 50 to 100 years. Reference design plans call for the repository to be closed and permanently sealed after this monitoring stage.

A recent reference design called for the outermost wall of these packages to be fabricated from a 20-mm thick shell of nickel base Alloy 22. (UNS N06022, nominal composition, by wt. 56% Ni, 22% Cr, 13% Mo, 2.5% Co, 3% W, and 3% Fe).\textsuperscript{1, 13} The second, or inner wall, of the packages is a 50-mm thick type 316NG stainless steel material. For design purposes, the Alloy 22 is primarily present for corrosion resistance and the 316NG stainless shell for providing mechanical strength.\textsuperscript{25} An earlier waste package design called for a 50-mm outer layer of plain carbon steel and a 20-mm inner layer of Alloy 22.\textsuperscript{2}

An additional engineered barrier in the reference design calls for use of drip shields to cover the waste packages in an effort to minimize water dripping onto the packages and to limit mechanical damage from possible falling debris. The reference design for the
drip shield calls for the covers and structural supports to be made from titanium and feet fabricated from Alloy 22. The reference design plans do not call for installation of the drip shields until completion of a long-term monitoring stage when the site is to be sealed and closed, after perhaps 100 years or more. The pallets for support of the waste packages are to be made from a welded assembly of Alloy 22. A concept drawing for the engineered barrier system is shown in Figure 5.

Alloy 22 material is a chromium-rich nickel base alloy. Nickel, chromium, and other important alloy components are not thermodynamically stable in the expected repository conditions. Alloy 22 derives its corrosion resistance from a phenomenon known as metallic passivity. When passive, a thin film sometimes only a few atomic layers deep, forms on the surface of the metal and separates the potentially reactive metal from the environment. The Alloy 22, 316NG stainless steel container, and the titanium drip shield materials all depend on passive behavior for corrosion resistance.

Projections of system performance indicate that the engineered barrier portion of the repository is critical to achieving the desired system performance. In the DOE viability assessment, the Alloy 22 outer wall of the waste package has been given primary credit for providing corrosion resistance through projected passive behavior. Corrosion rates in the passive state are often less than 0.01 \( \mu \text{m/year} \) and such rates will support a projected waste package design life in excess of 10,000 years. Since passivity is the key to the corrosion resistance of Alloy 22, it is essential that this portion of the waste package remain in the passive state over the extremely long service period. As an engineered material, however, Alloy 22 has only been in use for a few decades so predictions of the performance of Alloy 22 over the expected design life cannot be based on direct observation.\(^1\)\(^,\)\(^4\) In addition, there is only approximately 100 years of service
experience with engineered materials maintaining passive behavior (e.g. chromium stainless steels). In fact, documented examples of any metallic material maintaining passive behavior over many thousands of years do not seem to be available. Without direct evidence, the possibility exists for unknown mechanisms of deterioration to occur over many thousands of years. In summary, the relatively short service history of Alloy 22, and engineered passive metallic materials in general, brings into question the reliability of extrapolating the behavior of the material out to 10,000 years.  

In light of the above, a demonstration of metallic passive behavior of a suitable analogue material being maintained over many thousands of years would greatly increase confidence in the expectation that passive behavior could be maintained on the waste package materials.\textsuperscript{1, 4, 28, 45} The use of an analogue material would provide a look back in time to assess what type of corrosion behavior might have been responsible for a demonstrated long life. In searching for a demonstration of long-term passive behavior, it is important to recognize that metallic materials can be long lived for reasons other than passivity. For example, the material may have been immune to corrosion, or undergoing active corrosion at a very low rate.

Iron, copper, nickel, and alloys based on these metals are examples of long lived materials which have been identified in the literature as potential natural analogues to study for comparative behavior to modern day metals exhibiting passive behavior.\textsuperscript{4} The potential analogues are not directly representative of the waste package alloys, but are similar in that passive behavior may be responsible for a demonstrated long life.
3. PROJECT OBJECTIVE AND APPROACH

In light of the above issues associated with projections of such long-term passive behavior, this project was created to attempt to identify a metallic material that may have exhibited passive behavior over an extremely long period of time, and the environmental conditions leading to the behavior. To accomplish this, the following four tasks were established:

- Review the main characteristics of metallic passivity.
- Identify a candidate metallic material for use as an analogue in demonstrating long-term passive behavior. The candidate material must have demonstrated a long life in excess of 10,000 years. The candidate material would also have to be available for use in destructive corrosion and metallographic study. The candidate material could be either a natural or a manmade item.
- Assess the corrosion behavior of the selected candidate analogue and related metallic engineered modern materials under aqueous exposure conditions of controlled pH similar to those that may have been experienced by the analogue material in its environment. The experimental techniques utilized would need to be able to distinguish between immune, active, and passive behavior.
- Organize the information in an experimental potential-pH diagram using the general test methodology outlined by Verink.5.
4. REVIEW OF PASSIVE METALS

Jones\textsuperscript{15} has defined passivity as “a condition of corrosion resistance due to formation of thin surface films under oxidizing conditions with high anodic polarization”. Passive behavior is associated with the formation of a thin, thermodynamically stable oxide or hydroxide film on the surface of a metal. Many modern commercial metals owe their usefulness as structural materials to this passive behavior. Metals such as aluminum, nickel, chromium, titanium, and iron along with some of their alloys exhibit passive behavior. Iron containing a sufficient amount of chromium to become stainless steel is an example of one such alloy. While passive, these metals exhibit very low corrosion rates.

A metal or alloy showing passivity will typically display a transition from active corrosion to passive behavior when subject to anodic polarization. This transition will typically be exhibited by the formation of an S-shaped dissolution curve when plotting current, or current density, versus applied potential on a semi-logarithmic scale as shown in Figure 6. While undergoing anodic polarization, metals exhibiting a transition from active to passive behavior initially undergo exponentially increasing corrosion rates as measured by current density. On further increases in potential, the corrosion rate decreases to a much lower value and remains low over a considerable range of potential. The magnitude of the reduction in corrosion rate from the active to the passive regions can be on the order of $10^3$ to $10^6$.\textsuperscript{14, 15} Additional increases in potential lead to a marked increase in corrosion rate when the transpassive/oxygen evolution region of behavior is reached.
The initial zone of exponentially increasing corrosion rate is the region of active corrosion behavior. The zone of reduced corrosion rate is identified as the region of passive behavior.

Nickel based metals are well represented in the literature as a material for study of passive behavior. Researchers have experimentally identified a variety of films present on passive nickel base materials. MacDonald$^{16}$ reported on Surface Analysis by Laser Ionization (SALI) techniques performed using nickel specimens in both phosphate and borate buffer aqueous solutions. He reported Ni(OH)$_2$ as the primary constituent in the passive film formed with no significant difference between passive films formed in either of the buffer solutions. Graham$^{17}$ reported that the passive films on nickel are entirely NiO and 0.9 – 1.3\(\text{nm}\) thick. Macdougall$^{18}$ also indicated NiO as the passive film in borate buffer solutions. Hummel and Verink$^{19}$ provided a summary of various literature which suggested that a variety of films such as Ni(OH)$_2$, NiO, NiOOH, Ni$_3$O$_4$, Ni$_2$O$_3$, NiO$_2$, NiO$_{1.5-1.7}$, or chemisorbed oxygen were responsible for passive behavior. Their own research identified Ni(OH)$_2$ as the primary film with NiO and NiOOH identified at various pH/potential ranges with in-situ testing by use of differential reflectometry (DR).

Although the exact elemental compositions of the layer responsible for passive behavior are not resolved, $^{16}$ the effects of passive behavior can be experimentally observed by measuring changes in current. Despite the lack of resolution on the mechanism, Pourbaix$^6$ and Verink$^5$ have devised methods for mapping out conditions of active and passive corrosion behavior based on specimen potential and aqueous solution pH as discussed in the next section.
4.1 Potential/pH Diagrams

Pourbaix\textsuperscript{6} created a series of potential/pH diagrams that show reaction products that will be thermodynamically stable under equilibrium conditions in water of various pH. The diagrams may be thought of as a map showing whether a metal, metal ion, metal oxide or hydroxide, will be stable for various conditions of potential and pH in an aqueous electrochemical system. The diagrams show conditions of potential and pH where a metal in aqueous exposure can be immune to corrosion where the metal is stable, subject to corrosion where the metal ion is stable, or passive where an oxide or hydroxide form of the metal is stable. The diagrams are useful in identifying conditions of exposure where corrosion may be possible or where it is impossible. The diagram based on thermodynamic stability of nickel and its oxide or hydroxide forms is reproduced as Figure 7. Pourbaix developed the boundary lines of the theoretical diagram by use of the Nernst equation, with consideration provided for the activity levels of the metal ions in solution.\textsuperscript{15} The theoretical diagrams are published only for pure metals and do not predict rates of corrosion, or how quickly a metal may passivate.\textsuperscript{16} In addition to the theoretically based diagrams, Pourbaix also published a probable experimental potential/pH diagram for nickel using the corrosion behavior reported by various researchers.\textsuperscript{6} This diagram based on empirical information has been reproduced as Figure 8.

Verink\textsuperscript{5} outlined a method to produce potential/pH diagrams for metal alloys based on experimental testing. The general test methodology consisted of conducting a series of polarization scans on a specimen material in solutions of various pH and plotting the potentials at which active corrosion and passive behavior are observed. This method
permits creation of the potential/pH diagrams for metallic alloys and solutions other than pure water.
5. EXAMPLES OF LONG LIVED METALS

Johnson and Francis\textsuperscript{3} reported many examples of native metals, meteorites, and archeological objects that have survived quite well over extended periods of time. Their study included man-made items from alloys rich in metals such as gold, silver, copper, lead, iron and tin. The longest lived of the man-made items identified were gold artifacts from 6000 to 7000 B.C. Surviving iron and nickel based meteorites were estimated to have been exposed to terrestrial conditions for 5,000 to over 100,000 years. Manmade copper artifacts have been dated to 9,000 years old. Native copper deposits in Michigan have also been reported to be approximately 500 million years old. Abrasions on the copper deposits were linked to a glaciation period and dated to at least 8,000 years ago.

For surviving man-made artifacts, Johnson and Francis estimated a range of corrosion rates from 0.002 to 7.6 \( \mu \text{m/year} \) for iron specimens and 0.008 to 3 \( \mu \text{m/year} \) for copper specimens that were not submerged under water. For iron, both the high and low ends of the range occurred on artifacts buried in tombs in arid climates. Other iron specimens with corrosion rates between the extremes were found exposed in various atmospheric and aqueous environments. The copper specimens were reported buried in a variety of materials such as gravel, soil, clay, as well as under atmospheric exposure conditions. Johnson and Francis compared their estimates of corrosion rates to those published by Uhlig\textsuperscript{27} for materials under modern rural exposure conditions. Uhlig reported rates of 1.8 to 12.2 \( \mu \text{m/year} \) for iron and 0.4 to 1.3 \( \mu \text{m/year} \) for copper. Johnson and Francis commented that the modern rates reported by Uhlig corresponded with the mid-range of
their estimates, and that the most durable artifacts have been subject to exceptionally low corrosion rates.

Robbiola, Blengino, and Fiaud\textsuperscript{21} reported on natural patinas formed on archeological bronze (Cu-Sn) alloys buried for approximately 3,000 years. They estimated corrosion rates of 0.5 to 4 \(\mu\text{m}/\text{year}\) for exposure duration of 20 years or less and decreasing with time, tending towards zero. It should be noted however, that copper exhibits a large range of potential and pH conditions where it is immune to corrosion by having a thermodynamically stable metallic form. Review of a published potential/pH diagram\textsuperscript{15} for copper indicates that the range of metal stability is substantially larger than for other metals such as iron, nickel, aluminum, or chromium. With a significant range of stability, the possibility exists for the copper artifacts to have been in a condition where they were immune to corrosion.

It appears that little or no attention has been given in the literature as to whether the durability of these archeological and natural specimens was due to exposure conditions where the metals had been immune to corrosion, actively corroding, or exhibiting passive behavior in their environment. Thus there is much uncertainty as to whether any of the long lived metal specimens represent examples of long-term passive behavior.

5.1 The Josephinite Example

The potential of Josephinite as a natural analogue to demonstrate long term passive behavior has been pointed out by McNeil and Moody.\textsuperscript{4} Josephinite is a naturally occurring assemblage of metallic alloy of nickel and iron in conjunction with a host rock. The typical ratio of nickel to iron is approximately 3:1. Josephinite specimens are found in Josephine County in southwestern Oregon and were first described in 1892.\textsuperscript{9} Similar
mineral assemblages have been found at other locations in the world and have been identified as Awaruite.\textsuperscript{4,5} The variation in terminology in the literature appears to revolve around whether the mineral specimens from Josephine County are regarded as unique apart from similar specimens found elsewhere. For the purposes of this study the term Josephinite will refer to the metallic and host rock assembly of minerals found in and around Josephine County.

Naturally occurring deposits of both nickel and iron occur in various locations throughout the world, but they generally occur as metallic ores. The ores are typically sulfide or oxide forms of these metallic elements.\textsuperscript{33} Large iron ore deposits are located in the Ural Mountains of the former Soviet Union and near Lake Superior in the United States. Large nickel ore deposits are located in the Soviet Union and eastern Canada. Josephinite specimens are found as metallic nuggets instead of the ores more characteristic of the primary metal constituents.

Josephinite has been reported as placer deposits found in streams or streambeds, and as embedded deposits located within a host geological formation. Masses of Josephinite up to 50 kg have been reported.\textsuperscript{3} Centimeter sized nuggets are commercially available. The presence of large amounts of reduced metal in natural exposure, including oxidizing conditions, strongly suggest that passive behavior may have played an important role in the preservation of the metal alloy over geologic time frames.

Josephinite is reportedly found as irregularly shaped nuggets of the metal surrounded by harzburgite, serpentinized olivine, an ultramafic host rock.\textsuperscript{9,10} Ultramafic rocks are generally composed of ferromagnesium silicates, metallic oxides and sulfides, and native metals on rare occasions.\textsuperscript{9} Olivine is a mineral identified as being closely
associated with the Josephinite nuggets. Olivine is subject to serpentinization which occurs during exposure to water according to the following reaction ⁹:

\[
6 \text{Mg}_{1.5}\text{Fe}_{0.5}\text{SiO}_4 + 7 \text{H}_2\text{O} \rightarrow 3 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{H}_2 + \text{Fe}_3\text{O}_4
\]

(Olivine)  (Serpentine)

As shown above, the serpentinization occurs by the metamorphism (especially hydration) of a mineral, such as olivine. The most common serpentine color is reported as being green, however the rocks are reported to weather to an orange-brown color. ⁸ The serpentinization of the olivine host rock indicates that the Josephinite nuggets have been exposed to aqueous solutions for some portion of the geologic time frame.

Josephinite bearing placers were found by Dick ¹⁰ to be closely associated with serpentine shear zones and diabase dykes. Dykes are bodies of igneous rock cutting across the structure of adjacent rock and result from intrusion of magma. ⁸ Dykes associated with Josephinite nuggets have been dated by K-Ar methods to 150-155 million years. ⁹ ¹⁰ Dick ¹⁰ has suggested that the intrusion of the dykes caused an increase of hydrothermal activity and circulation of water in the adjacent rocks. He proposed that this hydrothermal activity led to the development of the serpentine and the formation of nickel-iron deposits by reduction of nickel sulfides and iron in the local vicinity of the dyke. This suggests a relatively close association of age between the formation of the dikes and the formation of the nickel-iron nuggets. Leavell ²⁹ expressed similar views on the origin of the material. Bird ⁴¹ suggested that the Josephinite metallic material had its origins in the earth mantle region and was deposited with the dykes. With either origin, the presence of serpentine, the formation of the nickel-iron deposits, and the presence of Josephinite placer deposits, suggest aqueous exposure which is
consistent with the suggestion that passive behavior may be responsible for the metal longevity.
Based on the reported longevity, availability, and reported exposure conditions of the deposits, Josephinite was selected as a material to use in examining the tendencies of this natural analogue towards passive or active corrosion behavior under aqueous exposure. Manmade artifacts of sufficient age (≈10,000 years) for this study were typically one of a kind museum type items and were not considered good candidates for destructive testing.  

Josephinite specimens from two sources were included in the study. A specimen nugget of Josephinite was obtained on loan from the Smithsonian Institute for the purposes of performing non-disruptive visual observations and elemental analysis using EDS techniques. Three additional specimens of Josephinite were obtained commercially for use in performing chemical, metallurgical, and corrosion testing. The commercial specimens were obtained from Excalibur Minerals, Inc. of Peekskill, New York. Detailed information on the Josephinite specimens is presented in Section 8.1.

Two modern alloys were selected for comparison of corrosion behavior against the Josephinite specimens. The composition of the two alloys was selected such that the nominal nickel/iron ratio of Josephinite fell between the nickel/iron ratio of the two alloys. One of the alloys was Nickel 200 (UNS N02200), a commercially pure nickel, which was supplied in the form of 1 cm diameter x 30 cm long rod. The second alloy was a nominal 55% nickel-45% iron core wire from a commercially available E-NiFe class of welding electrode within the American Welding Society A5.15 specification. The E-NiFe alloy
was supplied as 0.64 cm diameter x 58 cm long rod. Both of the modern materials were supplied in the mill-annealed condition, with mill test reports as provided in Appendix E. A summary of the elemental analysis as reported for the specimens on the respective mill test reports is shown in Table 1. Both the Nickel 200 and the E-NiFe specimens were supplied in a clean surface condition and were reported to have been pickled.
7. EXPERIMENTAL TECHNIQUES

A variety of techniques were used to examine and evaluate the specimens of this study. These techniques included: visual observations, metallographic observations, elemental analysis, potentiodynamic polarization, corrosion potential, and electrochemical impedance spectroscopy. Table 2 provides a matrix of the experimental techniques utilized on each type of specimen.

7.1 Visual Observations and Measurements of Josephinite Specimens

Densities of the commercial specimens were calculated by weighing them in air and immersed in water using a triple beam balance. Visual observations were made utilizing a reflected light microscope with magnifications up to 250x.

7.2 Metallographic Observations

The three commercial Josephinite specimens were sectioned for optical examination of the specimen interiors and for preparation of corrosion test specimens. Sections were cut using a low speed Buehler wafering wheel (diamond wheel cutting blade) and Buehler Metadi cutting fluid. One section from each nugget was mounted, polished and etched for metallographic examination. Buehler Bakelite thermosetting material was used for mounting. Etching was performed using Marble’s reagent, a mixture of hydrochloric acid and copper sulfate. Metallographic observations were made of the Nickel 200 and E-NiFe specimens for comparison.
Surface preparation for all of the metallographic work was performed by abrading the specimens with progressively finer silicon carbide paper discs through 600 grit and then progressively finer polishing through 0.05 micron alumina. After polishing, sections of each specimen were observed under magnification both with and without etching.

7.3 Elemental Analysis

Elemental analysis was performed on various areas of the Josephinite specimens using a JOEL JSM 840 scanning electron microscope (SEM), and a Tracor Northern TN 5500 energy dispersive x-ray spectrometer (EDS). Analysis was performed on the specimen exteriors before sectioning and interiors after sectioning. The Smithsonian specimen was not sectioned for analysis, however elemental analysis of the specimen exterior was performed.

In the SEM, a beam of electrons impinges on the surface of the specimen being analyzed. At the impingement point, electron and x-ray emissions are produced. EDS utilizes the energy spectrum of the x-rays given off by the specimen to identify the type and quantity of elements present on the material surface. The EDS process allows measurement of the elemental composition of the material specimen for elements heavier than sodium. Materials to be used in the SEM for EDS must be conductive or coated with a conductive sputtered layer. The specimen must be clean, and small enough to fit into the machine vacuum chamber.\(^{32}\)
7.4 Solutions Used in Corrosion Testing

A pH range of approximately 6 to 9 was reported for natural surface waters for areas near the location of Josephinite deposits in Oregon.\textsuperscript{34, 35} Aqueous solutions with pH bracketing and extending through this range were used to assess corrosion behavior of the Josephinite and modern material specimens. An assumption was made that these pH conditions have existed in the Oregon location for an extended period of time and are representative of the natural exposure conditions experienced by the Josephinite materials.

Buffered aqueous solutions of pH ranging from 4 to 12 were utilized for conducting potentiodynamic polarization scans, measurements of corrosion potential, and EIS of the Nickel 200, E-NiFe, and Josephinite specimens. The compositions of the buffered solutions utilized are summarized in Table 3. The compositions were taken from the CRC Handbook\textsuperscript{38} and were similar to those used by Verink\textsuperscript{5}. The pH of each solution used was verified to be within 0.1 units of the nominal value prior to use with a Corning 140 pH meter using commercial buffer solutions for system calibration. Resistivities of several of the buffered solutions were measured and are reported in Table 4. The measured resistivity of these solutions is lower than the values reported for natural waters in the vicinity of Josephine County. In the case of non-uniform active corrosion, the lower resistivity of these solutions may be expected to produce a higher corrosion rate than for the natural waters. However onset of passive behavior should result in extremely low corrosion rates independent of solution resistivity.

Temperature of the solutions during corrosion testing was 21 +/- 1.7 °C in all cases. The corrosion cell glassware used was in general accordance with the ASTM G5\textsuperscript{7} standard.
For potentiodynamic polarization, the solutions were stirred using a magnetic stirring plate and deareated. Deareation was performed by bubbling commercial, high-purity, nitrogen through the solution for a minimum of one hour prior to the start of the polarization scans.

The solutions used for measurements of corrosion potential and EIS were naturally aerated, being left open to the atmosphere. The solutions were not stirred during the course of the measurements.

A Gamry Instruments potentiostat was used in conjunction with a corrosion cell consisting of a saturated calomel electrode (SCE) reference electrode, Lugin probe, two graphite counter electrodes and the specimen being tested as the working electrode. The probe tip to specimen distance was typically ≈5mm. For this report, all measurements of electrochemical potential were converted to the standard hydrogen scale by adding 0.241 volts to the SCE measurement.

7.5 Specimens Used in Corrosion Testing

Corrosion test specimens of the modern nickel base alloys consisted of solid cylindrical specimens made from the supplied rods. The Nickel 200 corrosion specimens measured approximately 1.25 cm long by 0.93 cm diameter. The E-NiFe corrosion specimens measured approximately 2.25 cm long by 0.54 cm diameter. Exposed surface area of the specimens was approximately 5 cm² and 4 cm² for the Nickel 200 and E-NiFe specimens respectively, after subtracting the area of the Teflon gasket used in mounting the specimens. Mounting was in general accordance with ASTM G5. Photographs showing the configuration of the Nickel 200 and the E-NiFe corrosion specimens are provided in Figure 10.
Corrosion specimens for Josephinite consisted of cut cross sections of the supplied nuggets. The sectioned specimens of Josephinite were irregularly shaped and were estimated to have effective surface areas from 0.62 to 0.32 cm$^2$. The estimated metallic area of the sections was based on dimensional measurement of the approximately oval shaped sections. Based on the appearance of the unetched cross sections, it was estimated that approximately 75% of each cross section consisted of a metallic surface with the remainder assumed to be a non-conductive rock. To verify the assumption of non-conductivity, measurements of electrical resistance were made using pointed tips of probes placed on the rock and metallic areas of the cross sections and a multimeter at 200 ohm full scale reading. The meter indicated no conductivity between the rock and metallic areas on all of the specimens while readings of zero ohms were obtained within the metallic areas.

The Josephinite specimens were embedded in a two-part epoxy, Buehler Epoxide, to isolate the sectioned face as the exposed surface for corrosion testing. The specimens were in contact with a copper conductor buried within the epoxy. A schematic of the mounting is shown in Figure 9. Photographs showing the configuration of the embedded Josephinite specimens are provided in Figure 10.

All corrosion specimens were prepared by polishing with progressively finer silicon carbide paper down to 600 grit followed by a wash in distilled water and subsequent immersion into the various pH buffered solutions. The specimens were repolished and washed for each subsequent use.
7.6 Potentiodynamic Polarization

Potentiodynamic polarization scans were performed on the Nickel 200, E-NiFe, and Josephinite specimens. The test methodology was in general accordance with ASTM G5\(^7\), except for differences in the test solutions, and polarization scans were started at potentials below the hydrogen evolution potential at each pH level tested.

All potentiodynamic polarization specimens were prepared by polishing as described earlier within 30 minutes of specimen immersion. Polarization scans were started 55 minutes after specimen immersion as described in the ASTM G5 standard. Potentiodynamic scans were carried out in the anodic direction until passive behavior was established. Figure 6 depicts a plot of a generic potentiodynamic scan showing selected areas of interest in the potentiodynamic scans performed.

To verify the performance of the experimental potentiodynamic polarization techniques and equipment, specimens of type 430 stainless steel were run to the ASTM G5 standard. The standard addresses potentiodynamic polarization of type 430 stainless steel in an aqueous solution of 1N sulfuric acid. Standard results for type 430 stainless specimens are published in ASTM G5 for comparison against those measured to verify the techniques utilized. The specimens of 430 stainless steel were run at various times during the course of the experimental data collection to assure that the machine and techniques being utilized were reliably performing and recording the potentiodynamic scan. The test results were within the prescribed ASTM-G5 bands of laboratory performance.
7.7 Corrosion Potential
Nickel 200, E-NiFe and Josephinite specimens were immersed in naturally aerated, buffered solutions of various pH to measure the open circuit potential achieved. The Nickel 200 and E-NiFe specimens were tested in pH 4, 5, 6, 8, and 10 prepared solutions. Josephinite specimens were tested in solutions of pH 5, 6, 7, and 8.

7.8 Electrochemical Impedance Spectroscopy
Electrochemical Impedance Spectroscopy (EIS) was used as an additional test method to assess whether the Nickel 200, E-NiFe or Josephinite specimens were passive or actively corroding at the measured open circuit potentials. Specimens were immersed in buffered solutions of various pH and subjected to EIS to estimate the specimen corrosion rates. The testing apparatus was a Gamry Instruments with potentiostat and frequency response analyzer (FRA) using CMS-100 software.

The EIS scans were all run at zero applied DC voltage (at the open circuit potential), in a corrosion cell open to the atmosphere. The cell consisted of a glass corrosion cell and specimens in general accordance with ASTM G61. Two graphite counter electrodes were used, with a SCE reference electrode positioned close to the specimen through use of a Luggin probe. Testing was typically performed from 5000 Hz down to a 0.1 mHz frequency at an amplitude of 10 mV RMS.

To verify the performance of the EIS equipment, a Randle’s type dummy cell was created as a test circuit to provide a simulated model of a corroding electrode. The test circuit consisted of a nominal 1kΩ (measured 989 Ω) resistor connected in series to a parallel combination of a nominal 100µF capacitor and 850kΩ (measured 852 kΩ) resistor. A schematic diagram of the test cell is shown in Figure 11. An EIS scan was
performed on the test circuit. Plots of the modeled and recorded impedance response of the dummy cell are also provided in Figure 11. The respective plots show good agreement, indicating proper functioning of the measurement and test equipment. The modeling variables for the Rp and Rs resistors differed from the measured values by 0% and 0.8% respectively. Measurements for the capacitor portion of the circuit differed from the labeled capacitor value by 10%.

EIS measurements were performed on Nickel 200 specimens in pH 4, 5, 6, 7, 8, and 10 solutions. E-NiFe specimens were tested at pH 5, 6, 7, 8 and 9. Josephinite specimens were tested at pH 5, 6, 7, and 9. EIS measurements were made using the same specimens and corrosion cells that were being used for measurement of open circuit potential. EIS measurements were taken after various immersion times up to approximately 1000 hours. Specimen preparation was identical to that used for the potentiodynamic polarization specimens described earlier. The test data was analyzed by modeling as a simple corroding electrode represented by a resistor in series with a parallel combination of a resistor and a non-ideal capacitor. Circuit modeling was performed using Gamry Framework analysis software. The polarization resistance, Rp, was obtained as an output function of the models. Estimates of corrosion rate were obtained through the following equation as applies to cases of simple activation polarization but was used otherwise to obtain nominal values.\(^\text{30}\)
\[ I_{corr} = \frac{B}{Rp} \]

where:

\[ B = \frac{ba \cdot bc}{(2.303)(ba + bc)} \]

- \( I_{corr} \) = corrosion current density (a/cm\(^2\))
- \( B \) = composite Tafel parameter (V)
- \( Rp \) = polarization resistance (ohm-cm\(^2\))
- \( ba \) = anodic slope (V/decade), potential-log \( i_{corr} \)
- \( bc \) = cathodic slope (V/decade), potential-log \( i_{corr} \)

Values of 0.1V for the anodic and 0.1V for the cathodic slopes were used in the above equation from estimates provided by Jones.\(^{15}\) The resulting calculated value of the composite Tafel parameter, \( B \), was 0.022.
8. EXPERIMENTAL RESULTS AND DISCUSSION

8.1 Visual Observations and Measurements of Josephinite Specimens

The Smithsonian specimen was received with an adhesively attached paper tag identified with the number 149489. The specimen weighed 62.5 grams, was irregularly shaped, and measured approximately 5 by 4 by 2 cm. A photograph of the Smithsonian specimen is shown in Figure 12. The commercial specimens were smaller than the Smithsonian specimen with the largest dimension of the three specimens ranging from approximately 2.5 to 1 cm and mass ranging from 11.07 g to 2.56 g. A photograph of one of the commercial specimens is shown in Figure 13, the other two commercial Josephinite specimens were similar in appearance. Densities of the commercial specimens were calculated as 7.05 g/cm$^3$ for the largest specimen, and 5.51 and 5.56 g/cm$^3$ for the two smaller sized specimens. Measurements for density of the Smithsonian specimen were not performed to avoid potentially disruptive immersion of the specimen in water.

The exterior surfaces of all of the Josephinite specimens exhibited a polished luster with some portions having a shiny metallic appearance and other areas with a reddish-brown or black polished rock appearance. This is similar to Josephinite features reported in the literature$^{9,10,45}$. As shown in Figures 14 and 15, the specimens contained scratches and gouges with random orientations generally covering the metallic portions. The gouges may be due to abrasion or abrasion erosion$^{40}$ which might be caused by particle gouging action under either wet or dry conditions. Under magnification, the shiny metallic areas of the Josephinite surfaces were noted to have small black cavities.
8.2 Metallographic Observations

Typical unetched cross sections of the three commercial Josephinite nuggets are shown in Figure 16. Figure 17 shows a representative sample of inclusions observed in the cross sections. At least one section from each of the two larger nuggets contained copper colored inclusions. The largest specimen was noted to have the most prevalent copper colored inclusions. The copper colored inclusions were typically in close proximity to the black colored inclusions as can be seen in Figures 17 and 20. EDS analyses of one of the copper colored inclusions in Specimen L showed it to be nearly pure copper (see Table 5). All of the Josephinite specimens exhibited the internal black-colored inclusions. The copper and other inclusions appear similar to those reported by Botto. Based on visual observations of the unetched sections, it was estimated that approximately 75 percent of the typical cross-sectional area was metallic with the balance being inclusions.

The sectioned Nickel 200 and E-NiFe specimens were etched and observed under magnification up to 250X. The Nickel 200 specimens displayed grain sizes approximately 20 to 80 µm across. A representative micrograph of the Nickel 200 specimen is shown in Figure 18. The E-NiFe specimens displayed a much smaller grain size typically on the order of 5 to 10 µm per grain as shown in Figure 19. The appearance of the etched Nickel 200 and E-NiFe compared favorably with those reported in ASM Metals Handbook. The grains were generally equiaxed, with no evidence of cold work noted. The equiaxed grain structure tends to confirm the reported annealed state of the Nickel 200 and E-NiFe supplied material.
Metallographic etching of the Josephinite specimen revealed a variety of structures ranging from apparent complex mixture of phases to nearly equiaxed grains nominally 100 µm in size. Micrographs showing these features are provided in Figures 20 through 26. The black area at the center of Figure 20 is the dark area appearing at the center of Specimen L and highlighted by the arrow in Figure 16. Etching in some areas produced a banding effect as seen in Figures 25 and 26. The lack of homogeneity in the Josephinite etching behavior may be due to natural variations in the formation process of the material.

8.3 Elemental Analysis

The elemental analysis from various portions of the specimens is shown in Table 5. The table has been divided into four parts differentiating between specimen interiors, exteriors, metallic and non-metallic appearing regions. Elemental analysis of the Smithsonian and commercial Josephinite specimen exteriors showed good agreement with the reports of Josephinite and serpentine host rock reported in the literature

EDS analysis of the black inclusions showed some to be similar in composition to the mainly Mg-Si of the host rock noted on the specimen exteriors. Other similar appearing areas of the specimen interiors displayed differing ratios of Ni, Fe, Mg, Si, and Ca.

The elemental analysis results from interior portions of the three commercial specimens exhibited good agreement with the external portions as well as with the exterior of the Smithsonian specimen except in one regard. The largest commercial specimen, L, contained approximately 3% copper within the metallic portion along with isolated islands of almost pure copper. The mid-sized Josephinite specimen also had similar islands of copper colored inclusions but did not have the overall copper content observed in the larger specimen. The finding of native copper and copper inclusions in
association with Josephinite was reported by Botto. The copper colored inclusions appeared to be mainly located in association with dark colored inclusions internal to the metallic nuggets. The presence of copper was not noted on the exterior of the specimens. Copper may be present on the specimen exterior but buried under the host rock material, or may have been removed from the exposed surfaces by corrosion or erosion of the surrounding nickel-iron matrix.

The metallic areas noted on the exterior of the Josephinite specimens exhibited black spots as local depressions. The specimens also exhibited reddish/brownish areas as noted in the literature. The literature reports black colored magnetite surrounding some Josephinite specimens, however, EDS analysis of the Josephinite specimens used in this study showed no areas of high iron concentrations as would be expected out of a layer of magnetite ($\text{Fe}_3\text{O}_4$). It is suspected that the black/brown/red color variations may be due to a differing level of oxidation of the iron, or other elements present in the host rock.

8.4 Potentiodynamic Polarization

A compilation of typical polarization scans for the Nickel 200 specimens at various pH values are shown in Figure 27. Similar polarization scans for the E-NiFe and Josephinite specimens are shown in Figure 28 and 29 respectively. A summary of the $E_{\text{p}}$, $i_{\text{pass}}$, and $i_{\text{crit}}$ values obtained from the polarization testing is presented in Table 7.

It was noted that the $E_{\text{p}}$ values for the E-NiFe specimens were consistently lower than the corresponding values for Nickel 200 at pH values between 6 and 10. Comparison of the theoretical potential-pH diagram by Pourbaix for nickel and iron show that iron might be expected to passivate at a lower potential than nickel in this range. It is suspected
that the iron in the E-NiFe specimens is allowing them to passivate at lower potentials with more iron-like behavior characteristics than the Nickel 200 specimens.

It was also noted that the E-NiFe specimens generally exhibited a higher peak corrosion current density ($i_{\text{crit}}$, see Figure 6) than the Nickel 200 specimens, roughly by an order of magnitude. The passive current densities ($i_{\text{pass}}$, see Figure 6) measured were similar for the two materials. The data indicates that the E-NiFe specimens experienced a higher corrosion rate than the Nickel 200 specimens while actively corroding under the test conditions.

Review of the experimental and theoretical diagrams for nickel by Pourbaix indicates that the material should spontaneously passivate and not be subject to active corrosion at approximately pH 9 through 12. Figure 30 shows the measured peak and passive current densities obtained from the potentiodynamic polarization scans on Nickel 200, E-NiFe and the Josephinite specimens. The results show general convergence of the peak corrosion current density towards the passive current density as the solution pH approaches 10. The values of peak and passive current densities differ by less than 10 percent at pH 9. These experimental results provided general verification of spontaneous passive behavior indicated by Pourbaix’s delineation between active corrosion and passive behavior at pH 9 in Figure 8.

As shown in Figure 29, the Josephinite specimens exhibited a pattern of decreasing peak current densities as the solution pH increased from 6 to 9, similar to the Nickel 200 and E-NiFe specimens. Variations of approximately 50 percent in the corrosion current density with minimal change in the passivation potential were noted between duplicate specimens in the same pH. This may be due to naturally occurring variations in the
specimens, or interactions between the metallic Josephinite and the serpentine internal inclusions present in each section, or to variations in the true versus estimated surface areas of the exposed faces of the Josephinite specimens.

Jones\textsuperscript{15} reported a $b_a$ value of 0.10V for a nickel electrode in a 0.12 N NaOH solution. He reported experimental $b_a$ values from 0.06V to about 0.12V and $b_c$ values from 0.06V to infinity, with the later case corresponding to diffusion control by a dissolved oxidizer. Jones suggested use of a nominal value for $b_a$ and $b_c$ as 0.1V, which yields a composite Tafel parameter of 0.022V to obtain a reasonably good estimate of the corrosion rate. As discussed earlier, this value was used in making corrosion rate estimates from EIS experiments.

8.5 Corrosion Potential

The open circuit corrosion potential measured over time for the Nickel 200, E-NiFe and Josephinite specimens are plotted on Figure 31, 32, and 33. Figure 31 shows the measured potential for Nickel 200 specimens (converted to Standard Hydrogen Electrode Scale, SHE) on a linear time scale and shows a somewhat stable potential of approximately 0.2 volts SHE, or higher, being reached after 100 to 200 hours of immersion. However, when plotted with time on a logarithmic time scale as done in the bottom of Figure 31, the potentials were noted to continue on an upward trend through approximately 600 hours. The general upward trend was noted for the E-NiFe and Josephinite specimens as well. The upward trend is in agreement with predictions offered by MacDonald\textsuperscript{28} showing potentials increasing for one year on passive C22 material.
As shown in Figure 32, the open circuit corrosion potential measured for E-NiFe specimens in pH 6 solutions were noted to increase dramatically after formation of a dark gray or black film on the surface of the specimens. Film formation was noted after approximately 30 hours. Prior to formation of the film, the corrosion potentials were below the Epp values obtained from potentiodynamic polarization, indicating active corrosion behavior. After film formation, the corrosion potentials moved to values above the Epp, which suggests a transition to passive behavior. However, the EIS measurements discussed later in this report indicated that a substantially higher corrosion rate was still occurring on the specimens immersed in the pH 6 solution compared to the pH 7 and higher solutions. The film appeared to affect the measured corrosion potential, but did not appear to offer corrosion protection.

8.6 Electrochemical Impedance Spectroscopy

Curve modeling was performed using a Randles circuit modified to include a constant phase angle element (CPE) in place of a plain capacitor. The CPE is a fictitious circuit element related to charge storage at the metal-electrolyte interface. The circuit incorporates solution resistance, an interface capacitance, and polarization resistance values to model simple corrosion effects. A schematic diagram of the circuit is shown in Figure 34. The CPE element used in modeling the EIS behavior accommodates non-ideal interface capacitance. An ideal interface capacitance would be expected to show on the Nyquist plot as a semi-circle centered on the real impedance (Z) axis. The Nyquist plots obtained from the EIS tests on the tested specimens were typically semi-circles with the centers depressed below the real Z axis.

The Nyquist plots representing various exposure conditions for the Nickel 200, E-NiFe and two Josephinite specimens are shown in Figures 35, 36, 37 and 38, respectively.
Summary data from the EIS testing is provided in Table 8. In general, the plots show a trend of increasing semi-circle diameter (increasing Rp values) with increased exposure time and with increases in pH of the solutions.

Nyquist plots for the Josephinite specimens under exposure to pH7 solution for up to approximately 1000 hours are presented in Figures 37 and 38. Results generally indicate decreasing corrosion rate with increasing exposure time, similar to the Nickel 200 and E-NiFe specimens.

Figure 39 shows the change in the modeled value of Rp over time for the Josephinite specimens immersed in pH 7 solution for approximately 100 hours. The modeling results show increasing Rp values with increasing exposure times. This indicates decreasing corrosion rates as exposure time is increased. This behavior is in general agreement with the observations on passive behavior by Li.37

A photograph of Josephinite specimen M after 1,632 and 10,512 hours exposure in the buffered pH7 solution is provided in Figure 40. Although the specimens became electrically disconnected from the copper conductor used to make electrochemical measurements, specimens M and L2 were allowed to remain in pH7 solution, with observations made through 10,512 hours. The surfaces remained bright, with the original polish marks visible. No change was noted in the appearance after 10,512 hours of exposure. Similar behavior was noted for Specimen L2.

Estimated corrosion rates for the Nickel 200, E-NiFe and Josephinite specimens are presented graphically in Figure 41. For Nickel 200, the estimate of corrosion current density for solutions pH 5 or higher, was a very low rate of dissolution in order of
magnitude from $10^{-2}$ to $10^{-3}$ $\mu$A/cm$^2$, indicative of passive behavior. These rates correspond to a corrosion rate of less than 0.075 $\mu$m/year. The corrosion rate estimates show a value of approximately 3.5 $\mu$m/year at pH 4 and a decrease of approximately 2 orders of magnitude in the rate for pH 5 through 10. This marked decrease suggests a change from active corrosion to passive behavior between pH 4 and 5 as suggested by the experimental potential-pH diagram of Figure 43, which is discussed in the next section. It was also noted that the Nickel 200 specimens turned black in the pH 4 solution, but stayed bright and shiny in pH 5 through 10 solutions.

For the E-NiFe specimens in buffered solution above pH6, the estimated corrosion rates were less than 0.015 $\mu$m/year. These rates compare favorably to the rates estimated by Johnson and Francis$^3$ for long-lived metallic artifacts. The E-NiFe corrosion rate estimates at pH 6 show a value of approximately 15 $\mu$m/year and a decrease of approximately 3 to 5 orders of magnitude in the rate for pH 7 through 10. This marked decrease suggests a change from active corrosion to passive behavior between pH 6 and 7 as indicated by the experimental potential-pH diagram of Figure 44, which is discussed in the next section. Similar to the corroding Nickel 200 specimens in pH 4, the E-NiFe specimens turned black in the pH 6 solution, but stayed bright and shiny in the pH 7 through 10 solutions.

Estimated corrosion rates for the Josephinite specimens ranged from 28 to 0.24 $\mu$m/year in the tested solutions. The results showed a similar behavior as the Nickel 200 and E-NiFe electrode specimens with a one to two order of magnitude decrease in corrosion rate as pH was increased to higher values. The large decrease in rate suggests a change from active corrosion to passive behavior between pH 5 and 6 as indicated by
the experimental potential-pH diagram of Figure 45, which is discussed in the next section. As additional confirmation of this behavior, the exposed face of the Josephinite specimens turned black in pH 5, but stayed shiny in the pH 6 through 9 solutions.

Corrosion rates estimated from the EIS measurements for the Josephinite specimens were higher than the corresponding rates for the Nickel 200 or the E-NiFe specimens by factors of 10 to 100. This may be due to variations in the naturally occurring specimens, or interactions between the metallic Josephinite and the serpentine host material present in each section. Some of the difference may also be attributed to an assumption made that 75 percent of the exposed Josephinite specimen surface area being metallic. The presence of crevices may substantially add to the exposed surface areas that were not taken into account in the estimates. As an additional factor, it was noted that the EIS modeling results for the Josephinite specimens required use of Alpha correction values between 0.5 and 0.6 while the Nickel 200/E-NiFe specimens required Alpha values typically much closer to unity. This indicates significant depression of the center of the Nyquist plot semi-circles below the real Z axis. McKubre\textsuperscript{43} listed several causes for the depression as: reference electrode shielding, current divergence at the electrode perimeter, poor reference probe placement, electrode surface heterogeneity, poor electrode orientation, and surface roughness. As discussed in the section on visual observations, the Josephinite electrode surfaces used in these experiments were noted to have highly heterogeneous features with non-symmetric geometry, particularly when compared to the manufactured Nickel 200 and E-NiFe specimens. Sagues\textsuperscript{42} and McKubre have suggested that significant error may be present in the impedance results due to this depression effect. It is suspected that these conditions may be resulting in a significant overestimation of corrosion rate for the Josephinite specimens.
The Josephinite specimens exhibited similar general trends as the Nickel 200 and E-NiFe. Namely, that the corrosion rates in low pH solutions were several orders of magnitude higher than at higher pH solutions. The demarkation between higher and lower rates occurred at different pH with an apparent dependence on the nickel content. The occurrence of higher corrosion rates versus pH appeared to follow the inverse of the nickel content; that is, the higher the nickel content, the lower the pH where passive behavior was observed. The relationship is shown graphically in Figure 42. Nickel 200 appears to be actively corroding in the pH 4 solution, while the material appears to demonstrate passive behavior from pH 6 to pH 12. For Josephinite with approximately 70% nickel, the specimens were active in pH 5, but appeared to be passive in pH 6 to pH 9. For the E-NiFe electrode with approximately 55% nickel, the specimens were active in pH 6, but appeared to be passive in pH 7 to pH 10.
9. EXPERIMENTAL POTENTIAL/PH DIAGRAM

Figure 43 shows the values of the open circuit potentials and primary passive potentials (Epp) obtained from the series of polarization scans conducted on Nickel 200 specimens immersed in various buffered pH solutions. The Epp values were taken as the measured potential at the point of peak current density, indicating the onset of passive behavior. In cases where two peak current density values were present, such as seen for Nickel 200 in pH 6 solution (Figure 27), the more noble potential was taken as the Epp value. Figure 43 shows the Epp values obtained from these experiments overlaid on the experimental nickel potential-pH diagram from Pourbaix for comparison showing good agreement. This comparison provided confidence that the technique could provide results corresponding to other researchers and could reasonably delineate areas of active and passive behavior.

As indicated by the measured open circuit potentials, the experimental potential-pH diagram for Nickel 200 as shown in Figure 43 suggests that a Nickel 200 specimen will be actively corroding in pH 4 but passive in pH 5 through 12 under the test conditions. The results are in agreement with estimated corrosion rates from EIS presented in Figure 41. This figure shows a marked decrease in the estimated corrosion rates as pH changes from 4 to 5.

In a similar manner as used for Nickel 200, values of the open circuit potentials and primary passive potential (Epp) from the E-NiFe specimens were plotted in Figure 44. This experimental potential-pH diagram includes the experimental diagram for nickel
from Pourbaix for reference. The diagram suggests that the E-NiFe specimens were actively corroding in pH 6, but passive in pH 7 through 12. This is in agreement with the estimated corrosion rates shown in Figure 41, which shows a high rate of corrosion in pH 6, but substantially lower rates in the higher pH solutions.

Values of the open circuit potentials and primary passive potential (Epp) from the Josephinite specimens were plotted in Figure 45. This potential-pH diagram includes the experimental diagram for nickel from Pourbaix for reference. The diagram suggests that the Josephinite specimens were actively corroding in pH 5, but passive in pH 6 through 9. This is in agreement with the estimated corrosion rates shown in Figure 41, which shows a high rate of corrosion in pH 5, but substantially lower rates in the higher pH solutions.

A range of pH from 6 to 9 has been previously identified for natural waters in the geographic region where Josephinite specimens are found in southwest Oregon. The results of this project indicate that the Josephinite metallic material displays passive behavior in the controlled, buffered, aqueous solutions under oxidizing conditions used in these experiments and therefore may be a useful natural analogue material representing long term passive behavior.
10. CONCLUSIONS

The experimental results indicate that the Nickel 200, and E-NiFe specimens tested exist in the passive state in the tested naturally aerated, buffered solutions of various pH equal to or greater than approximately 5 for Nickel 200 and 7 for the E-NiFe specimens tested. Potentiodynamic polarization, open circuit potential measurements and EIS methods have tended to confirm this behavior. The behavior of the Josephinite specimens showed similar trends with passive behavior indicated for the tested pH 6 and greater solutions. Information on the pH of natural waters in areas surrounding the Josephinite deposits suggests that passive behavior may be expected in the native waters.

Within the range of pH 6 to 9, the open circuit potential achieved by the Josephinite specimens indicates significant anodic polarization takes place in the tested solutions. The measured open circuit potentials place the behavior in the corrosion prone area of the theoretical potential-pH diagram by Pourbaix for both nickel and iron. Despite the anodic polarization and the thermodynamic tendency for the primary constituent materials of nickel and iron to corrode, the metallic Josephinite displays a substantial resistance to corrosion as indicated by the EIS results. This shows substantial conformance to the definitions of passive behavior presented by Uhlig.

The estimated corrosion rates from EIS measurements for the Josephinite were less consistent than for the Nickel 200 and the E-NiFe electrode specimens. True surface area, non-homogeneous electrode surfaces, non-uniform geometry, as well as
interactions between the inclusions and crevices are considered possible sources of some of the inconsistencies.

Potential-pH diagrams were constructed using the results from potentiodynamic polarization techniques, and measured open circuit potentials with the materials tested. The potential-pH diagram produced for Nickel 200 was similar to that produced by other researchers.

The potential-pH diagrams resulting from these tests show a more restrictive zone of active corrosion for the E-NiFe specimens than the experimental diagram for nickel produced by Pourbaix. The experimental diagrams produced for nickel were similar to the theoretical zone shown by Pourbaix and others in the regions of corrosion behavior.

Measurement of open circuit potential alone is not adequate to differentiate between active and passive behavior. EIS measurements in conjunction with the OCP were more accurate at defining the regions of behavior. The OCP achieved by the E-NiFe electrode and the Josephinite specimens under what appeared to be corroding conditions where a visible corrosion product formed, placed the behavior in the passive regions of the respective experimental potential-pH diagrams. Despite the OCP, EIS results indicated that a high rate of corrosion was being experienced by the specimens.

A significant feature noted in review of the corrosion rates was the marked decrease in rate for Nickel 200 as the solution pH changed from 4 to 5, for Josephinite from pH 5 to 6, and for the E-NiFe electrode from pH 6 to 7. The marked decrease provides an indication of the onset of passive behavior in the higher pH solutions. As reported
previously, aqueous solutions with pH from approximately 6 to 9 have been reported in the vicinity of Josephine County. This suggests that passive behavior may be expected from Josephinite under field exposure conditions.
11. RECOMMENDED ADDITIONAL WORK

Additional analyses to better characterize the metallurgical structure of the Josephinite material. Etching characteristics in some areas were very different from the Nickel 200 and the E-NiFe alloys tested. Some specimens were heavily banded when etched. Judging by composition alone, the effects of etching was expected to have produced features similar to the Nickel 200 and E-NiFe specimens. SEM work at higher resolutions than used in the optical microscopy employed and additional EDS analysis traversing the banded areas is recommended.

Continue measurement of the open circuit corrosion potential and corrosion rates over longer periods of time. Work by Sagues and Li\textsuperscript{37} indicates that the corrosion rate may be expected to decrease over time. This information may be useful in demonstrating long life of Josephinite specimens.

Perform potentiodynamic scans and open circuit potential measurements on additional specimens of Josephinite in buffered solutions of pH 5 to 9 to obtain a better representation of the available nuggets.

Additional work is recommended to isolate the cavities and inclusions in the Josephinite specimens from areas of the metallic surface and obtain a more homogenous electrode. Removal of the inclusion areas, or isolating them by coating are two possibilities, as well as restricting the exposed surface to perhaps a circular area. Another route would be to prepare the Nickel 200 and the E-NiFe specimens as planer electrode surface in lieu of
the cylindrical ones utilized. This should act to minimize the differences between the specimens due to geometric factors. These would remove the possible effect of these conditions on the metallic corrosion rate estimates by EIS and provide a better measure of the corrosion rate by removing possible significant errors due to these factors.

Perform similar experiments using aqueous specimens from the area of Josephine deposits in southwest Oregon. These waters are reported to have higher resistivity than the buffered solutions used in these experiments. Other ionic species, such as chlorides are likely present in the natural waters, which may affect the results.

Perform elemental analysis of the corrosion product observed on the Josephinite and the E-NiFe electrode specimens in pH 5 and 6 respectively to identify the primary constituents. Testing for elements such as nickel and iron as metallic elements and sodium, potassium, and phosphate as elements from the buffer solutions used in testing.
REFERENCES


13 Reference Design Description for a Geologic Repository, Revision 2, January 1999, Civilian Radioactive Waste Management System


23 Silverman, David C., Revised EMF-pH Diagram for Nickel, Corrosion, Volume 37, No. 9, pp. 546-548, September 1981


25 DiBella, Carl, Memorandum to participants in International Workshop on Long-Term Extrapolation of Passive Behavior, Background information on Waste Package Environment, June 9, 2001


27 Uhlig, H, Corrosion and Corrosion Control, John Wiley and Sons, 1985
<table>
<thead>
<tr>
<th>Page</th>
<th>Reference</th>
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<tr>
<td>31</td>
<td>Kern, Raymond and Weisbrod, Alain, <em>Thermodynamics for Geologists</em>, Freeman, Cooper &amp; Company, 1967</td>
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<td>35</td>
<td>Private Communication, Chris Anderson of the Illinois Valley Soil and Water Conservation District, District covers Josephine County, Oregon</td>
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<td>37</td>
<td>Sagues, A., Li, Lienfang, <em>Metallurgical Effects on Chloride Ion Corrosion Threshold of Steel in Concrete</em>, Report to Florida Department of Transportation, 2001</td>
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Table 1 – Elemental analysis of tested modern specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Ni</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>C</th>
<th>Ti</th>
<th>Cr</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel 200</td>
<td>99.69</td>
<td>0.01</td>
<td>0.21</td>
<td>0.05</td>
<td>0.03</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>0.003</td>
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<tr>
<td>AWS A5.15, E-NiFe</td>
<td>55.25</td>
<td>44.07</td>
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<td>0.05</td>
<td>0.04</td>
<td>0.06</td>
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- not reported, data from mill test reports

Table 2 – Test matrix of specimens

<table>
<thead>
<tr>
<th>Test</th>
<th>pH</th>
<th>Nickel 200</th>
<th>E-NiFe</th>
<th>Josephinite Specimen S</th>
<th>Josephinite Specimen M</th>
<th>Josephinite Specimen L*</th>
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</thead>
<tbody>
<tr>
<td>Visual</td>
<td>N/A</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>Metallographic Analysis</td>
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<td>X</td>
<td>X</td>
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<td>X</td>
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<td>Elemental Analysis</td>
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<td>X</td>
<td>X</td>
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<td>Potentiodynamic Polarization</td>
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<td>Corrosion Potential</td>
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<td>X</td>
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<td>Electrochemical Impedance</td>
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<td>X</td>
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<td></td>
<td>X</td>
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<tr>
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<td>10</td>
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<td></td>
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<td>X</td>
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</tbody>
</table>

*Josephinite Specimen L was divided into two sections for corrosion testing, L1 and L2*
Table 3 – Buffered solutions used in testing

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffered Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>500 ml of 0.1 molar Potassium Hydrogen Phthalate (KH₂C₆H₄O₄) and 13 ml of 0.1 molar Sodium Hydroxide (NaOH) plus distilled water for 1 liter volume</td>
</tr>
<tr>
<td>5</td>
<td>500 ml of 0.1 molar Potassium Hydrogen Phthalate (KH₂C₆H₄O₄) and 226 ml of 0.1 molar Sodium Hydroxide (NaOH) plus distilled water for 1 liter volume</td>
</tr>
<tr>
<td>6</td>
<td>500 ml of 0.1 molar Potassium Phosphate Monobasic (KH₂PO₄) and 56 ml of 0.1 molar Sodium Hydroxide (NaOH) plus distilled water for 1 liter volume</td>
</tr>
<tr>
<td>7</td>
<td>500 ml of 0.1 molar Potassium Phosphate Monobasic (KH₂PO₄) and 294 ml of 0.1 molar Sodium Hydroxide (NaOH) plus distilled water for 1 liter volume</td>
</tr>
<tr>
<td>8</td>
<td>500 ml of 0.1 molar Potassium Phosphate Monobasic (KH₂PO₄) and 467 ml of 0.1 molar Sodium Hydroxide (NaOH) plus distilled water for 1 liter volume</td>
</tr>
<tr>
<td>9</td>
<td>500 ml of 0.1 molar Sodium Borate (Na₂B₄O₇) and 9 ml of 0.1 molar Sodium Hydroxide (NaOH) plus distilled water for 1 liter volume</td>
</tr>
<tr>
<td>10</td>
<td>500 ml of 0.1 molar Sodium Borate (Na₂B₄O₇) and 183 ml of 0.1 molar Sodium Hydroxide (NaOH) plus distilled water for 1 liter volume</td>
</tr>
<tr>
<td>12</td>
<td>500 ml of 0.1 molar Sodium Phosphate Dibasic (Na₂HPO₄) and 269 ml of 0.1 molar Sodium Hydroxide (NaOH) plus distilled water for 1 liter volume</td>
</tr>
</tbody>
</table>

Solutions prepared and verified for pH using pH meter prior to use.
Buffered solution mixtures are as published in the CRC Handbook.³⁸

Table 4 – Resistivity of aqueous solutions

<table>
<thead>
<tr>
<th>pH</th>
<th>Data Source</th>
<th>Resistivity, Ω/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Measured buffered solution</td>
<td>167</td>
</tr>
<tr>
<td>6.2</td>
<td>Reference 34, Oregon water</td>
<td>6,600</td>
</tr>
<tr>
<td>7</td>
<td>Measured buffered solution</td>
<td>146</td>
</tr>
<tr>
<td>8</td>
<td>Measured buffered solution</td>
<td>119</td>
</tr>
<tr>
<td>8.45</td>
<td>Reference 34, Oregon water</td>
<td>2,805</td>
</tr>
<tr>
<td>9</td>
<td>Measured buffered solution</td>
<td>505</td>
</tr>
<tr>
<td>7 to 8.91</td>
<td>Reference 35, Oregon waters in nearby counties</td>
<td>12 – 4.8</td>
</tr>
<tr>
<td>Location</td>
<td>Ni</td>
<td>Fe</td>
</tr>
<tr>
<td>---------------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Metallic-Sm</td>
<td>67.79</td>
<td>30.16</td>
</tr>
<tr>
<td>Metallic-Sm</td>
<td>71.37</td>
<td>27.48</td>
</tr>
<tr>
<td>Metallic-Sm</td>
<td>71.31</td>
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<tr>
<td>Metallic-Sm</td>
<td>69.02</td>
<td>30.54</td>
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<tr>
<td>Metallic-M</td>
<td>73.77</td>
<td>26.23</td>
</tr>
<tr>
<td>Metallic-S</td>
<td>62.43</td>
<td>25.77</td>
</tr>
</tbody>
</table>

**Metallic areas – Specimen Interior**

<table>
<thead>
<tr>
<th>Location</th>
<th>Ni</th>
<th>Fe</th>
<th>Mg</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Cu</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section –L</td>
<td>66.75</td>
<td>28.40</td>
<td>-</td>
<td>0.76</td>
<td>-</td>
<td>0.49</td>
<td>3.60</td>
<td>-</td>
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<tr>
<td>Section –M</td>
<td>73.60</td>
<td>25.81</td>
<td>-</td>
<td>0.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Section –S</td>
<td>63.24</td>
<td>33.59</td>
<td>0.62</td>
<td>2.21</td>
<td>-</td>
<td>0.34</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Literature</td>
<td>68.2</td>
<td>28.9</td>
<td>&lt;0.02*</td>
<td>-</td>
<td>&lt;0.008*</td>
<td>0.21*</td>
<td>0.041*</td>
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</tr>
<tr>
<td>Section-L near copper</td>
<td>22.49</td>
<td>72.93</td>
<td>-</td>
<td>0.53</td>
<td>-</td>
<td>0.46</td>
<td>3.58</td>
<td>-</td>
</tr>
<tr>
<td>Section-L near copper</td>
<td>9.89</td>
<td>25.27</td>
<td>-</td>
<td>16.03</td>
<td>0.80</td>
<td>25.7</td>
<td>22.33</td>
<td>-</td>
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<tr>
<td>Section-L copper area</td>
<td>2.48</td>
<td>0.56</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>96.69</td>
<td>-</td>
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</table>

**Dark areas – Specimen Exterior**

<table>
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<th>Fe</th>
<th>Mg</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Cu</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brown-Sm</td>
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<td>33.13</td>
<td>42.70</td>
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<td>0.46</td>
<td>-</td>
<td>0.26</td>
</tr>
<tr>
<td>Brown-Sm</td>
<td>5.77</td>
<td>15.59</td>
<td>35.02</td>
<td>43.29</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Black-Sm</td>
<td>11.95</td>
<td>11.59</td>
<td>35.94</td>
<td>39.15</td>
<td>Nd</td>
<td>1.07</td>
<td>-</td>
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</tr>
<tr>
<td>Black-Sm</td>
<td>5.07</td>
<td>8.17</td>
<td>40.68</td>
<td>45.8</td>
<td>Nd</td>
<td>Nd</td>
<td>-</td>
<td>0.29</td>
</tr>
<tr>
<td>dark-L</td>
<td>2.99</td>
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<td>1.52</td>
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**Dark areas – Specimen Interior**

<table>
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<th>Mg</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Cu</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section-L</td>
<td>19.29</td>
<td>30.56</td>
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<td>5.72</td>
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<td>Section-M</td>
<td>20.5</td>
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<td>-</td>
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<td>Literature</td>
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<td>12.35</td>
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<td>3.99</td>
<td>3.46</td>
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</table>

Nd (not detected), - (not reported), * (reported as oxide)

Sm – Smithsonian specimen, L, M, S – Commercial specimens
<table>
<thead>
<tr>
<th>Specimen</th>
<th>pH</th>
<th>Value</th>
<th>Slope, volts/decade</th>
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<tr>
<td>Nickel 200</td>
<td>4</td>
<td>bc</td>
<td>0.15</td>
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<td>6</td>
<td>bc</td>
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<td></td>
<td>8</td>
<td>bc</td>
<td>0.17</td>
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<tr>
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<td>12</td>
<td>bc</td>
<td>0.14</td>
</tr>
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<td>Nickel 200 Average</td>
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<td>bc</td>
<td>0.17</td>
</tr>
<tr>
<td>Nickel 200</td>
<td>4</td>
<td>ba</td>
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<td>Nickel 200 Average</td>
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<td>0.19</td>
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<td>bc</td>
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<tr>
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<tr>
<td>E-NiFe</td>
<td>4</td>
<td>ba</td>
<td>0.07</td>
</tr>
<tr>
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<td>ba</td>
<td>0.09</td>
</tr>
<tr>
<td>E-NiFe Average</td>
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<td>ba</td>
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<tr>
<td>Nickel 200 and E-NiFe group average</td>
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<td>bc</td>
<td>0.16</td>
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<tr>
<td></td>
<td></td>
<td>ba</td>
<td>0.14</td>
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<tr>
<td>Nominal values suggested by Jones</td>
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<tr>
<td></td>
<td></td>
<td>ba</td>
<td>0.1</td>
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<tr>
<td>Composite Tafel Parameter using nominal values suggested by Jones</td>
<td></td>
<td>( B = \frac{ba \times bc}{(2.303)(ba + bc)} )</td>
<td>0.022</td>
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</table>
Table 7 – Summary of potentiodynamic polarization test results

<table>
<thead>
<tr>
<th>Solution</th>
<th>Scan Rate, mV/sec</th>
<th>Epp, volts SHE</th>
<th>Ipeak, Amps/cm²</th>
<th>Ipass, Amps/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel 200</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>pH4</td>
<td>0.167</td>
<td>0.156</td>
<td>3.48E-5</td>
<td>1.40E-6</td>
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<td>pH4</td>
<td>0.778</td>
<td>0.166</td>
<td>5.10E-5</td>
<td>4.70E-6</td>
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<tr>
<td>pH4</td>
<td>0.167</td>
<td>0.271</td>
<td>2.97E-5</td>
<td>4.50E-6</td>
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<tr>
<td>pH6</td>
<td>0.167</td>
<td>0.186</td>
<td>6.29E-6</td>
<td>1.31E-6</td>
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<tr>
<td>pH6</td>
<td>0.778</td>
<td>0.144</td>
<td>1.50E-5</td>
<td>4.26E-6</td>
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<tr>
<td>pH6</td>
<td>0.167</td>
<td>0.141</td>
<td>3.95E-6</td>
<td>1.07E-6</td>
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<tr>
<td>pH8</td>
<td>0.167</td>
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<td>6.87E-6</td>
<td>1.46E-6</td>
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<tr>
<td>pH8</td>
<td>0.778</td>
<td>-0.08</td>
<td>1.37E-5</td>
<td>5.53E-6</td>
</tr>
<tr>
<td>pH8</td>
<td>0.778</td>
<td>-0.08</td>
<td>1.56E-5</td>
<td>5.50E-6</td>
</tr>
<tr>
<td>pH9</td>
<td>0.167</td>
<td>-0.244</td>
<td>1.03E-6</td>
<td>9.77E-7</td>
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<tr>
<td>pH9</td>
<td>0.778</td>
<td>-0.285</td>
<td>5.95E-6</td>
<td>3.54E-6</td>
</tr>
<tr>
<td>pH10</td>
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Table 8 – Summary of EIS test and modeling results

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Figure 1 - Geographic distribution of Nuclear Waste needing long-term storage

Figure 2 - DOE projected flow of Nuclear Waste to disposal site
Figure 3 - Reference design waste package

Figure 4 - Reference design natural barrier system
Figure 5 - Reference design for engineered barrier system

Figure 6 - Typical potentiodynamic polarization curve
Figure 7 – Theoretical potential-pH diagram for nickel, from Pourbaix
Figure 8 – Experimental potential-pH diagram for nickel, from Pourbaix \(^6\)
1. Embed Josephinite sample in epoxy.
2. Drill and tap into Josephinite sample for 3-38 threads.
3. Insert threaded end of copper wire with some insulation removed.
4. Cover exposed copper wire to sound insulation with 2nd layer epoxy.
5. Check for electrical continuity between exposed Josephinite face and opposite end of copper wire.

Figure 9 – Schematic of mounting for Josephinite corrosion specimens
Figure 10 – Corrosion specimen mounting. E-NiFe at top left, Nickel 200 at top right, Josephinite at bottom
Figure 11 – Test circuit used for verification of EIS instrumentation. Modeling results are shown in the three top graphs and consisted of three representative variables: Rs – Solution Resistance, ohms; Rp – Polarization Resistance, ohms; Rc – Interface Capacitance, µ farads.

- Rs = 989 ohm resistor model as 996.6 ohm
- Rp = 852 k ohm resistor model as 852 k ohm
- Ru = 100 mF capacitor model as 110 micro Farad
Figure 12 - Smithsonian Josephinite specimen, scale in inches

Figure 13 - Commercial Josephinite specimen, scale in inches
Figure 14 - Scratches on exterior metallic portion of Smithsonian Josephinite specimen. 25x. Scale at lower right is 10µm/division

Figure 15 - Scratches on exterior metallic portion of commercial Josephinite specimen. 25x. Scale at lower right is 10µm/division
Figure 16 - Cross sections of commercial specimens, M, L, S, top to bottom. Arrow points to dark area seen at center of Figure 20. Scale at bottom is 1mm/division.

Figure 17 - Copper inclusions in specimen L, unetched. 25x. Scale at lower right is 10µm/division.
Figure 18 - Nickel 200 specimen microstructure, Marbles reagent, 250x. Scale at lower right is 10µm/division

Figure 19 – E-NiFe electrode specimen microstructure, Marbles reagent, 250x. Scale at lower right is 10µm/division
Figure 20 - Specimen L etched in Marbles reagent. Large inclusion at center, numerous copper inclusions visible. 6.25x. Arrow is area magnified in Figure 16. Scale at lower right is 1mm/division

Figure 21 - Specimen L magnified from arrow area of Figure 20. 100x. Arrow is area magnified in Figure 19. Scale at lower right is 10µm/division
Figure 22 - Specimen L magnified view of arrow area from Figure 21. 250x. Scale at lower right is 10μm/division

Figure 23 - Specimen L, microstructure of additional area. 250x. Scale at lower right is 10μm/division
Figure 24 - Specimen M microstructure. 250x. Scale at lower right is 10μm/division

Figure 25 - Specimen L etching revealed banding features. 25x. Scale at lower right is 10μm/division
Figure 26 - Specimen L showing banding at copper inclusion. 250x. Scale at lower right is 10µm/division
Figure 27 – Typical potentiodynamic polarization scans of Nickel 200 specimens
Figure 28– Typical potentiodynamic polarization scans for E-NiFe electrode specimens
Figure 29 – Typical potentiodynamic polarization scans for Josephinite specimens
Figure 30 – Peak and passive current densities for: Top - Nickel 200, Center - E-NiFe, Bottom - Josephinite Specimens
Figure 31 – Open circuit corrosion potential for Nickel 200 specimens, Top - linear time scale, Bottom logarithmic time scale
Figure 32 - Open circuit corrosion potential for E-NiFe electrode specimens, Top - linear time scale, Bottom – logarithmic time scale
Figure 33 - Open circuit corrosion potential for Josephinite specimens. Note the marked difference between the specimens in pH5 and the other solutions.
Top - linear time scale, Bottom – logarithmic time scale
Figure 43 – Randles circuit used for modeling EIS behavior. Model consists of four variables:
- Rs – Solution resistance, ohms
- Rp – Polarization resistance, ohms
- Rc – Interface capacitance, µFarads
- Alpha – factor for non-ideal interface capacitance
Figure 35 – Nyquist diagram for Nickel 200 specimens in various pH solutions, typical EIS plots and curves used for modeling shown
Figure 36 – Nyquist diagram for E-NiFe electrode specimens in various pH solutions, typical EIS plots shown
Figure 37 - Nyquist diagram for Josephinite specimen L1 in pH 7 solution
Figure 38 - Nyquist diagram for Josephinite specimen S in pH 7 solution
Figure 39 – Rp value over time for two specimens in pH7 buffered solution
Figure 40 – Top - Josephinite specimen M after 1,632 hours exposure in naturally aerated pH7 solution.
Bottom – Same specimen after approximately 10,512 hours
Estimated Corrosion Rate by EIS, um/year

Figure 41 - Estimated corrosion rate for Nickel 200, E-NiFe and Josephinite Specimens based on EIS measurements. Note Josephinite rates are average of at least two specimens.
Figure 42 - Corrosion behavior dependence on Nickel Content and Solution pH
Figure 43 - Experimental potential-pH diagram produced for Nickel 200 specimens

Approximate range of measured open circuit potentials in naturally aerated solutions in pH range 6 - 12

O2 Stability
Experimental Line from Pourbaix

Passive

Corrosion

H2 Stability

Inert

Spontaneous Passivation

Potential, (SHE)

pH
Figure 44 – Experimental potential-pH diagram for E-NiFe electrode specimens. Corrosion potential values for pH 6 specimens are prior to formation of dark film on specimen surfaces. After film formation, the corrosion potentials shifted to above the NiFe Epp line.
Figure 45- Experimental potential-pH diagram for Josephinite specimens. Corrosion potential values for pH 5 specimen are prior to formation of dark film on specimen surfaces. After film formation, the corrosion potentials shifted to above the nickel passive/corrosion boundary line.
APPENDICES
Appendix A: Nickel 200 Potentiodynamic Polarization Results

Nickel pH4 Buffered Polarization Scan

Figure A1 - Nickel 200 pH4
Appendix A: (Continued)

Nickel pH6 Buffered Polarization Scan

Figure A2 - Nickel 200 pH6
Appendix A: (Continued)

Nickel pH8 Buffered Polarization Scan

Figure A3 - Nickel 200 pH8
Appendix A: (Continued)

Figure A4 - Nickel 200 pH9
Appendix A: (Continued)

Nickel pH10 Buffered Polarization Scan

Figure A5 - Nickel 200 pH10
Appendix A: (Continued)

Nickel pH12 Buffered Polarization Scan

![Graph showing Nickel pH12 Buffered Polarization Scan with markers for O2 stability and H2 stability.]

Figure A6 - Nickel 200 pH12
Appendix B: E-NiFe Potentiodynamic Polarization Results

E-NiFe pH4 Buffered Polarization Scan

Figure B1 - E-NiFe pH4
Appendix B: (Continued)

E-NiFe pH6 Buffered Polarization Scan

Figure B2 - E-NiFe pH6
Appendix B: (Continued)

E-NiFe pH8 Buffered Polarization Scan

![Graph of E-NiFe pH8 Buffered Polarization Scan](image)

Figure B3 - E-NiFe pH8
Figure B4 - E-NiFe pH9
E-NiFe pH10 Buffered Polarization Scan

Potential vs. SHE

Current Density (A/cm²)

-1.5  -1.0  -0.5  0.0  0.5  1.0  1.5

pH10NiFe .167 a
pH10 NiFe .778
Linear (O2 Stability)
Linear (H2 stability)

Figure B5 - E-NiFe pH10
Appendix B: (Continued)

E-NiFe pH12 Buffered Polarization Scan, 0.167mV/sec

Figure B6 - E-NiFe pH12
Appendix C: Josephinite Potentiodynamic Polarization Results

Figure C1 - Josephinite pH 6, 7 and 9
Appendix D: Nickel 200 EIS results

Figure D1 – Nickel 200, pH4, 48 hours
Appendix D: (Continued)

Figure D2 – Nickel 200, pH5, 504 hours
Figure D3 – Nickel 200, pH6, 100 hours
Figure D4 – Nickel 200, pH6, 360 hours
Appendix D: (Continued)

Figure D5 – Nickel 200, pH8, 192 hours
Figure D6 – Nickel 200, pH10, 96 hours
Appendix E: E-NiFe EIS Results

Figure E1 - E-NiFe – pH6, 137 hours
Figure E2 - E-NiFe, pH6, 213 hours
Appendix E: (Continued)

Figure E3 – E-NiFe, pH7, 504 hours
Appendix E: (Continued)

Figure E4 – E-NiFe. pH8, 234 hours
Figure E5 – E-NiFe, pH10, 131 hours
Figure E6 – E-NiFe, pH10, 560 hours
Appendix F: Josephinite EIS Results

Figure F1 – Josephinite S, pH5, 216 hours
Figure F2 – Josephinite S, pH6, 120 hours
Figure F3 – Josephinite S, pH7, 95 hours
Figure F4 – Josephinite S, pH7, 123 hours
Figure F5 – Josephinite S, pH7, 144 hours
Figure F6 – Josephinite S, pH7, 168 hours
Figure F7 – Josephinite S, pH7, 240 hours
Figure F8 – Josephinite S, pH7, 318 hours
Appendix F: (Continued)

Figure F9– Josephinite S, pH7, 960 hours
Figure F10 – Josephinite S, pH9, 264 hours
Appendix F: (Continued)

Figure F11 – Josephinite L1, pH5, 120 hours
Figure F12– Josephinite L1, pH5, 342 hours
Figure F13 – Josephinite L1, pH7, 117 hours
Appendix F: (Continued)

Figure F14 – Josephinite L1, pH7, 141 hours
Figure F15 - Josephinite L1, pH7, 168 hours
Figure F16 - Josephinite L1, pH7, 240 hours
Figure F17 - Josephinite L1, pH7, 288 hours
Figure F18 - Josephinite L1, pH7, 1008 hours
Appendix F: (Continued)

Figure F19 - Josephinite L1, pH9, 120 hours
Figure F20 - Josephinite L1, pH9, 316 hours
Appendix F: (Continued)

Figure F21 - Josephinite M, pH6, 120 hours
Figure F22– Josephinite M, pH6, 318 hours
Appendix F: (Continued)

Figure F23 – Josephinite M, pH7, 120 hours
**Figure G1 – E-NiFe Material Certification**

**CERTIFIED MATERIAL TEST REPORT**

- **No.**: 97715
- **Order No./Item**: 10376A
- **Page**: 1 of 2
- **Quantity**: 1
- **Mark Order No.**: 10376A
- **Material**: Ni Fe 256 HR Rod
- **Manufacturer**: COIL PKL ANN
- **Quality Certification Representative**: [Signature]

**SPECIFICATIONS**:

- **Quality System Certification**: ISO 9002 (ABS-QE Cert. 30125);
  - ISO/IEC Guide 25 (ASME Cert. 10/1021); EN 10 204/DIN 50049 (Cert. 3.1.8).

**CHEMICAL ANALYSIS (wt. %)**

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<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Ti</th>
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<td>0.002</td>
<td>0.05</td>
<td>0.04</td>
<td>55.75</td>
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**Total Other Elements**: 0.50% Maximum

**Tested by IAIIL, 3200 Riverside Dr., Huntington, WV 25701; Accredited for Fastener Quality Act**

**Melt Method**: Air

**MECHANICAL PROPERTIES**

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<th>Heat/Lot</th>
<th>Quantity</th>
<th>Gross</th>
<th>Net</th>
<th>Dia</th>
<th>Yield</th>
<th>Tensile</th>
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<td>0814</td>
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**Yield Strength was determined using a Stress Strain Curve**


Any subcontracted work also complies with Customer & ASME Section III, NCA 3800 Requirements.
Appendix G – (Continued)

Figure G2 – Nickel 200 Material Certification
Figure G3 – Nickel 200 Additional Material Certification
Figure G4 – Josephinite Supplier Certification
Ray Monson

From: "Monson,Ray"
To: remjim@att.net
Sent: Wednesday, February 13, 2002 5:15 PM
Subject: josephinite

telecon with Chris Anderson of the Illinois Valley Soil and Water Conservation Dist at 541-592-3731; Closest areas to Josephine creek pH and Cond are:
83 to 197 mS/cm pH 7-7.49
100.3 to 205 mS/CM pH 8.1 - 8.91.
pH of just under 9 is highest he has seen

suggested website of Oregon DEQ about Rogue River Basin. Mouth of Illinois River

Ray Monson
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Law Engineering and Environmental Services
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813-282-8585 fax