

**AN ELECTROCHEMICAL STUDY ON PASSIVATION OF
ALLOY 22 IN CHLORIDE-CONTAINING SOLUTIONS
WITH AND WITHOUT SULFUR**

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ABSTRACT

This report documents the results of a previously unpublished set of experiments that evaluated the effects of sulfur on the passivation behavior of Alloy 22 (Ni-22Cr-13Mo-4Fe-3W) in chloride-containing solutions with and without sulfur species at low temperatures {e.g., less than 100 °C [212 °F]}. In earlier studies, an increase in the anodic current had been observed for Alloy 22 exposed to chloride solutions containing sulfur. The purpose of the additional experiments reported here was to use electrochemical methods to evaluate the hypothesis that the observed increase in anodic current was due to the oxidation of sulfur species dissolved in the test solution.

The results in this study showed more than an order of magnitude increase in the anodic current when 0.01 M Na₂S was added to either 0.5 M NaCl solution or simulated concentrated water at 20, 50 and 95 °C [72, 140, and 203 °F]. The use of an electrode made of platinum, an inert metal, as a reference indicated that the observed increase was mainly due to the oxidation of sulfur species in solution and did not result from the active dissolution of Alloy 22. The Alloy 22 specimens passivated in the presence of the sulfur-containing solutions, and the passive film on Alloy 22 was not compromised due to the presence of sulfur. There was no observable evidence of enhanced passive dissolution (i.e., general corrosion rate) of Alloy 22 due to sulfur. If there was a mechanism to enhance passive dissolution, the effect should be minimal.

The information obtained in this study has resulted in an improved understanding of the corrosion behavior of Alloy 22 as an engineered material in various low-temperature geochemical environments characterized by the presence of aqueous species of sulfur and chloride. High concentrations of alloying elements (i.e., more than 22 wt% of chromium and 13 wt% of molybdenum) in Alloy 22 keep the accumulation of sulfur on the alloy surface at a low enough concentration to maintain the passive film stability.

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: All CNWRA-generated original data contained in this report meet the quality assurance requirements described in the Geosciences and Engineering Division Quality Assurance Manual. Sources for other data should be consulted for determining the level of quality for those data. Computational calculations have been recorded in CNWRA Scientific Notebook 900 (Jung and Ellis, 2008).

Reference

Jung, H. and C. Ellis. "Effects of Sulfur on Passivation and Repassivation of Alloy 22 Using Scratch Test." Scientific Notebook No. 900. San Antonio, Texas: CNWRA. pp. 48-53 and 56-71. 2008.

1 INTRODUCTION

This report is part of the knowledge management activities for the U.S. Nuclear Regulatory Commission (NRC) high-level waste repository safety program. The report provides previously undocumented results from recent corrosion tests that used electrochemical methods and thermodynamic computations to evaluate the potential for enhanced passive dissolution (i.e., general corrosion rate) of Alloy 22 (Ni-22Cr-13Mo-4Fe-3W) in the presence of sulfur.

1.1 Background Information

The U.S. Department of Energy (DOE) identified the long lifetime of Alloy 22 waste packages as an important attribute for isolating nuclear waste in a potential high-level waste repository at Yucca Mountain, Nevada, because corrosion of the waste package is considered to be an important potential degradation process under nominal repository conditions (DOE, 2002). The corrosion behavior of Alloy 22 has been the topic of many NRC/CNWRA investigations during the pre-licensing and licensing phases of the Yucca Mountain repository program (e.g., Jung, et al., 2009, 2007; Ahn, et al., 2008; Dunn, et al., 2005, 1998; Pensado, et al., 2002; Cragolino and Sridhar, 1991).

In the absence of environments leading to localized corrosion, Alloy 22 is expected to corrode uniformly (i.e., general corrosion) in an aqueous environment with low corrosion rates under the potential repository conditions (Jung, et al., 2009, 2007; Ahn et al., 2008; Dunn, et al., 2005; Pensado, et al., 2002). The low corrosion rates are attributed to the presence of protective passive oxide film on the alloy surface.

General corrosion rates could increase substantially, however, if the passive film became unstable, which would depend on material alteration states, such as alloy chemistry, structure, and exposure conditions during the disposal period. Such unstable passive film on Alloy 22 could come from sulfur-induced corrosion (Ahn, et al., 2008; Yang, et al., 2004). Sulfur species present either in the alloy or in the environment could have a detrimental effect on the corrosion resistance of Alloy 22 by enhancing localized corrosion (i.e., pitting corrosion) susceptibility or general corrosion rate.

Previously, Jung, et al. (2009) evaluated localized corrosion susceptibility of Alloy 22 due to sulfur-induced corrosion. Specifically, sulfur segregation by anodic dissolution of Alloy 22 and the resultant breakdown of the passive film were evaluated using two techniques: the scratch repassivation technique and the electrochemically accelerated dissolution process. For scratch repassivation tests, the passive film on Alloy 22 was mechanically removed by scratching the alloy surface in sulfur-containing solutions, and the resultant repassivation rates of Alloy 22 were measured by recording current changes with time. The results showed that Alloy 22 repassivated within a few seconds and the anodic current measured after scratching returned to its prescratch level. The results from the accelerated dissolution tests indicated that sulfur segregation could not affect the long-term stability of the passive film on Alloy 22. Based on test observations, Jung et al. (2009) concluded that sulfur segregation might not have any significant detrimental effect on the long-term passive film stability of Alloy 22.

Another aspect of sulfur-induced corrosion could be a potential enhancement of the general corrosion rate of Alloy 22. In the presence of sulfur during the scratch repassivation tests, a relatively high anodic current was observed compared to in the absence of sulfur during the potentiostatic polarization before and after a scratch. An example is shown in Figure 1-1. Based on the literature information on inert materials' electrochemical reactions to platinum (Al-Kharafi, et al., 2010), gold (Zhang and Nicol, 2003), and graphite (Ateya and Al-Kharafi, 2002), the increase of anodic current was considered to be caused by oxidation of sulfur species (mainly hydrogen sulfide) dissolved in the solution. In Al-Kharafi, et al. (2010), the

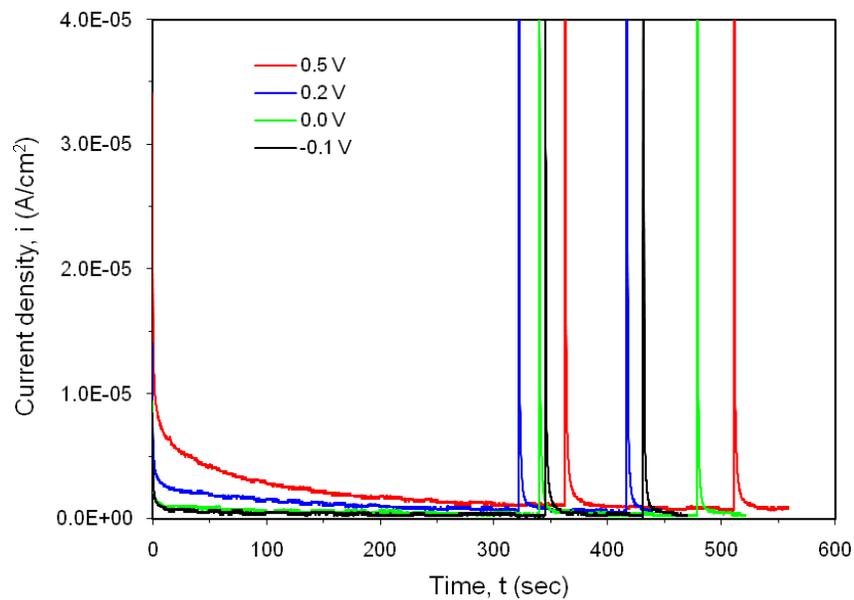
anodic current measured on the platinum electrode in the absence of sulfide ions was negligible compared to that measured in the presence of sulfide ions (0.15 M HS^-) in 3.5 percent NaCl solutions at $25 \text{ }^\circ\text{C}$ [$77 \text{ }^\circ\text{F}$]. Al-Kharafi, et al. (2010) concluded that an increase in anodic current resulted from sulfide ion oxidation. Therefore, it is possible that the increase in the anodic current observed in the scratch repassivation tests in Alloy 22 could be due to oxidation of sulfur species (i.e., mainly hydrogen sulfide) present in the solution.

Sulfate reducing bacteria (SRB) are also a potential source for corrosive sulfur species (i.e., hydrogen sulfide), as metabolites in the proposed Yucca Mountain, Nevada, repository environment that could contact the surface of Alloy 22 waste packages (Yang, et al., 2004; Yang and Cragolino, 2004). Yang, et al. (2004) evaluated microbially influenced corrosion—specifically, the potential detrimental effect of SRB to induce localized corrosion for Alloy 22. Yang et al. (2004) also observed an increase in anodic current on the polarization curves for platinum and stainless steel when SRB or sulfide was present in the solution. The increase was believed to be caused by the oxidation of adsorbed sulfur species on the surfaces of platinum and stainless steel. However, the potential effect of sulfur on the anodic current of Alloy 22 was not confirmed by experiments.

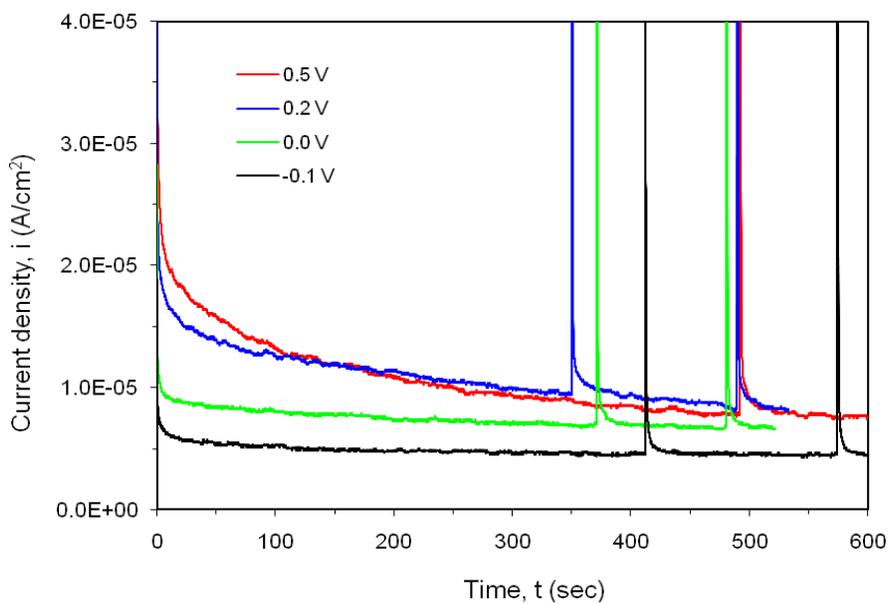
1.2 Objective and Scope

The objective of the present work is to evaluate whether sulfur species oxidation affects the anodic current of Alloy 22 at low temperatures {e.g., below $100 \text{ }^\circ\text{C}$ [$212 \text{ }^\circ\text{F}$]}. In addition, the thermodynamic stability of metal sulfides is examined by utilizing the potential-pH diagrams for nickel-, chromium-, and molybdenum-sulfur-water systems at 25 and $90 \text{ }^\circ\text{C}$ [77 and $140 \text{ }^\circ\text{F}$]. Finally, the effect of sulfur on the general corrosion rate of Alloy 22 is assessed.

To evaluate the effects of oxidation of sulfur species on the anodic current of Alloy 22, corrosion tests were conducted using electrochemical methods in the chloride-containing solutions with and without sulfur at 22 , 60 , and $95 \text{ }^\circ\text{C}$ [72 , 140 , and $203 \text{ }^\circ\text{F}$]. Platinum was used as a reference for comparison of polarization curves for Alloy 22.



(a)



(b)

Figure 1-1. Potentiostatic Polarization Curves at Various Potentials in Deaerated 0.5 M NaCl Solution at 22 °C [72 °F] (a) Without Sulfur and (b) With 0.01 M Na₂S (Jung, et al., 2009)

2 EXPERIMENTAL DETAILS

2.1 Materials

The working electrodes for the tests were either cylindrical Alloy 22 or platinum flag samples (purity of 99.95 percent). Alloy 22 samples were machined from a thick plate with a diameter of 12.075 mm [0.48 in] and a height of 10.16 mm [0.4 in]. Alloy 22 samples were polished to a 600 grit finish, cleaned with ethanol, and dried. The chemical composition of mill-annealed Alloy 22 (HT 2277-3-3266) is shown in Table 2-1.

2.2 Test Solutions

Two test solutions (0.5 M NaCl and simulated concentrated water, the composition of which is shown in Table 2-2) containing 0 and 0.01 M Na₂S were prepared from analytical-grade chemicals and deionized water. The initial pH of 0.5 M NaCl solutions without sulfur addition was approximately 6.7, while the initial pH of 0.5 M NaCl solutions with sulfur addition was approximately 10. The 0.5 M NaCl solutions containing 0.01M Na₂S were adjusted to an initial pH of 7 with dilute HCl solution. The test solution was aerated by opening it to air. The test was conducted at the solution temperatures of 22, 60, and 95 °C [72, 140, and 203 °F].

2.3 Test Procedures

Tests were conducted in a 1-liter [0.22 gal] glass cell. The saturated calomel, used as a reference electrode, was connected to the solution through a Lugging probe with a porous silica tip. A platinum mesh was used as a counter electrode. The exposed surface areas of the working electrodes for Alloy 22 and platinum flag samples were 3.851 and 10 cm² [0.597 and 1.55 in²], respectively. Polarization tests were made using an electrochemical interface and frequency response analyzer controlled by a personal computer. Unless otherwise indicated, potentiodynamic measurements were performed at the potential scan rate of 0.2 mV/s. During the tests, the test samples were either rotated at a speed of 60 rpm or not rotated at all. Impedance measurements were carried out in the frequency range of 100 kHz to 10 mHz with an alternating current voltage amplitude of 10 mV at the open circuit potential. The potentials, except the potential-pH diagrams, were measured; potentials are reported in this report against a saturated calomel reference electrode (SCE) via the conversion

$$E (V_{SCE}) = E (V_{SHE}) - 0.242V \quad (2-1)$$

Table 2-1. Chemical Composition of Mill-Annealed Alloy 22 (in Weight Percent)											
Ni*	Cr*	Mo*	W*	Fe*	Co*	Si*	Mn*	V*	P*	S*	C*
Bal†	22.15	12.90	2.81	3.82	1.37	0.01	0.30	0.15	0.012	0.002	0.004
*Ni—nitrogen; Cr—chromium; Mo—molybdenum; W—tungsten; Fe—iron; Co—cobalt; Si—silicon; Mn—manganese; V—vanadium; P—phosphorous; S—sulfur; C—carbon †Bal—balance											

Table 2-2. Chemical Composition of Simulated Concentrated Water in This Study									
Ion	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
mg/L	3,400	40,900	<1	<1	1,400	6,700	6,400	16,700	70,000

3 RESULTS AND DISCUSSION

This section summarizes and discusses the Alloy 22 experiment results. The polarization behaviors of Alloy 22 both in the presence and absence of sulfur in the test solutions (i.e., 0.5 M NaCl or simulated concentrated water) are evaluated, and the results are compared to those of platinum. Finally, the potential effect of sulfur-induced corrosion on the general corrosion rate of Alloy 22 is assessed.

High anodic currents for Alloy 22 (Jung, et al., 2009) and stainless steel (Yang, et al., 2004) were observed when sulfur species were present in the solution. This increase was considered to be caused by the oxidation of the sulfur species present in the solution, rather than active dissolution of Alloy 22 or stainless steel. To confirm this hypothesis, experiments were conducted on Alloy 22 using electrochemical methods.

3.1 Passivation Behavior of Alloy 22 in 0.5 M NaCl Solution With and Without Sulfur Addition

Figure 3-1 shows the polarization behavior of the rotating Alloy 22 samples in aerated 0.5 NaCl solution with and without 0.01 M Na₂S addition at 60 and 95 °C [140 and 203 °F]. In the absence of Na₂S, Alloy 22 showed a passive behavior at both 60 and 95 °C [140 and 203 °F] up to about 0.4 V_{SCE}. The corrosion current at 95 °C [203 °F] appears slightly higher than at 60 °C [140 °F], which was confirmed from the impedance spectra measured at the open circuit potential (Appendix A, Figure A-1). The polarization resistances of Alloy 22 samples were 241 and 144 kohms at 60 and 95 °C [140 and 203 °F], respectively. The impedance spectra were fitted using a simple Randle's circuit.

When 0.01 M Na₂S was added, the polarization curves shifted to a high anodic current range and Alloy 22 appeared to be depassivated. The anodic currents increased more than an order of magnitude from the results in the solution without sulfur. This increase could be due to the enhanced anodic dissolution of Alloy 22 with the addition of Na₂S and/or the anodic oxidation of the sulfur species dissolved in the solution, which could have contributed to the resultant anodic current observed.

Because it was not clear whether the passivation of Alloy 22 was preserved when Na₂S was added (as shown in Figure 3-1), a cyclic polarization scan was conducted to check for the presence of passivation. Figure 3-2 shows the cyclic polarization behavior of Alloy 22 without rotation in aerated 0.5 NaCl solution with 0.01 M Na₂S addition at 60 °C [140 °F]. The anodic current obtained during the reversed scan was lower than that obtained during the forward scan, indicating that Alloy 22 was passivated and not actively corroded by the high anodic current during the forward scan up to 0.75 V_{SCE}. If Alloy 22 had been actively dissolved, the anodic current obtained during the reversed scan should have been higher than the current obtained during the forward scan. Other investigators (Cragnolino, 2008) reported similar behavior showing higher current. When active dissolution or pitting occurs during the forward scan, the anodic current obtained during the reversed scan is usually higher than the value obtained during the forward scan at potentials above the repassivation potential. Figure 3-3 shows an

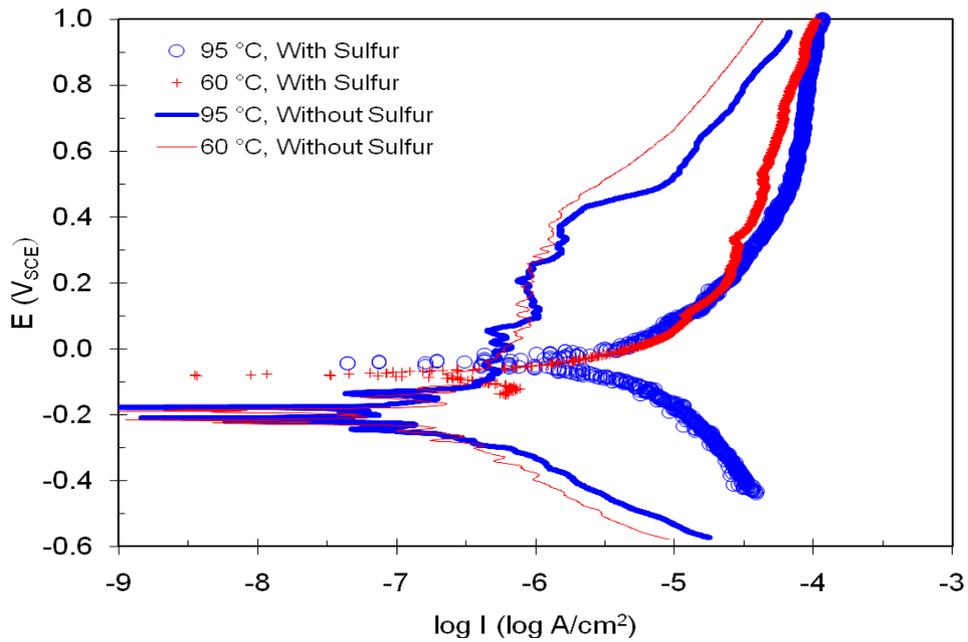


Figure 3-1. Polarization Curves of the Rotating Alloy 22 Electrodes Tested in Aerated 0.5 M NaCl Solution With and Without 0.01 M Na₂S Addition at 60 and 95 °C [140 and 203 °F] (Scan Rate of 0.2 mV/s)

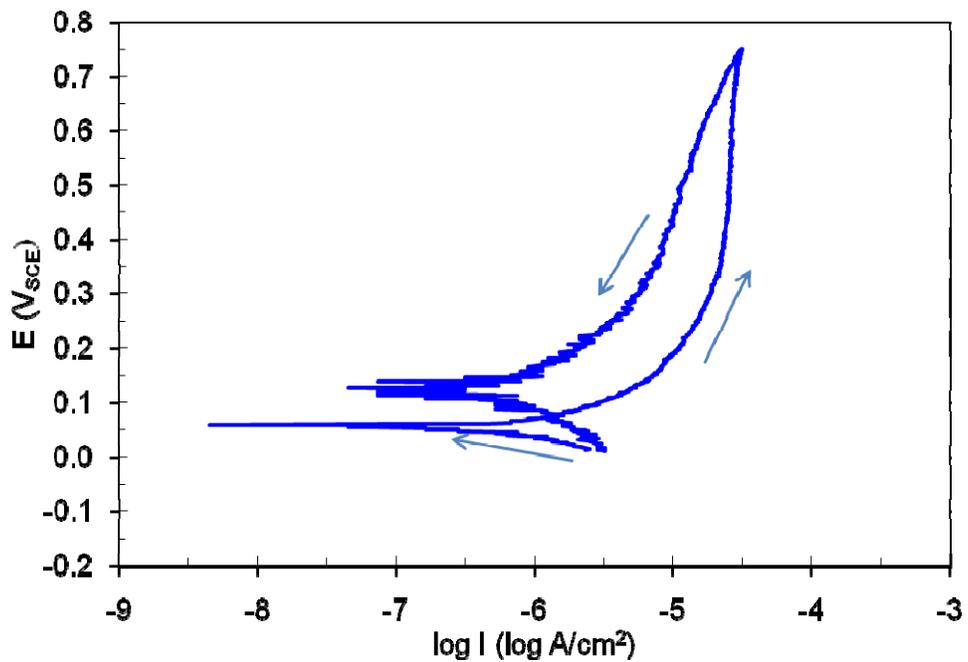


Figure 3-2. Cyclic Polarization Curve of the Alloy 22 Electrode Without Rotation in 0.5 M NaCl Solution Containing 0.01 M Na₂S at 60 °C [140 °F] (Scan Rate of 0.5 mV/s)

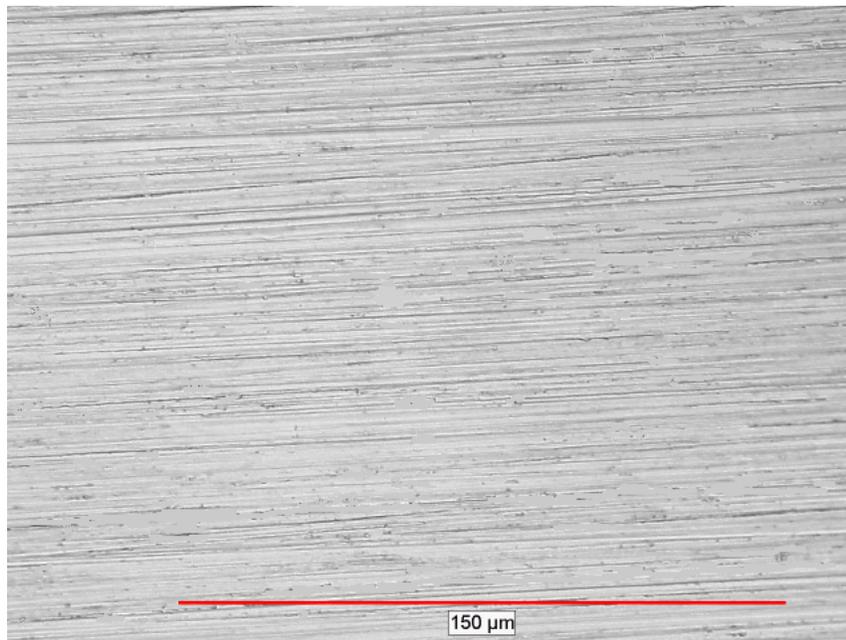


Figure 3-3. Optical Micrograph of the Alloy 22 Surface After Cyclic Polarization Test in 0.5 M NaCl Solution Containing 0.01 M Na₂S at 60 °C [140 °F]

optical micrograph of the general surface of Alloy 22 after a cyclic polarization scan. As seen in the figure, the surface is bright and polishing marks from a 600-grit finish are still present. If there had been active dissolution, the surface would have been rough and polishing marks would have been much less prominent or eliminated. No active dissolution or pitting corrosion on Alloy 22 was evident.

3.2 Effect of Sulfide Oxidation on Anodic Current of Platinum

Platinum was used as a reference to compare the polarization behaviors of Alloy 22 and to evaluate the net effect of sulfur species on the anodic current. Because platinum is a noble metal and inert to corrosion, it is reasonable to assume that the current measured during the polarization of platinum is from electrochemical reactions of dissolved sulfur species on the surface of platinum, not from the dissolution of platinum. Figure 3-4 shows the polarization curves on platinum without rotation obtained with and without 0.01 M Na₂S addition to 0.5 M NaCl solution. Similar to Alloy 22 in the same solutions, the anodic current obtained in the presence of Na₂S is approximately two orders of magnitude higher than the anodic current obtained in the absence of Na₂S. Because platinum is expected to be electrochemically inert in the NaCl and Na₂S test solutions, the enhanced anodic current should be a result of sulfide oxidation.

Al-Kharafi, et al. (2010) also observed an increase in the anodic current of platinum when sulfide was present in the solution at 25 °C [77 °F]. Al-Kharafi, et al. (2010) showed that the anodic current of platinum was low when it was polarized in a 3.5 wt% NaCl solution at room temperature, but the anodic current increased when 0.15 M Na₂S was added. The current

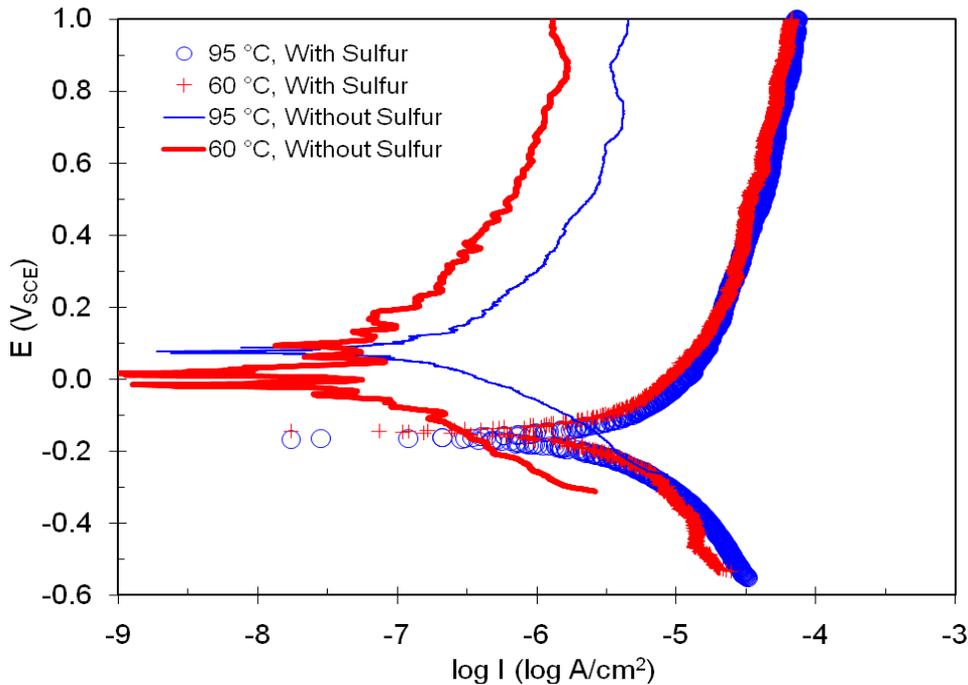
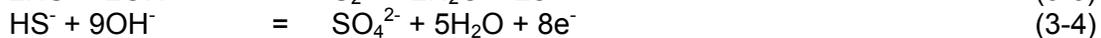


Figure 3-4. Polarization Behaviors of Platinum Electrode in 0.5 M NaCl Solution With and Without 0.01 M Na₂S Addition at 60 and 95 °C [140 and 203 °F] (Scan Rate of 0.2 mV/s)

density near 0.0 V_{Ag/AgCl}¹ was approximately 4×10^{-1} A/cm² [2.6 A/ft²] with Na₂S addition at the potential scan rate of 10 mV/s. Al-Kharafi et al. (2010) concluded that the high anodic current in the presence of Na₂S was due to the oxidation of the sulfide ions. In addition, three anodic current peaks during the forward scan were observed at the potentials of -0.1, 0.475, and 1.0 V_{Ag/AgCl}. These three peaks were attributed to (i) the formation of platinum sulfide and polysulfide; (ii) the deposition of elemental sulfur; and (iii) the oxidation of the deposited sulfur to form soluble sulfate ions (SO₄²⁻).

In the oil and gas industry, hydrogen sulfide and associated sulfide ions have been shown to contaminate geothermal brines due to their toxicity and corrosiveness to the metal structures (Tuttle and Kane, 1981). One way hydrogen sulfide can be removed from the aqueous stream is by an electrochemical oxidation method: inert materials such as platinum, graphite, or gold are used as the working electrode to convert sulfide to elemental sulfur or sulfate, which is environmentally benign. Several electrochemical reactions can occur during sulfur species oxidation (Al-Kharafi, et al., 2010; Ateya and Al-Kharafi, 2002), including



¹ Note: E (V, SCE) = E (V, Ag/AgCl) + 0.045V

In a neutral range of the test solutions for this study (about pH 7), hydrogen sulfide (HS^-) ion could be a thermodynamically stable species (Langmuir, 1997). These ions have been recognized as the reducing agents and can be readily oxidized by O_2 , Cl_2 , and H_2O_2 (Weil and Sandler, 1991). Therefore, upon anodic oxidation, hydrogen sulfide can oxidize to elemental sulfur (S), polysulfide (S_2^{2-}), or sulfate (SO_4^{2-}) depending on the applied potential and pH, as seen in Appendix B, Figures B-1 through B-3.

3.3 Comparison of Polarization Curves of Alloy 22 and Platinum

Figure 3-5 shows the comparison of the polarization curves of the platinum electrodes shown in Figure 3-4 and the Alloy 22 electrodes shown in Figure 3-1 when 0.01 M Na_2S was added to the 0.5 M NaCl solution at 60 and 95 °C [140 and 203 °F]. The anodic polarization curves for these two types of electrodes have approximately the same shape and absolute value of anodic current between 0 and 0.6 V_{SCE} . Because Alloy 22 was rotated at 60 rpm, while the platinum electrode was not rotated (i.e., 0 rpm), the anodic currents of Alloy 22 obtained with rotation should be higher than those obtained without rotation. This rotation-speed-base difference could be attributed to a different degree of diffusion-controlled process, resulting in different limiting currents. Similarly, the anodic current of platinum would be expected to be higher with rotation. Ateya and Al-Kharafi (2002) reported that the oxidation of sulfide on the surface of a graphite electrode was diffusion controlled in 0.58 M NaCl with 0.001 or 0.005 M Na_2S . When the solution was stirred, the anodic-limiting current increased at least one order of magnitude. Again, because platinum is a noble metal and inert to corrosion, it is reasonable to assume that the current measured during platinum polarization should be due to the results of electrochemical reactions of dissolved sulfur species (i.e., sulfide oxidation) on the surface of platinum, not from platinum dissolution. Any contribution from platinum dissolution should be negligible, as Al-Kharafi, et al., (2010) observed.

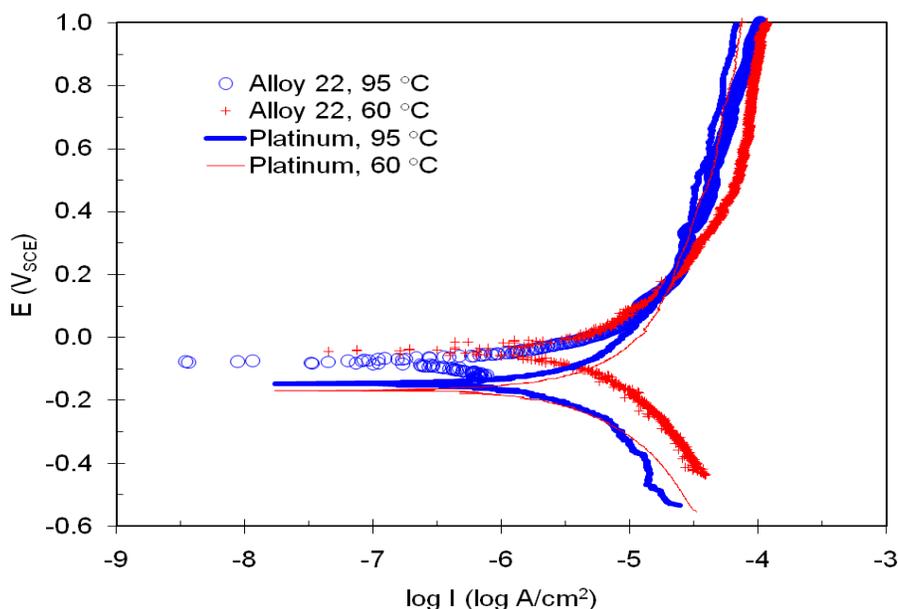


Figure 3-5. Comparison of Polarization Curves on Alloy 22 and Platinum Electrodes in 0.5 M NaCl Solution Containing 0.01 M Na_2S at 60 and 95 °C [140 and 203 °F]

Note that the corrosion potential measured for the Alloy 22 electrode was similar to that measured for the platinum electrode, indicating that Alloy 22 was not actively corroding in the presence of 0.01 M Na₂S.

3.4 Passivation Behavior of Alloy 22 in Simulated Concentrated Water With and Without Sulfur Addition

Figure 3-6 shows the polarization curves of the rotating Alloy 22 electrodes in the simulated concentrated water with and without 0.01 M Na₂S addition tested at 22, 60, and 95 °C [72, 140, and 203 °F]. In the absence of Na₂S, both anodic and corrosion currents increased gradually as the temperature increased from 22 to 60 and 95 °C [72 to 140 and 203 °F], which is consistent with the previous polarization test results on Alloy 22 in the literature (Dunn, et al., 2005; Pensado, et al., 2002; Lloyd, et al., 2003).

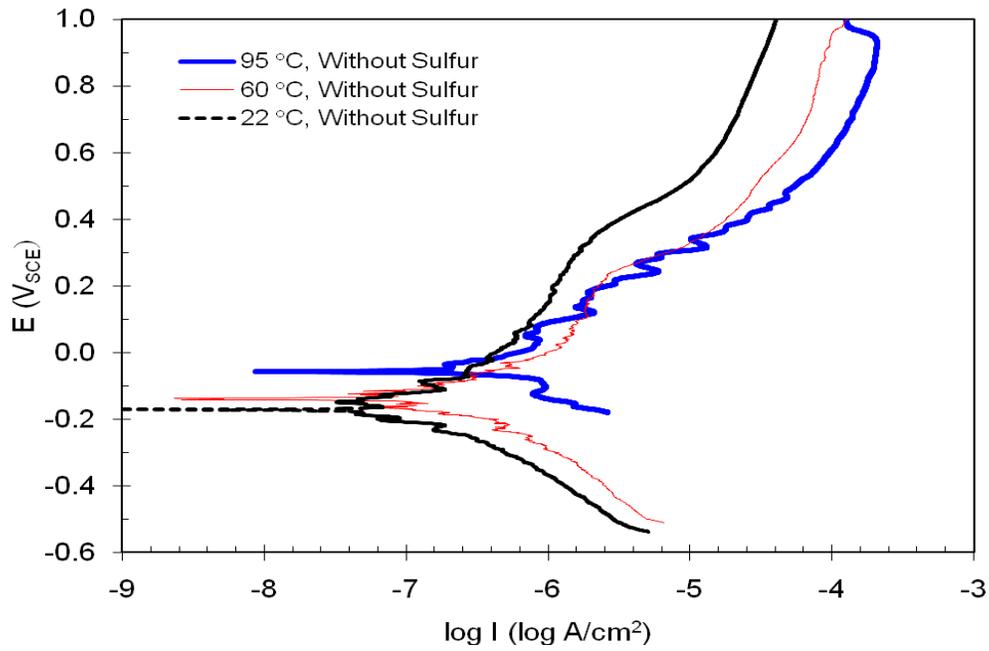
Similar to the polarization curves obtained in 0.5 M NaCl solution, the anodic currents in simulated concentrated water containing 0.01 M Na₂S were more than an order of magnitude higher than the anodic current obtained in the absence of Na₂S. Even if there is a difference in the solution chemistry between the 0.5 M NaCl solution and simulated concentrated water (e.g., pH of 7 for 0.5 M NaCl and pH of ~10 for simulated concentrated water), the higher anodic current is most likely due to the anodic oxidation of sulfur species, rather than from the dissolution of Alloy 22, according to the discussions of and findings for the 0.5 M NaCl solution in the previous sections.

3.5 Thermodynamic Stability of Sulfur-Metal (Ni, Cr, Mo)-Water Systems Below 100 °C [203 °F]

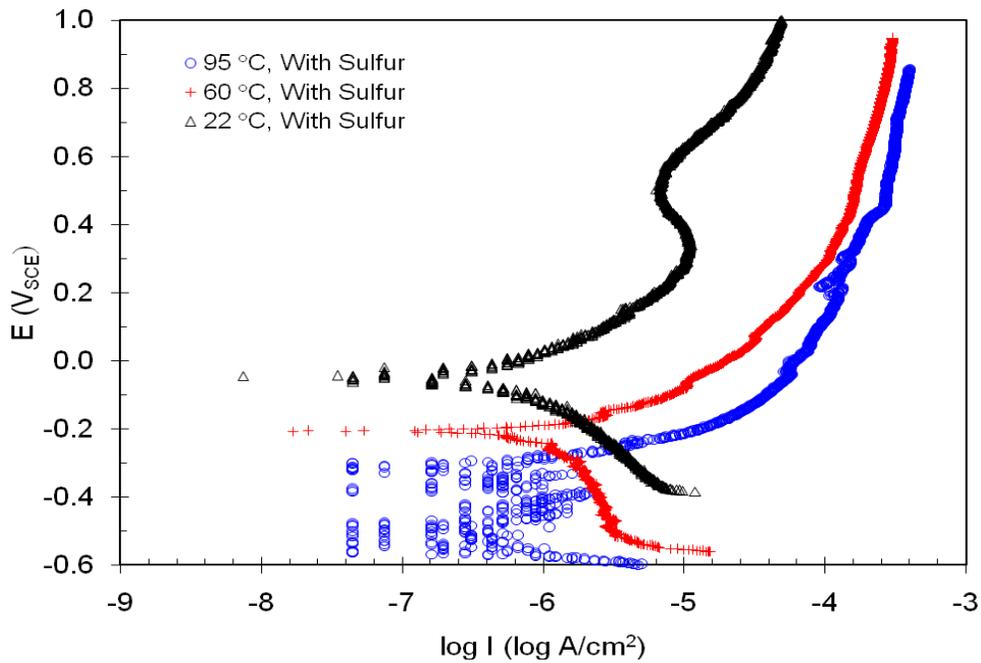
In the previous report (Jung, et al., 2007), several metal sulfides, including nickel and molybdenum sulfides, were identified as the stable phases at 25 and 90 °C [77 and 194 °F]. As seen in the thermodynamic stability diagrams for the nickel-sulfur-water system (Appendix B, Figure B-1), nickel can oxidize to form different phases of nickel sulfides (e.g., Ni₃S₂, NiS, and Ni₃S₄) in a wide range of potential and pH regions at both temperatures. These nickel sulfides can inhibit formation of a protective passive oxide film on Alloy 22.

To the contrary, there are no stable phases of chromium sulfides, as seen in Appendix B, Figure B-2. Chromium can form chromium oxide (Cr₂O₃) rather than sulfides in a wide range of potentials and pHs. The superior stability of chromium oxide may be one reason Alloy 22 could repassivate quickly after scratching and could also maintain passivation when the polarization scan was reverse tested in the sulfur-containing solutions, as seen in Figure 3-3.

In the case of molybdenum, the calculated stability diagrams at 25 and 90 °C [77 and 194 °F] (Appendix B, Figure B-3) indicate that there is a strong tendency to form metal molybdenum sulfides such as MoS₂ and MoS₃. However, molybdenum plays a beneficial role in passivation of nickel-molybdenum alloys (Marcus and Moscatelli, 1989) and stainless steel (Elbiache and Marcus, 1992) by reducing sulfur content on the alloy surface. Several mechanisms were proposed to reduce sulfur content, including removing sulfur as the dissolved forms of compounds (e.g., molybdenum sulfides or clusters) (Marcus and Moscatelli, 1989) or reducing the residence time of the adsorbed sulfur on the alloy surface by desorbing sulfur occupying the active sites present on the metal surface (Betts and Newman, 1993).



(a)



(b)

Figure 3-6. Polarization Curves of the Rotating Alloy 22 Electrodes in Simulated Concentrated Water (a) Without and (b) With 0.01 M Na₂S Addition at 22, 60, and 95 °C [72, 140, and 203 °F] (Scan Rate of 0.2 mV/s)

4 SUMMARY

To evaluate a potential effect of sulfur on the passivation and general corrosion rate of Alloy 22, electrochemical testing was conducted in the solutions containing sulfur species at low temperatures {e.g., below 100 °C [212 °F]}. Thermodynamic stability of metal sulfides was also examined utilizing the potential-pH diagrams for nickel-, chromium- and molybdenum-sulfur-water systems. The electrochemical testing results indicate that the increase in the anodic current on Alloy 22 was mainly due to oxidation of sulfur species, not the active dissolution of Alloy 22. The passive film of the Alloy 22 was not compromised by the presence of sulfur.

Thermodynamic calculations predicted the formation of a stable chromium oxide (Cr_2O_3) on the alloy surface over a wide range of potentials and pH at low temperatures (Appendix B, Figure B-2). High concentrations of alloying elements (>22 wt% of chromium and 13 wt% of molybdenum) in Alloy 22 are believed to keep accumulated sulfur content at a low enough concentration on the Alloy 22 surface to maintain stability of the passive film on the alloy surface. As long as the beneficial roles of these alloying elements in Alloy 22 passivation were maintained, potential deleterious effects of sulfur present in the environment, if in existence, would be minimal. To further enhance our understanding and quantify any potential enhancement in the general corrosion rate of Alloy 22 from sulfur, weight loss measurements could be used to separate the net contribution of metal dissolution from the measured anodic current due to oxidation of sulfur species dissolved in the solution.

The corrosion tests and thermodynamic calculations in the present study provide no observable evidence of sulfur affecting the passivation of Alloy 22 and increasing its general corrosion rate.

5 CONCLUSIONS

In this report, the potential effect of sulfur presence on passivation of Alloy 22 at low temperatures {e.g., below 100 °C [212 °F]} was evaluated through scoping corrosion tests and thermodynamic computation. There are three main conclusions of the study.

- Polarization test results showed that there was an increase greater than an order of magnitude in the anodic current on Alloy 22 when 0.01 M Na₂S was added to either 0.5 M NaCl solution or simulated concentrated water at 22, 60, and 95 °C [72, 140, and 203 °F]. By utilizing platinum, it was found that this increase was mainly due to oxidation of sulfur species dissolved in the solution. The increase was not from the active dissolution of Alloy 22.
- Even if a high concentration of sulfide (0.01 M Na₂S) was present in the solution, Alloy 22 could passivate. The passive film stability was not compromised due to sulfur in the solution. No evidence was observed that indicated enhancement of passive dissolution (i.e., general corrosion rate) of Alloy 22 due to sulfur presence in the environment. If there was a mechanism to enhance passive dissolution, the effect should be minimal.
- High concentrations of alloying elements (i.e., >22 wt% of chromium and 13 wt% of molybdenum) could contribute to keeping the accumulated sulfur content on the alloy surface low enough to maintain passive film stability of Alloy 22. As long as the beneficial roles of alloying elements are maintained, the passive film on Alloy 22 will not likely deteriorate due to the presence of sulfur.

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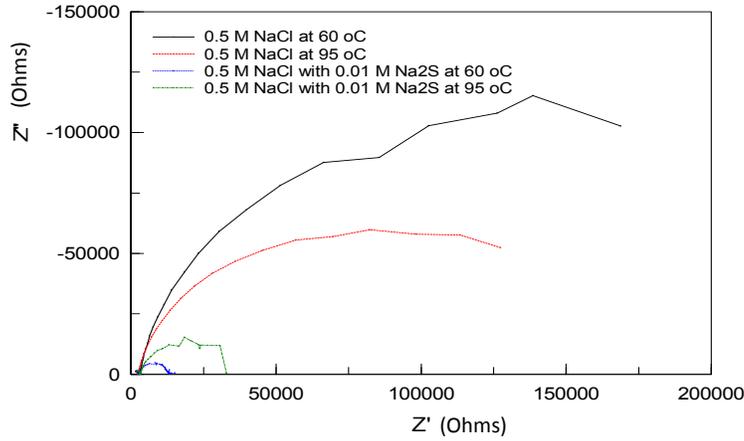
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APPENDIX A

**IMPEDANCE SPECTRA OF ALLOY 22 MEASURED AT
OPEN CIRCUIT POTENTIAL AT 60 AND 95 °C [140 AND 103 °F]**

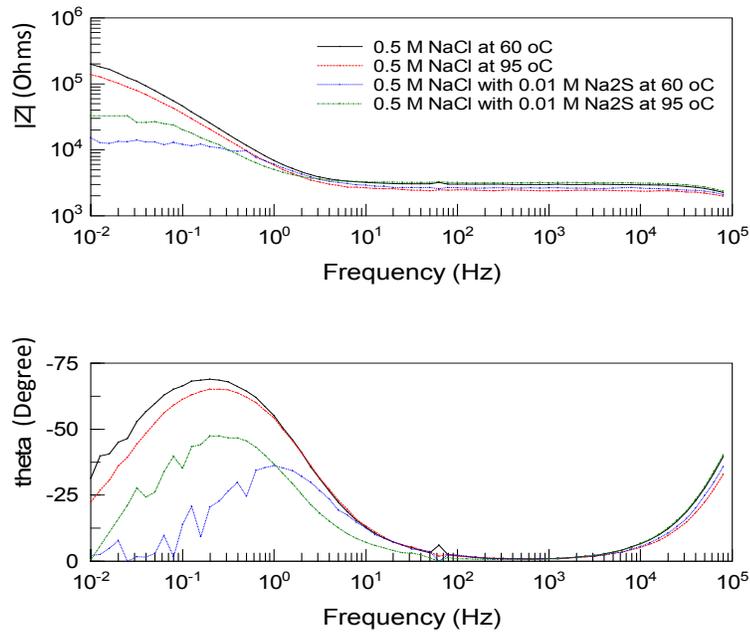
IMPEDANCE SPECTRA OF ALLOY 22 MEASURED AT OPEN CIRCUIT POTENTIAL AT 60 AND 95 °C [140 AND 103 °F]

Nyquist Plot



(a) Nyquist Plot

Bode Plot



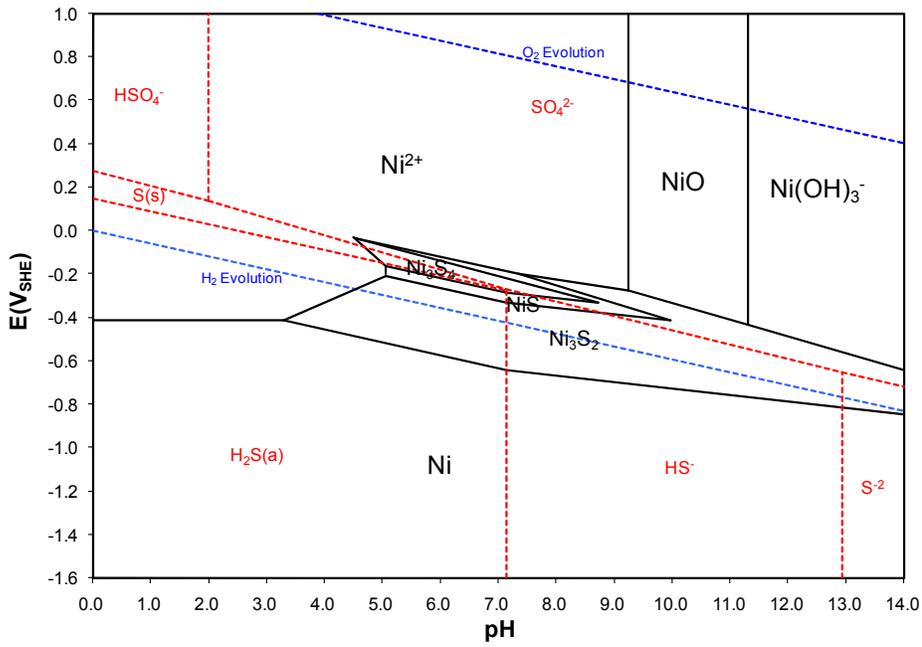
(b) Bode Plot

Figure A-1. Impedance Spectra of Alloy 22 Measured at Open Circuit Potential in 0.5 M NaCl With and Without 0.01 M Na₂S Addition at 60 and 95 °C [140 and 203 °F]; (a) Nyquist Plot, (b) Bode Plot

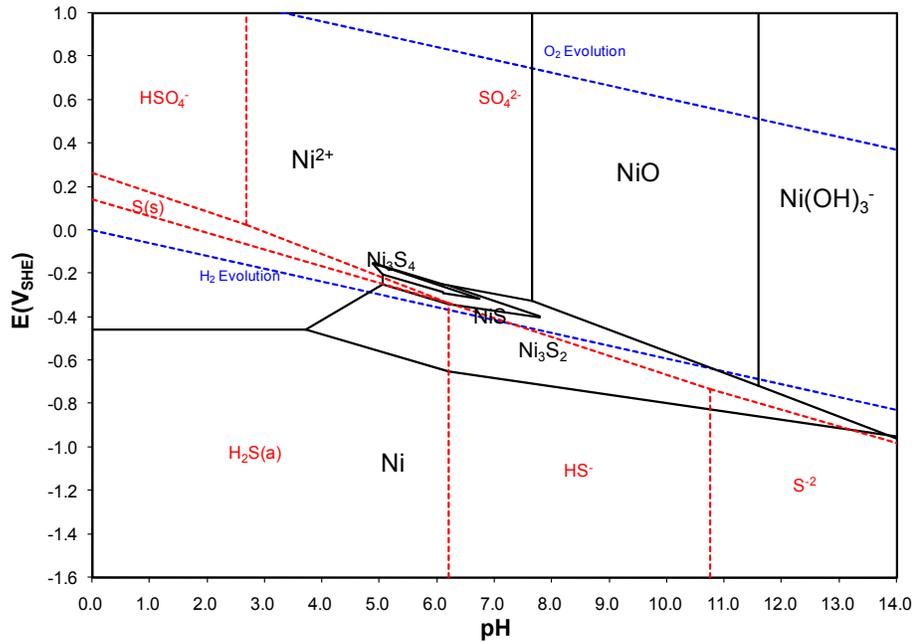
APPENDIX B

**POTENTIAL-PH DIAGRAMS FOR METALS (NI, CR, AND MO)-S-H₂O
SYSTEM AT 25 AND 90 °C [77 AND 194 °F]**

POTENTIAL-PH DIAGRAMS FOR METALS (NI, CR, AND MO)-S-H₂O SYSTEM AT 25 AND 90 °C [77 AND 194 °F]

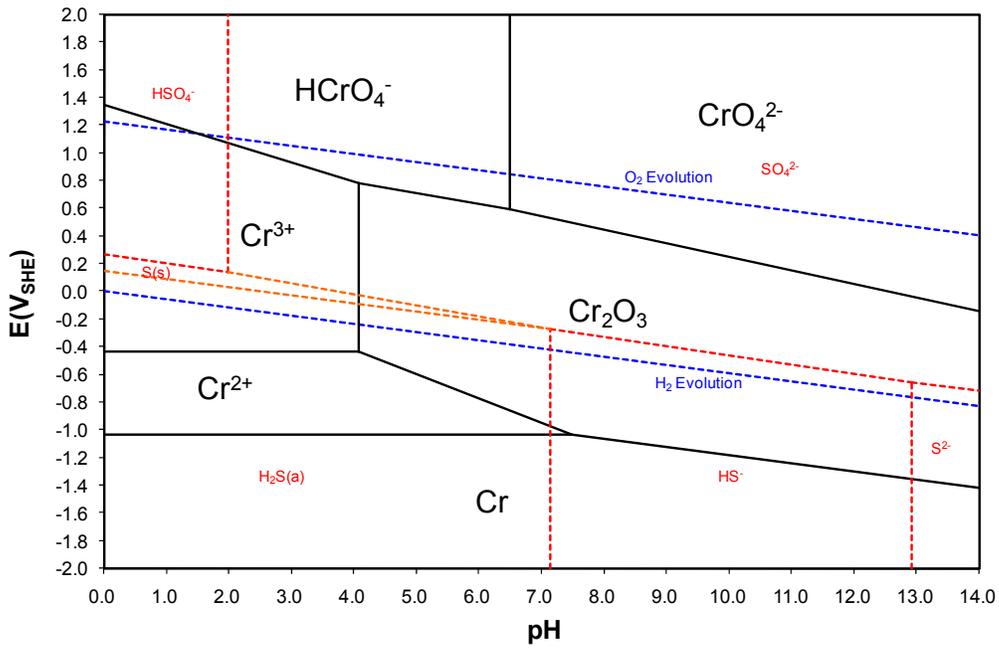


(a)

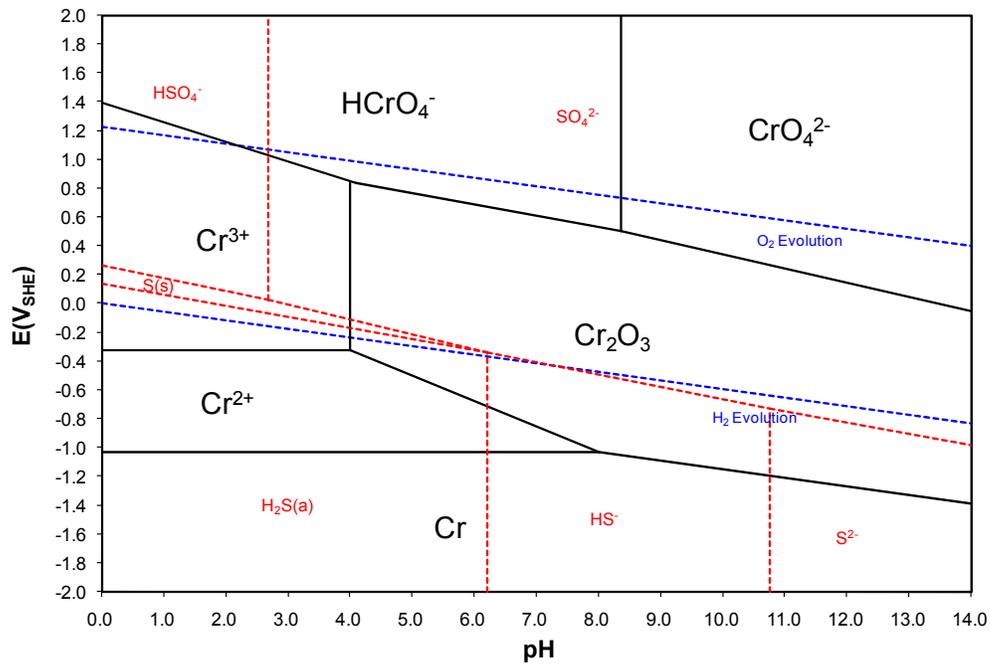


(b)

Figure B-1. Potential-pH Diagram for Ni-S-H₂O System at (a) 25 °C [77 °F] and (b) 90 °C [194 °F] for 10⁻⁶ M of Ions (Jung, et al., 2007)



(a)



(b)

Figure B-2. Potential-pH Diagram for Cr-S-H₂O System at (a) 25 °C [77 °F] and (b) 90 °C [194 °F] for 10^{-6} M of Ions (Jung, et al., 2007)

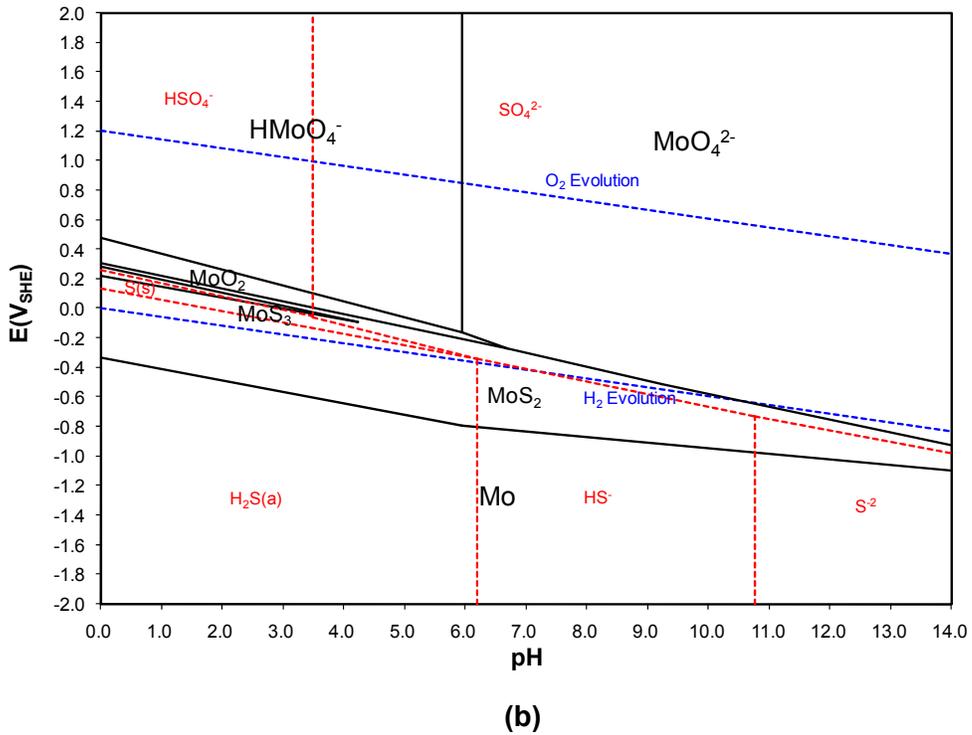
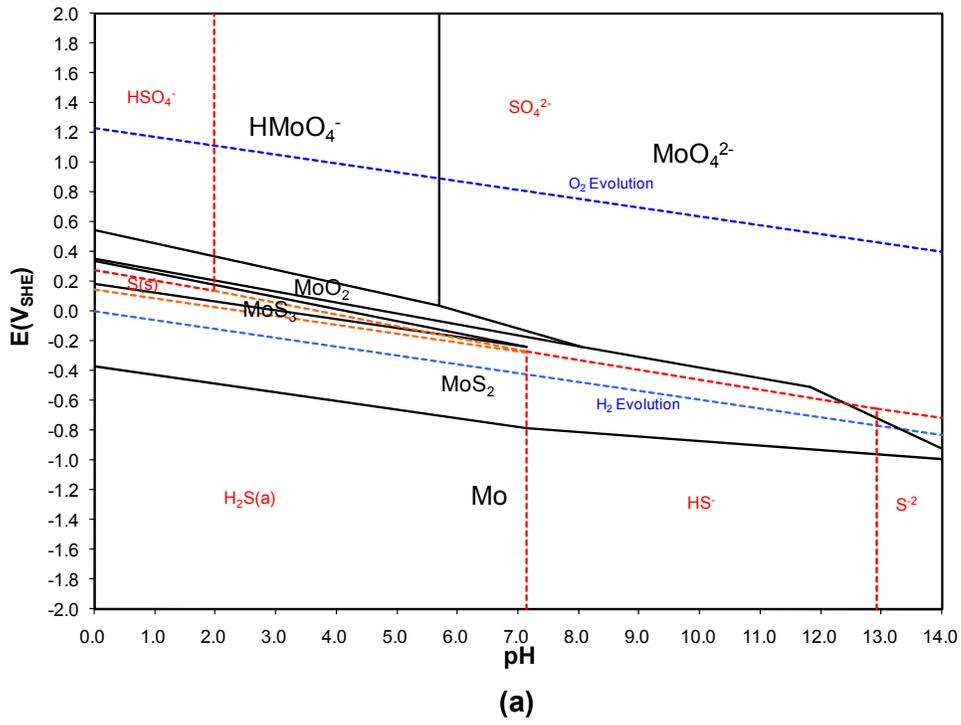


Figure B-3. Potential-pH Diagram for Mo-S-H₂O System at (a) 25 °C [77 °F] and (b) 90 °C [194 °F] for 10⁻⁶ M of Ions (Jung, et al., 2007)

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