NRC Form 390A
(12-2003)
NRCMD 3.9

U.S. NUCLEAR REGULATORY COMMISSION

RELEASE TO PUBLISH UNCLASSIFIED NRC CONTRACTOR SPEECHES, PAPERS, AND JOURNAL ARTICLES
(Please type or print)

1. TITLE (State in full as it appears on the speech, paper, or journal article) Assessment of Nickel-Based Alloy Passive Film Stability Through Thermodynamic Modeling

2. AUTHOR(S) P. Shukla, R. Pabalan, and L. Yang

3. NAME OF CONFERENCE, LOCATION, AND DATE(s) NACE 2009 Annual Conference & Exposition, Atlanta, Georgia, March 22-26, 2009

4. NAME OF PUBLICATION
NACE Conference Proceedings

5. NAME AND ADDRESS OF THE PUBLISHER
NACE International
1440 South Creek Drive
Houston, TX 77084-4906

TELEPHONE NUMBER OF THE PUBLISHER
(281) 228-6200

6. CONTRACTOR NAME AND COMPLETE MAILING ADDRESS (Include ZIP code)
Dr. Pavan Shukla
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute
6220 Culebra Road
San Antonio, TX 78238

TELEPHONE NUMBER OF THE CONTRACTOR
(210) 522-6534

YES	NO	7. CERTIFICATION (*ANSWER ALL QUESTIONS*)		
	X	A. COPYRIGHTED MATERIAL – Does this speech, paper, or journal article contain copyrighted material: If yes, attach a letter of release from the source that holds the copyright.		
	X	B. PATENT CLEARANCE – Does this speech, paper, or journal article require patent clearance? If yes, the NRC Patent Counsel must signify clearance by signing below.		
		NRC PATENT COUNSEL (*Type or Print Name*)	SIGNATURE	DATE
X		C. REFERENCE AVAILABILITY —	Is all material referenced in this speech, paper, or journal article available to the public either through a public library, the Government Printing Office, the National Technical Information Service, or the NRC Public Document Room? If no, list below the specific availability of each referenced document.	
		SPECIFIC AVAILABILITY		
X		METRIC UNIT CONVERSION —	Does this speech, paper, or journal article contain measurement and weight values? If yes, all must be converted to the International System of Units, followed by the English units in brackets, pursuant to the NRC Policy Statement implementing the Omnibus Trade and Competitiveness Act of 1988, Executive Order 12770, July 24, 1991.	

8. AUTHORIZATION

The signatures of the NRC project manager and the contractor official certify that the NRC contractor speech, paper, or journal article is authorized by NRC, that it has undergone appropriate peer review for technical content and for material that might compromise commercial proprietary rights, and that it does not contain classified, sensitive unclassified, or nonpublifc information (NRC MD 3.9, Part II(A)(1)(d))

A. CONTRACTOR AUTHORIZING OFFICIAL (*Type or print name*)	SIGNATURE	DATE
Sitakanta Mohanty, Assistant Director		
B. NRC RESPONSIBLE PROJECT MANAGER (*Type or print name*)	OFFICE/DIVISION	MAIL STOP

TELEPHONE NUMBER	E-MAIL I.D.	Did you place the speech, paper, or journal article in ADAMS? If so, provide the ADAMS Accession No. (Use Template OCIO 099)	YES ☐ NO ☐ _____

SIGNATURE	DATE
K Ashe For S.M.	9-18-08

ASSESSMENT OF NICKEL-BASED ALLOY PASSIVE FILM STABILITY THROUGH THERMODYNAMIC MODELING

Pavan K. Shukla,[1] Roberto T. Pabalan,[1] and Lietai Yang[2]
[1]Center for Nuclear Waste Regulatory Analyses
[2]Southwest Research Institute®
6220 Culebra Road
San Antonio, Texas 78238-5166

ABSTRACT

Nickel-based alloys such as Alloy 600, Alloy 22, and C-276 exhibit better corrosion resistance compared to iron-based alloys such as stainless steel. For this reason, nickel-based alloys are preferred in nuclear systems. The corrosion resistance of nickel-based alloys can be attributed to the stability of the protective passive oxide film that forms on the metal surface. The passive film acts as a barrier between the metal surface and corrosive salt solutions present in the environment. However, the corrosion resistance of nickel-based alloys can be compromised in aggressive environments where the passive film constituents dissolve. In this paper, it is hypothesized that the dissolution of the passive film in a given environment would correlate with a diminished corrosion resistance of nickel-based alloys. This hypothesis is tested by using thermodynamic modeling to evaluate the thermodynamic stability of the passive films of various nickel-based alloys in various salt solutions. A chemical thermodynamic software is used to determine the potential passive film constituents and, subsequently, to calculate the solubility of those constituents in different chemical environments. The calculated solubilities are compared with published experimental data. The results of this study show that the marked increase in the solubility of passive film constituents correlates well with the decrease in corrosion resistance of nickel-based alloys.

INTRODUCTION

Nickel-based alloys exhibit superior corrosion resistance in various aggressive environments compared to iron-based alloys. For example, nickel-based alloys have superior corrosion resistance in neutral and alkaline salt solutions compared to stainless steel.[1] These nickel-based alloys tend to have protective passive films on the surface consisting of oxides of nickel, chromium, and iron. The passive film acts as a barrier between the metal surface and corrosive salt solutions present in the environment. The corrosion resistance of the alloys depends on the stability of the passive oxide films. Therefore, the thermodynamic stability of passive film constituents in a given aqueous environment can provide insight into the corresponding corrosion resistance of nickel-based alloys. The objective of this paper is to evaluate the stability of nickel-based alloy passive films under different chemical and physical conditions using thermodynamic modeling. The evaluation is supported by comparisons of calculated passive film solubilities with experimental data for the three nickel-based alloys Alloy 600, Alloy 22, and C-276. The chemical compositions of these alloys are provided in Table 1.

Alloy 600 is used in steam generator tubing in pressurized water reactor secondary systems. Sakai, et al.[2] investigated the effect of lead on stress corrosion cracking of Alloy 600. In particular, Sakai, et al.[2] studied the effect of the chemistry of lead-bearing water on the passive film of Alloy 600. The authors reported that stress corrosion cracking of Alloy 600 could occur at

280 °C [536 °F] and 65 bar [64 atm] in lead-containing solutions. Sakai, et al.[2] measured the relative amount of nickel in the passive film and in the solution contacting the passive film. They observed that the presence of lead in the solution causes a decrease in nickel concentration in the passive film and a corresponding increase in nickel concentration in the solution. The authors further observed that the dissolved nickel concentration increases with increasing lead in the solution. In this paper, thermodynamic simulations were conducted to determine the dissolved concentration of nickel in solutions containing varying amounts of lead. The calculated results were compared with the experimental data Sakai, et al.[2] reported.

C-276 is used in nuclear, chemical, and aerospace industries due to its high corrosion resistance and high strength at elevated temperature.[3] In the nuclear industry, C-276 is used to make agitator blades and heat exchanger tubes. Pawel[4] conducted a systematic study to measure the corrosion rate of the C-276 in different concentrations of hydrofluoric acid (HF) solutions. The author measured the corrosion rate in 0.05, 1, and 10 weight percent HF acid solution at 24, 50, and 76 °C [75, 122, and 169 °F]. The author reported that the C-276 corrosion rate does not change with temperature in 0.05 weight percent HF solution; however, the corrosion rate markedly increases in 1 and 10 weight percent HF solution with increasing temperature. In this paper, we investigated the solubility of C-276 passive film constituents in 0.05, 1, and 10 weight percent solutions at 50 and 76 °C [122 and 169 °F]. The solubility of the passive film constituent was compared with the general corrosion rates Pawel[4] reported.

Alloy 22 is also a highly corrosion-resistant nickel-based material and is expected to be used for nuclear waste disposal containers. Yang, et al.[5] measured the general corrosion rate of Alloy 22 in triple-salt brines consisting of NaCl, $NaNO_3$, and KNO_3 salts whose concentrations were selected such that the solution boiling point varied between 130 and 220 °C [266 and 428 °F]. Yang, et al. (2008) maintained the system at ambient pressure and vented it to the atmosphere through a vent bubbler, which was used to condense the vapor exiting the test vessel. Yang, et al.[5] reported that the general corrosion rates are invariant with solution pH as long as its value is greater than ~5. However, the corrosion rate increases exponentially with decreasing pH when the pH is less than 4.5. In another study, Gray, et al.[6] reported that the Alloy 22 passive film becomes unstable in 1 M NaCl solution at 90 °C [194 °F] when the solution pH is adjusted to 2.0 by adding HCl. The instability of the passive film was manifested in the form of high general corrosion rates when the solution pH is close to 2.0. In this paper, the solubility of Alloy 22 passive film constituents was determined using thermodynamic simulations. The trend in calculated solubilities was compared with that of general corrosion rates that Yang, et al.[5] and Gray, et al.[6] reported.

The objective of this paper is to test the hypothesis that an increase in corrosion susceptibility of nickel-based alloys can be attributed to the dissolution of their passive film constituents. The hypothesis was tested by conducting thermodynamic stability evaluations for the following systems:

- Alloy 600 in contact with solutions containing different lead concentrations
- C-276 in contact with solutions of different HF concentrations and at different temperatures
- Alloy 22 in contact with triple-salt solutions whose boiling points are between 130 and 220 °C [266 and 428 °F], or in contact with a 1 M NaCl solution at 95 °C [203 °F] whose pH is adjusted with hydrofluoric acid.

If the thermodynamic stability calculations confirm the hypothesis, the approach can be used as a guiding methodology for predicting the corrosion resistance of nickel-based alloys in a given environment.

APPROACH

Thermodynamic calculations are performed using a chemical thermodynamic software.[7] The approach consists of two steps. First, the possible constituents of the passive film on Alloy 22 in a given environment are determined from Pourbaix diagrams generated using the software. Subsequently, the software is used to calculate the solubility of the passive film constituents under various physical and chemical conditions.

RESULTS AND DISCUSSION

Alloy 600

The Pourbaix stability diagrams, where the x-axis represents solution pH and the y-axis represents oxidation/reduction potential, of Alloy 600 in contact with pure water at 280 °C [536 °F] and 65 bar [64 atm] are presented in Figure 1. For clarity, the Pourbaix diagrams are presented in terms of the stability of chromium and nickel elements present in Alloy 600. The two Pourbaix diagrams indicate that CrO(OH) and $NiFe_2O_4$ are stable over a wide pH and oxidation/reduction potential range; hence, these solid oxides are the possible passive film constituents of Alloy 600. Additional Pourbaix diagrams were generated for Alloy 600 in contact with 0.0333 m lead chloride ($PbCl_2$) solution {equivalent to 6,900 parts per million (ppm) Pb in solution}. The latter analysis indicates that CrO(OH) and $NiFe_2O_4$ are still the passive film constituents; however, lead oxide (PbO) and lead dioxide (PbO_2) are also stable over a wide range of pH and oxidation/reduction potential. The calculated Pourbaix diagram depicting the stability of lead in the system consisting of Alloy 600 in contact with $PbCl_2$ solution at 280 °C [536 °F] and 65 bar [64 atm] is presented in Figure 2.

The solubilities of CrO(OH) and $NiFe_2O_4$ at 280 °C [536 °F] and 65 bar [64 atm] in solutions with different $PbCl_2$ concentrations were calculated using the chemical thermodynamic software.[7] The dissolved ionic concentrations of nickel (Ni^{2+}), chromium (Cr^{3+}), and iron (Fe^{3+}) were obtained. The results show that the dissolved Ni^{2+} concentration is significantly higher than the Cr^{3+} and Fe^{3+} concentrations. Furthermore, in contrast to Cr^{3+} and Fe^{3+}, the dissolved Ni^{2+} concentration changes significantly with varying $PbCl_2$ concentration. The calculated Ni^{2+} concentrations are presented in Figure 3(a). As shown in the figure, the dissolved Ni^{2+} concentration increases by three orders of magnitude when the $PbCl_2$ solution concentration is increased from 10 to 10,000 ppm. Notice also that the calculated equilibrium pH of the solution decreases with increasing $PbCl_2$ concentration. To compare the simulation results with the measured concentration of Ni^{2+} Sakai, et al.[2] reported, additional thermodynamic calculations were conducted. Sakai, et al.[2] measured the Ni^{2+} concentration in solution when Alloy 600 was brought into contact with solutions of different $PbCl_2$ concentrations at 280 °C [536 °F] and 65 bar [64 atm]. The authors reported dissolved Ni^{2+} concentrations equal to 220, 55, 26, and 18 ppm for 0.24, 0.033, 0.018, and 1.4×10^{-3} m $PbCl_2$ solutions, respectively. The calculated Ni^{2+} concentrations obtained from thermodynamic simulations are listed in Table 2 and plotted in Figure 3b. The figure shows that the calculated Ni^{2+} concentrations are lower compared to the values Sakai, et al.[2] measured. For example, Sakai, et al.[2] reported a dissolved Ni^{2+} concentration of 220 ppm in 0.24 m $PbCl_2$ solution, whereas the calculated value is 47 ppm. Nonetheless, the trend in calculated and measured Ni^{2+} concentration as a function of $PbCl_2$

concentration is the same. This result indicates that thermodynamic simulations provide a useful approach for qualitatively analyzing passive film stability—hence corrosion susceptibility—of Alloy 600.

C-276

A thermodynamic analysis was conducted for C-276 in contact with different concentrations of hydrofluoric acid at 24, 50, and 76 °C [75, 122, and 169 °F]. The Pourbaix stability diagrams for C-276 immersed in water at 50 °C [122 °F] are presented in Figures 4(a) and 4(b) in terms of the stability of nickel and chromium elements present in C-276. The two diagrams indicate that CrO(OH) and $NiFe_2O_4$ are stable over a wide pH and oxidation/reduction potential range. Additional Pourbaix diagrams generated for C-276 in contact with 0.05 weight percent HF solution indicated that CrO(OH) and $NiFe_2O_4$ are still the dominant passive film constituents for C-276 immersed in the HF solution. This result contradicts Pawel[4] who stated that nickel fluoride will form as an adherent passive film when nickel-based alloys are brought into contact with HF solutions.

Pawel[4] conducted experimental studies to measure the corrosion rate of several nickel-based alloys in different concentrations of HF solution. Pawel[4] reported the general corrosion rate of C-276 in 0.05, 1.0, and 10 weight percent HF solutions at 24, 50 and 76 °C [75, 122, and 169 °F]. Pawel[4] stated that the HF concentration did not affect the general corrosion rate at 24 °C [75 °F], but that the general corrosion rate increased significantly with HF concentration at 50 and 76 °C [122 and 169 °F]. The C-276 general corrosion rates Pawel[4] reported are compared with general corrosion rates calculated with the thermodynamic software[7] in Figure 5(a). The software also was used to calculate the solubility of CrO(OH) and $NiFe_2O_4$ in contact with different concentrations of HF acid solutions at 24, 50, and 76 °C [75, 122, and 169 °F]. The calculated dissolved Cr^{3+} and Ni^{2+} concentrations as a function of HF concentration at 24, 50, and 76 °C are presented in Figures 5(b) and 5(c), respectively. The results indicate that the Ni^{2+} concentration is about an order of magnitude higher than the Cr^{3+} concentration for different HF concentrations. It is also observed that dissolved Ni^{2+} and Cr^{3+} concentrations decrease with increasing temperature at a fixed HF concentration, whereas the C-276 general corrosion rate Pawel[4] measured increases with temperature at a fixed HF concentration. This analysis indicates that thermodynamic stability of passive film constituents correlate well with the general corrosion rate data as a function of HF concentration at a fixed temperature; however, the same is not true when HF concentration is fixed and temperature is varied.

Alloy 22

The chemical thermodynamic software was also used to determine the possible constituents of the passive film on Alloy 22 in contact with $NaCl–NaNO_3–KNO_3$ brines, which have sufficiently high salt concentrations such that the boiling point is between 130 and 220 °C [266 and 428 °F]. The Pourbaix diagrams calculated for Alloy 22 at 130 °C [266 °F] are shown in Figure 6. For clarity, the stability fields for the chromium and nickel subsystems are plotted separately and the iron and molybdenum subsystems are not plotted. Figure 6 indicates that over a wide range of pH and oxidation/reduction potential, three solids—CrO(OH), $NiFe_2O_4$, and $NiCr_2O_4$—are stable. These three solid oxides possibly represent constituents of the passive film protecting Alloy 22 from corrosion in $NaCl–NaNO_3–KNO_3$ brines.

To assess the stability of passive oxide films on Alloy 22 in brines saturated with NaCl, $NaNO_3$, and KNO_3, the thermodynamic software[7] was used to calculate the solubility of CrO(OH) and $NiFe_2O_4$ in contact with these brines. The solubility of $NiCr_2O_4$ was not explored, because the $NiCr_2O_4$ thermodynamic parameters in the current software version are not well constrained by solubility data. Furthermore, $NiCr_2O_4$ appears as a stable phase when solution pH is greater than 8 {see Figure 6(a)}, whereas experimental evidence suggests that passive film is unstable when solution pH is less than 5. Hence, the solubility of $NiCr_2O_4$ cannot influence the stability of Alloy 22 passive film in the range of pH solution considered in the paper. The CrO(OH) and $NiFe_2O_4$ solubilities were calculated at 130 °C [266 °F] and over the pH range of 3.5 to 9.0. In the calculations, the brine was specified to be saturated with the three salts NaCl, $NaNO_3$, and KNO_3, and the pH was varied by the addition of HCl or NaOH. Under these conditions, the brine is very concentrated, with calculated concentrations of sodium, potassium, chloride, and nitrate ions equal to 47, 59, 3, and 103 moles/kg H_2O, respectively. Yang, et al.[5] measured Alloy 22 general corrosion rates at 130 °C [266 °F] in these concentrated brines. The measured values Yang, et al.[5] reported are presented in Figure 7(a).

The calculated CrO(OH) and $NiFe_2O_4$ solubilities are plotted in Figures 7(b) and 7(c), respectively, as total dissolved Cr^{3+}, Ni^{2+}, and Fe^{3+} concentrations versus pH. The figure shows that the dissolved metal concentrations are relatively constant at pHs higher than 5.0. However, the CrO(OH) and $NiFe_2O_4$ solubility markedly increases when the solution pH is close to 4.5 and there is a steep increase in dissolved concentration of Cr^{3+}, Ni^{2+}, and Fe^{3+} with decreasing pH below ~4.5. This trend of increasing Cr^{3+}, Ni^{2+}, and Fe^{3+} concentration with decreasing pH is consistent with the trend in Alloy 22 corrosion rates Yang, et al.[5] reported {shown in Figure 7(a)}. The results indicate that the passive film starts to dissolve when the solution pH is equal to or less than 4.5, which makes it unable to protect the nickel-based alloy from corrosion.

Another set of solubility calculations was carried out to test the hypothesis regarding the stability of Alloy 22 passive film components in NaCl solutions with varying pH. Gray, et al.[6] conducted a series of experiments at 90 °C [194 °F] to measure the Alloy 22 general corrosion rate in 1 M NaCl solutions. Gray, et al.[6] varied the solution pH by adding HCl to the NaCl solution. The authors reported that the breakdown of the passive film occurred when solution pH was close to 2. The breakdown in passive film was indicated by a marked increase in general corrosion rate and corresponding open circuit potential. Both corrosion rate and open circuit potential values increased as solution pH was lowered with the addition of HCl. The open circuit potential increased somewhat linearly with decreasing pH, whereas corrosion rate increased exponentially with decreasing pH. The Pourbaix diagrams generated using the chemical thermodynamic software indicated that CrO(OH) and $NiFe_2O_4$ are the passive film constituents. The solubilities of CrO(OH) and $NiFe_2O_4$ in 1 M NaCl solution were calculated as a function of pH. The calculated results are presented in terms of Cr^{3+} concentration in Figure 8(a) and in terms of Ni^{2+} and Fe^{3+} concentration in Figure 8(b). As seen in these two figures, the Cr^{3+}, Ni^{2+}, and Fe^{3+} concentrations start to increase when the solution pH is 2.8 or less. These solubility results provide another confirmation that dissolution of passive film constituents coincides with marked increases in general corrosion rate. Hence, the thermodynamic solubility calculations can be used as a qualitative method to determine passive film stability in a given environment.

SUMMARY AND CONCLUSIONS

In this paper, it was hypothesized that an increase in corrosion susceptibility of nickel-based alloys can be attributed to the dissolution of passive film constituents on the alloy surface. This hypothesis was tested by determining the thermodynamic stability of passive films for three nickel-based alloys—Alloy 600, C-276, and Alloy 22—exposed to different environments. The

thermodynamic stability fields of an alloy placed in a given environment were obtained in the form of Pourbaix diagrams using a chemical thermodynamic software. The Pourbaix diagrams were used to determine the possible passive film constituents. The stability of the passive film constituents was analyzed by determining their solubilities in the respective environments. The calculated solubilities were quantitatively compared with experimental data on Alloy 600 and qualitatively compared with experimental data on C-276 and Alloy 22.

The passive film constituents for Alloy 600 in contact with $PbCl_2$ solutions are CrO(OH), $NiFe_2O_4$, PbO, and PbO_2. The solubilities of CrO(OH) and $NiFe_2O_4$ in contact with different concentrations of $PbCl_2$ solution at 280 °C [536 °F] and 65 bar [64 atm] were calculated using the software.[7] The solubility calculations showed that dissolved Ni^{2+} concentrations are significantly higher than those of Cr^{3+} and Fe^{2+} and that dissolved Ni^{2+} increases with the concentration of $PbCl_2$ in solution. The calculated solubilities of CrO(OH) and $NiFe_2O_4$ in $PbCl_2$ solutions were compared with the Ni^{2+} concentration Sakai, et al.[2] measured in $PbCl_2$ solutions in contact with Alloy 22 at 280 °C [536 °F] and 65 bar [64 atm]. Although the measured Ni^{2+} concentration values are higher than the calculated values, both measured and calculated values show the same trend of increasing dissolved Ni^{2+} concentration with increasing $PbCl_2$ concentration.

The possible passive film constituents for C-276 in contact with HF solution are CrO(OH) and $NiFe_2O_4$. The solubilities of these two solids in HF solutions were determined using the software and were compared with the C-276 general corrosion rates measured in HF solutions by Pawel.[4] The Pawel[2] data show that the C-276 general corrosion rate increases with increasing HF concentration and temperature. The calculated CrO(OH) and $NiFe_2O_4$ solubilities increase with increasing HF concentration, consistent with the trend of the C-276 general corrosion rate Pawel[4] observed. However, the calculated CrO(OH) and $NiFe_2O_4$ solubilities decrease with temperature, which is inconsistent with the observed increase in C-276 general corrosion rate with temperature.

The passive film constituents for Alloy 22 in contact with saturated salt solutions of NaCl, $NaNO_3$, and KNO_3 are CrO(OH) and $NiFe_2O_4$. The solubilities of these two oxides in the triple-salt solution at 130 °C [266 °F] were determined over the pH range 3.5 to 9.0 using the thermodynamic software and were qualitatively compared with measured Alloy 22 general corrosion rates.[5] There is positive correlation between the calculated dissolved Cr^{3+}, Ni^{2+}, and Fe^{3+} concentration and the Alloy 22 general corrosion rates with decreasing solution pH. The dissolved Cr^{3+}, Ni^{2+}, and Fe^{3+} concentrations increase sharply with decreasing solution pH; a similar trend with pH is also observed for the Alloy 22 general corrosion rate. The solubility of Alloy 22 passive film constituents in 1 M NaCl solution with varying pH was also explored, and the calculated CrO(OH) and $NiFe_2O_4$ solubilities were compared with measured Alloy 22 general corrosion rates.[6] Gray, et al.[6] reported that the Alloy 22 passive film broke down when solution pH was close to 2 and that the breakdown in passive film was manifested by a marked increase in general corrosion rate and corresponding open circuit potential. The calculated Pourbaix diagrams for Alloy 22 immersed in 1 M NaCl solution indicate that CrO(OH) and $NiFe_2O_4$ are the constituents of the passive film. The CrO(OH) and $NiFe_2O_4$ solubilities in 1 M NaCl solutions calculated using the software showed the same trend with pH as that observed for the Alloy 22 general corrosion rate.

The thermodynamic analyses of the passive films for three nickel-based alloys indicate there is a correlation between the solubility of passive film constituents and the corrosion susceptibility of nickel-based alloys. This approach can be used as a screening analysis before

experimentally verifying the stability of passive film of nickel-based alloys in a given environment.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the reviews of Drs. H. Jung and S. Mohanty, the editorial review of L. Mulverhill, and the assistance of J. Gonzalez in the preparation of the manuscript.

This paper describes work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) and its contractors for the U.S. Nuclear Regulatory Commission (USNRC) under Contract No. NRC-02-07-006. The activities reported here were performed on behalf of the USNRC Office of Nuclear Materials Safety and Safeguards, Division of High-Level Waste Repository Safety. This paper is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the USNRC.

REFERENCES

1. R.E. Kirk and D.F. Othmer. Encyclopedia of Chemical Technology. Vol. 17, 4th Edition. New York City, New York: Wiley International. 1997.

2. T. Sakai, K. Akoi, T. Shigemitu, and Y. Kishi. "Effect of Lead Water Chemistry on Oxide Thin Film of Alloy 600." *Corrosion*. Vol. 48, No. 9. pp. 745–750. 1992.

3. M. Ahmad, J.I. Akhter, M. Iqbal, M. Akhtar, E. Ahmed, M.A. Shaikh, and K. Saeed. "Surface Modification of Hastelloy C-276 by SiC Addition and Electron Beam Melting." *Journal of Nuclear Materials*. Vol. 336. pp. 120–124. 2005.

4. S.J. Pawel. "Corrosion of High-Alloy Materials in Aqueous Hydrofluoric Acid Environments." *Corrosion*. Vol. 50, No. 12. pp. 963–971. 1994.

5. L. Yang, R.T. Pabalan, P.K. Shukla, M. Juckett, X. He, K.T. Chiang, and T. Ahn. "Corrosion of Alloy 22 Induced by Dust Deliquescence Brines." San Antonio, Texas: CNWRA. 2008.

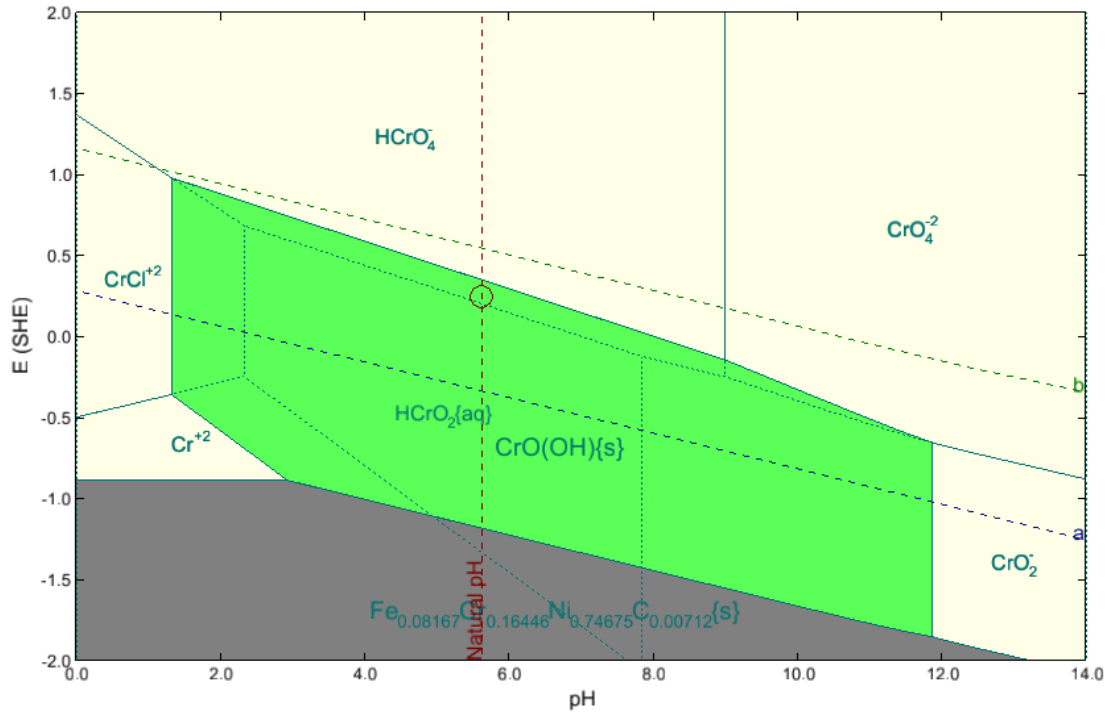
6. J.J. Gray, J.R. Hayes, G.E. Gdowski, B.E. Viani, and C.A. Orme. "Influence of Solution pH, Anion Concentration, and Temperature on the Corrosion Properties of Alloy 22." *Journal of the Electrochemical Society*. Vol. 153, No. 3. pp. B61–B67. 2006.

7. OLI Systems, Inc. "A Guide to Using the OLI Software for Version 2.0 of the Analyzers." Morris Plains, New Jersey: OLI Systems, Inc. 2005.

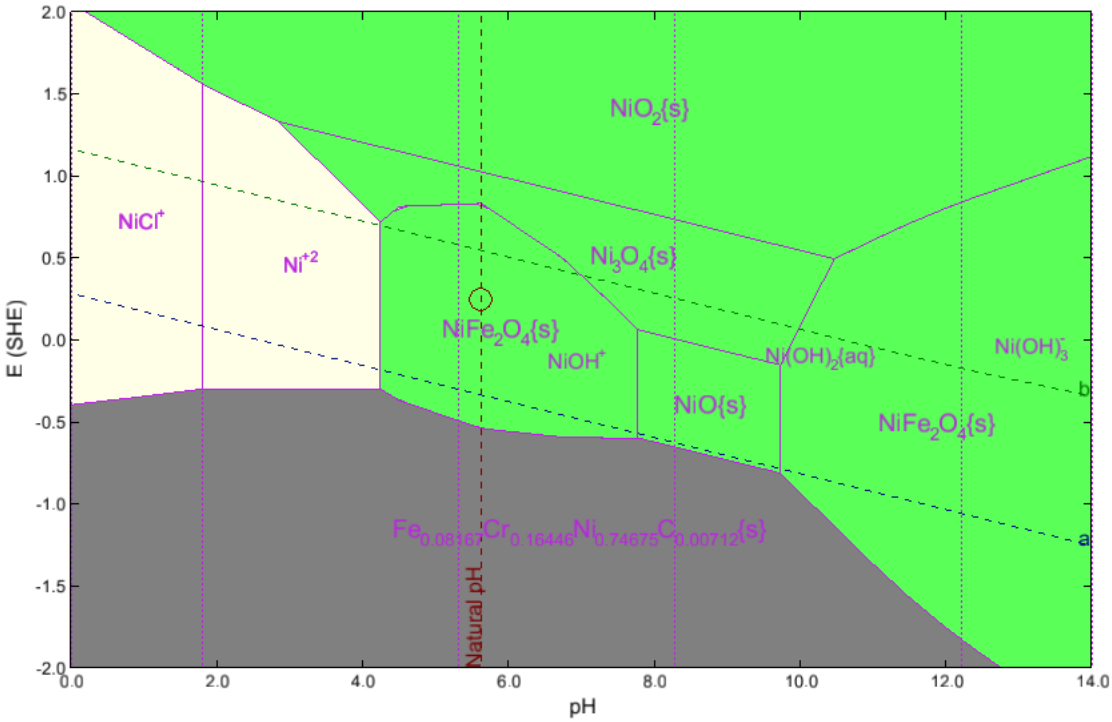
Table 1. Chemical Composition (in Weight Percent) of Alloy 600, C-276, and Alloy 22			
Element*	**Alloy 600**	**C-276**	**Alloy 22**
Fe	9.17	6.19	4.1
Cr	15.18	21.1	21.1
Ni	74.63	56.6	56.7
Mo	—	15.78	13.8
Cu	0.35	—	—
Mn	0.42	0.47	0.28
Si	0.23	0.02	0.03
W	—	3.4	2.9
Co	—	1.79	0.93
V	—	0.09	0.14
Al	—	—	—
Ti	—	—	—
Nb	—	—	—
C	0.002	0.002	0.002
S	0.001	0.003	0.002

*Fe, iron; Cr, chromium; Ni, nickel; Mo, molybdenum; Cu, copper; Mn, manganese; Si, silicon; W, tungsten; Co, cobalt; V, vanadium; Al, aluminum; Ti, titanium; Nb, niobium; C, carbon; and S, sulfur.

Table 2. Calculated Dissolved Concentrations of Cr^{3+}, Ni^{2+}, and Fe^{3+} in $PbCl_2$ Solutions in Contact with Alloy 600 at 280 °C [536 °F] and 65 bar [64 atm]	
Condition: 0.0333 m $PbCl_2$ solution (6,900 ppm Pb) with pH fixed at 3.0 at 25 °C [77 °F]. The pH of the solution was adjusted by adding HCl.	
Ion	**Concentration (ppm)**
Cr^{3+}	4.9803E-06
Ni^{2+}	3.4631E+01
Fe^{3+}	1.8127E-06
Condition: 0.01834 m $PbCl_2$ solution (3,800 ppm Pb) with pH fixed at 4.5 at 25 °C [77 °F]. The pH of the solution was adjusted by adding sodium hydroxide.	
Ion	**Concentration (ppm)**
Cr^{3+}	4.8572E-06
Ni^{2+}	6.1367E+00
Fe^{3+}	1.7341E-06
Condition: 1.448×10^{-3} m $PbCl_2$ solution (300 ppm Pb) with pH fixed at 7.0 at 25 °C [77 °F]. The pH of the solution was adjusted by adding HCl.	
Ion	**Concentration (ppm)**
Cr^{3+}	4.7797E-06
Ni^{2+}	1.4801E-02
Fe^{3+}	1.9689E-06
Condition: 0.2413 m $PbCl_2$ solution (50 g/L Pb) with pH fixed at 3.0 at 25 °C [77 °F]. The pH of the solution was adjusted by adding HCl.	
Ion	**Concentration (ppm)**
Cr^{3+}	4.9880E-06
Ni^{2+}	4.7448E+01
Fe^{3+}	1.8249E-06



(a)



(b)

Figure 1. Calculated stability diagrams for (a) chromium and (b) nickel present in Alloy 600 in contact with pure water at 280 °C [536 °F] and 65 bar [64 atm]

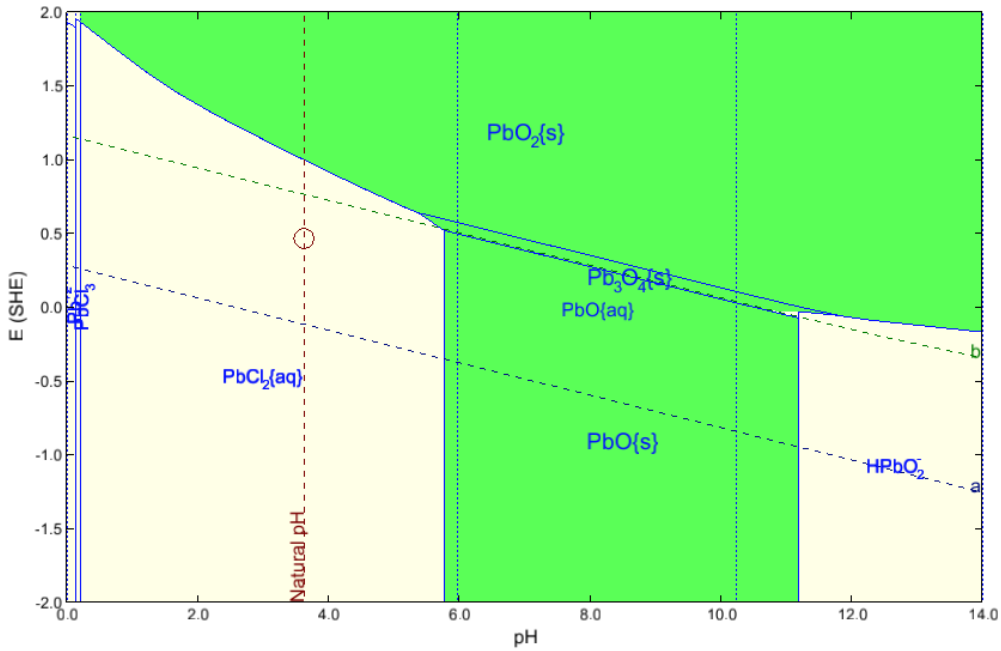
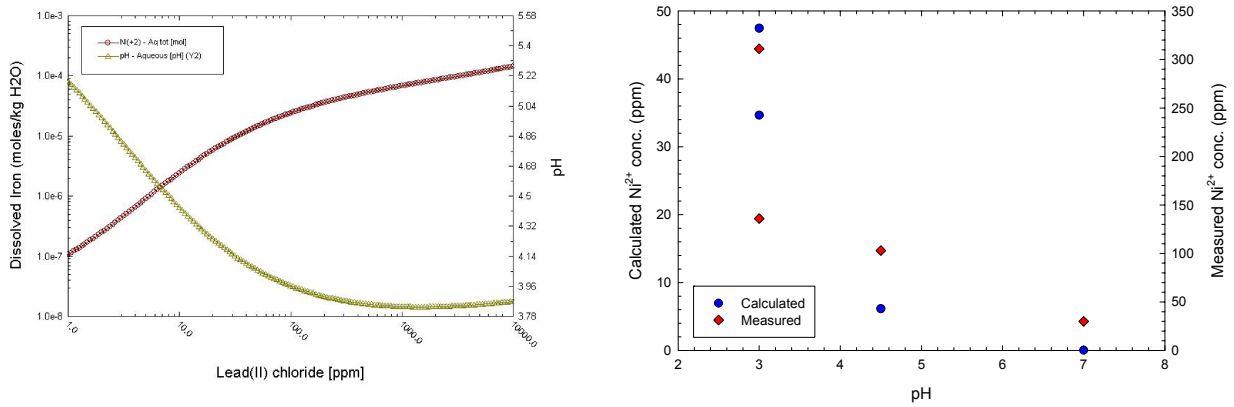
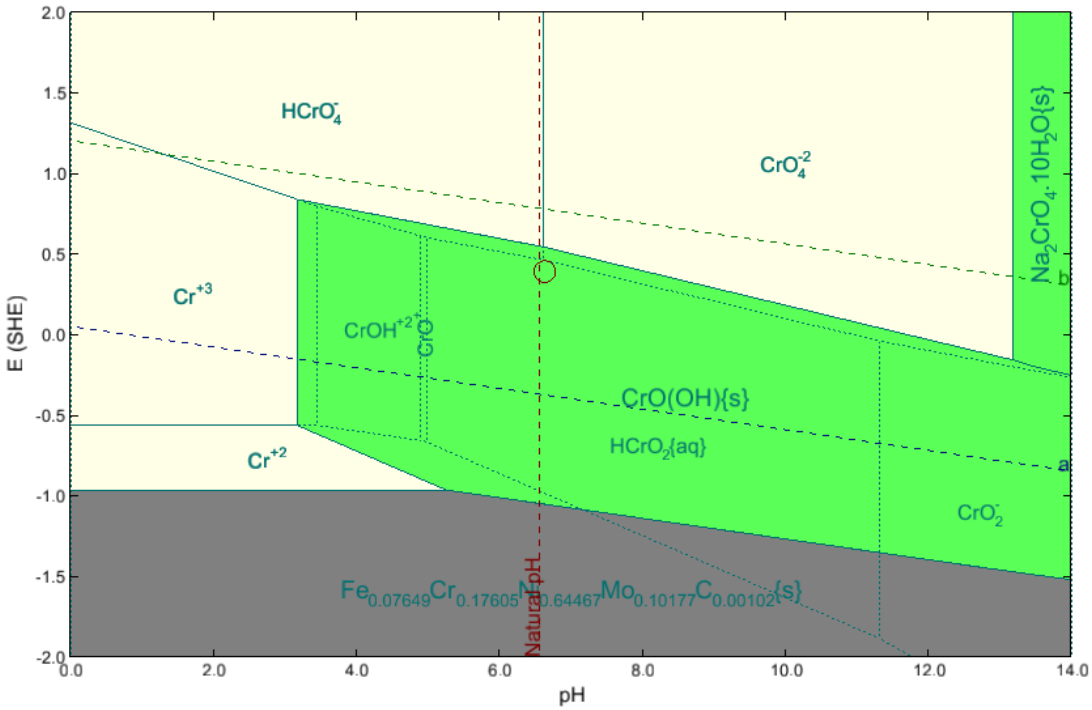


Figure 2. Calculated stability diagram for lead (Pb) present in a system consisting of Alloy 600 in contact with 0.0333 m lead chloride ($PbCl_2$) solution at 280 °C [536 °F] and 65 bar [64 atm]. The figure indicates that lead will precipitate as PbO or PbO_2 over a wide pH and oxidation/potential range.

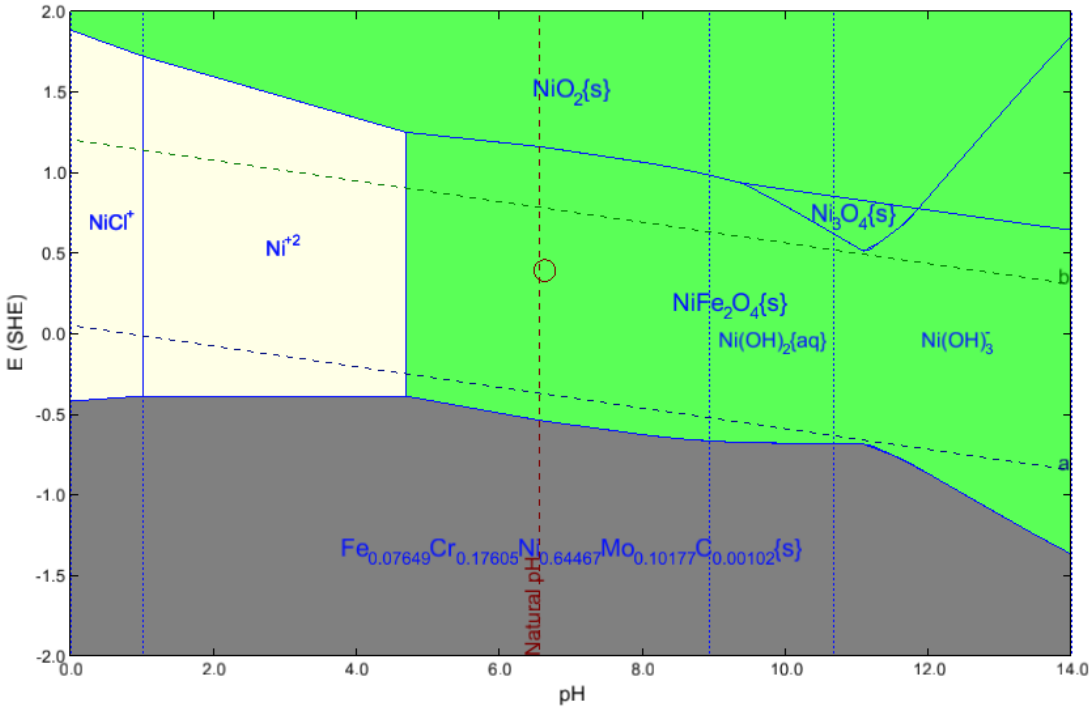


(a) **(b)**

Figure 3. (a) Dissolved nickel ion concentration as a function of $PbCl_2$ concentration derived by calculating the solubility of $NiFe_2O_4$ in $PbCl_2$ solutions at 280 °C [536 °F] and 65 bar [64 atm]. (b) Calculated nickel ion concentration (circles) in $PbCl_2$ solutions as a function of pH compared with measured values (diamonds) Sakai, et al.[2] reported.



(a)



(b)

Figure 4. Calculated stability diagrams for (a) chromium and (b) nickel in C-276 in contact with pure water at 50 °C [122 °F] and 1 bar [0.99 atm]

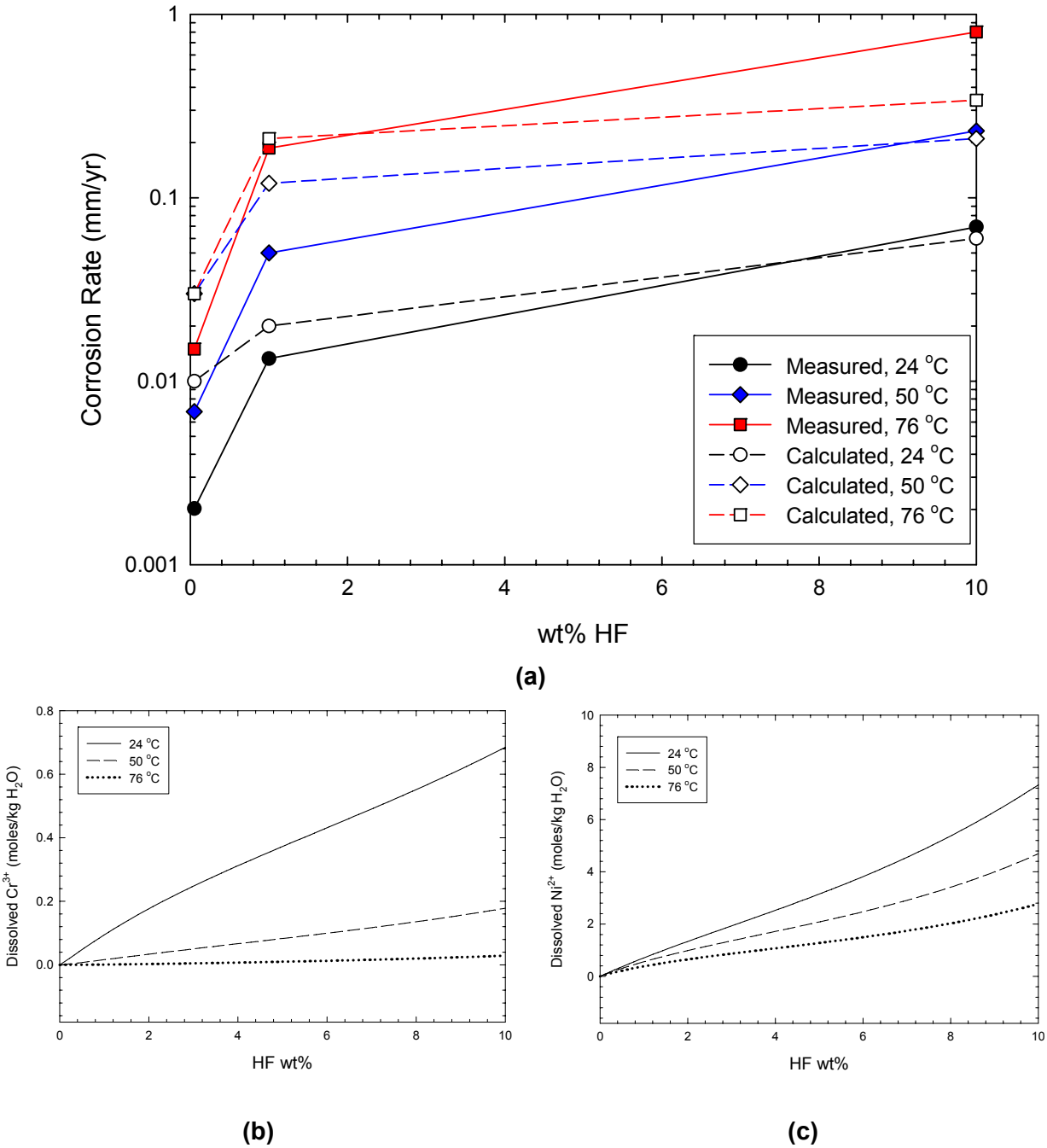
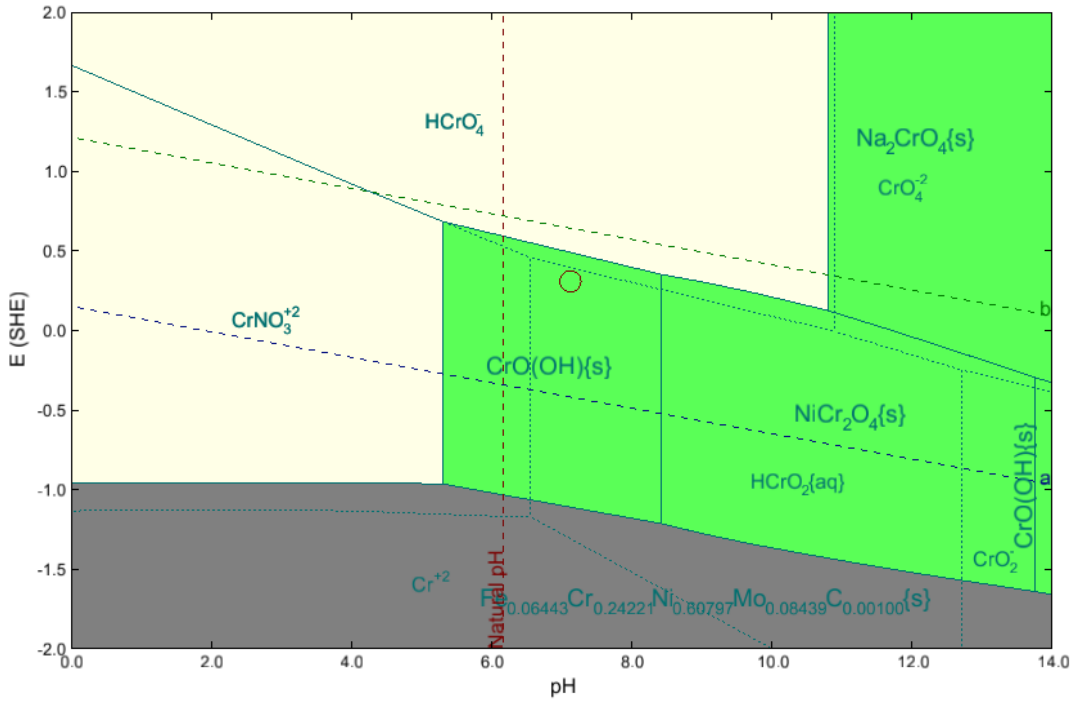
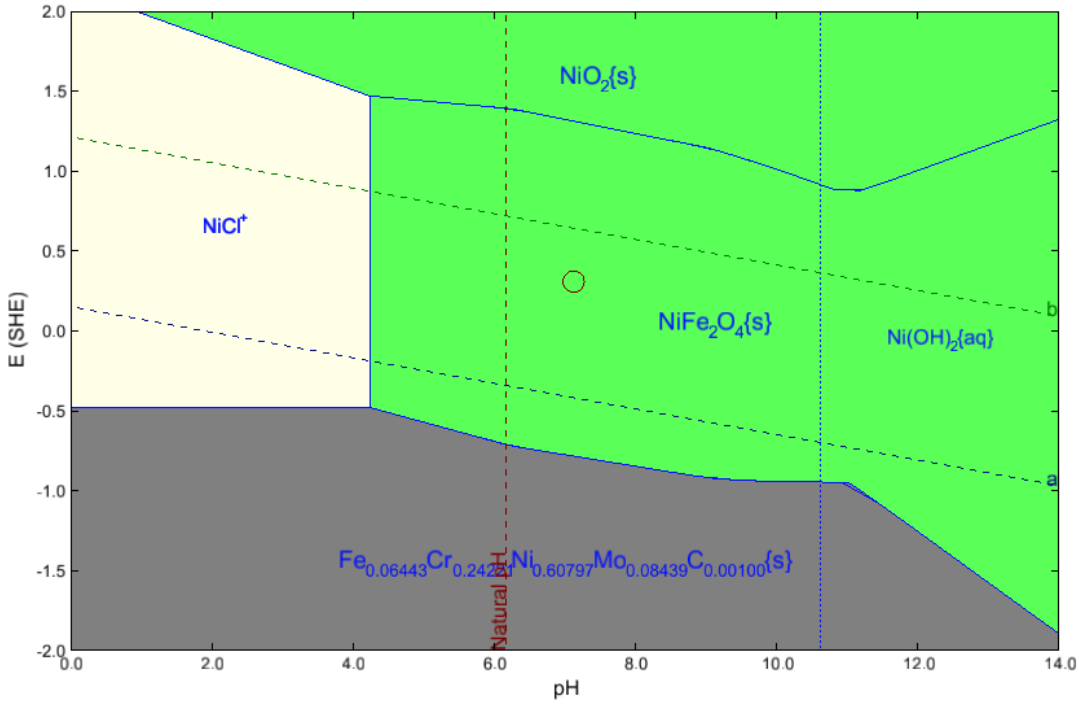


Figure 5. (a) Measured and calculated general corrosion rate of C-276 in 0.05, 1.0, and 10 weight percent HF solutions at 24, 50, and 76 °C [75, 122, and 169 °F]. (b) Dissolved Cr^{3+} concentration as a function of HF concentration at 24, 50, and 76 °C [75, 122, and 169 °F] based on the calculated solubility of CrO(OH) in HF solutions. (c) Dissolved Ni^{2+} concentration as a function of HF concentration at 24, 50, and 76 °C [75, 122, and 169 °F] based on the calculated solubility of $NiFe_2O_4$ in HF solutions.

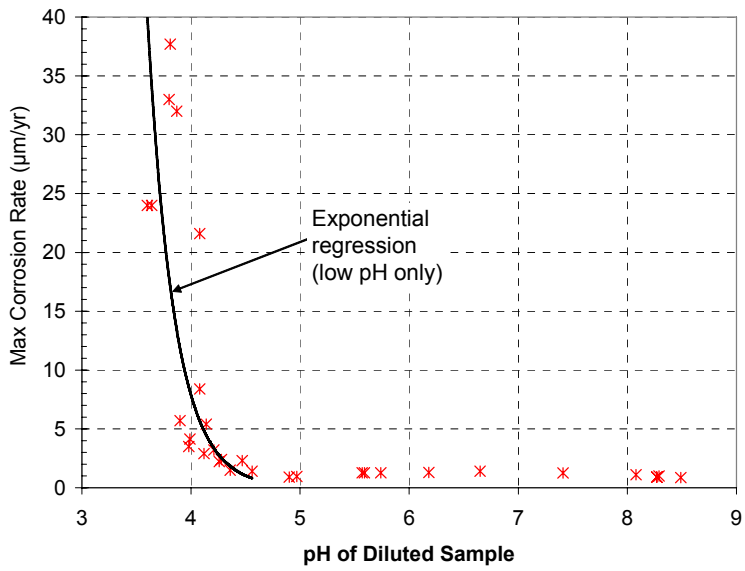


(a)

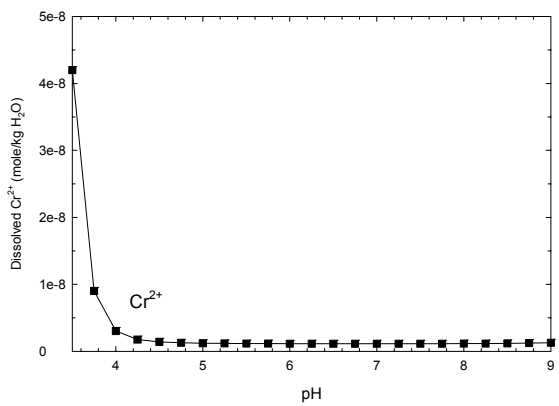


(b)

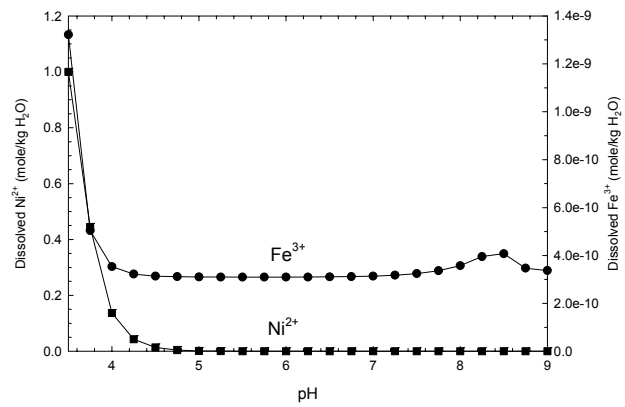
Figure 6. Calculated stability diagrams for (a) chromium and (b) nickel in Alloy 22 in contact with a brine saturated with NaCl, $NaNO_3$, and KNO_3 salts



(a)



(b)



(c)

Figure 7. (a) Measured general corrosion rates of Alloy 22 at 130 °C [266 °F] in an NaCl–$NaNO_3$–KNO_3 brine at varying solution pH (Yang, et al.[5]). Calculated solubility of (b) CrO(OH) and (c) $NiFe_2O_4$ at 130 °C [266 °F] as a function of pH in brines saturated with NaCl, $NaNO_3$, and KNO_3 salts.

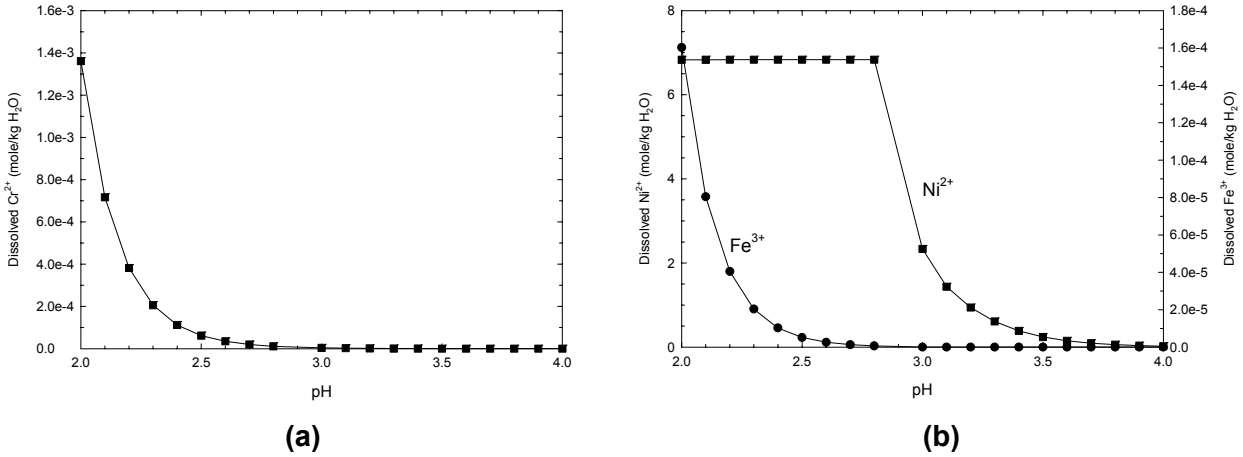


Figure 8. Calculated solubilities at 90 °C [203 °F] of (a) CrO(OH) and (b) $NiFe_2O_4$ in 1 M NaCl solution with HCl added to adjust the pH