Electrochemical Evaluation and Surface Characterization of Josephinite as a Natural Analog for Container Materials

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BACKGROUND

- Natural analogs have been considered appropriate instruments for increasing confidence in the assessment of waste package performance for the potential high-level radioactive waste repository at Yucca Mountain, NV.
- This investigation was conducted using a sample of "new josephinite" collected by Professor J. Bird (Cornell University) in the proximity of Cave Junction in Oregon.

OBJECTIVES

- Evaluate the electrochemical and passive behavior of josephinite in simulated groundwaters and compare it with that of a cast Ni_3Fe alloy
- Assess the validity of josephinite as an appropriate natural analog

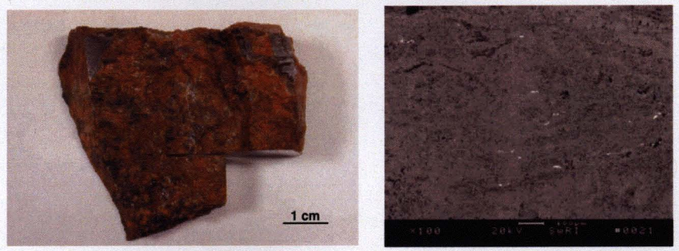

Figure 1. Views of the josephinite sample **(left)** exterior surface covered with alteration minerals and **(right)** polished surface showing Ni_3As_2 phase (white spots) dispersed in Ni_3Fe phase (gray area) and voids filled with serpentine (black spots).

EXPERIMENTAL METHODS

ELECTROCHEMICAL EVALUATION

- Cyclic potentiodynamic polarization (scan rate 0.167 mV/s) and potentiostatic tests in deaerated solutions at room temperature
- Test solutions (Table 1): simulated groundwater (pH 8.3 and higher adjusted by adding NaOH) and basic saturated water (pH 13.0)

XPS PASSIVE FILM ANALYSIS

- Wide-energy surveys for surface elemental composition measurement and high-resolution scans for oxidation state determination
- Concentration depth profiles obtained after Ar ion sputtering with a rate of 2.3 nm/min relative to the sputtering rate of SiO_2

Table 1. Chemical composition of test solutions used in this study

Ionic Species	Simulated Groundwater mg/L	Simulated Groundwater mM	Basic Saturated Water mg/L	Basic Saturated Water mM
Na^+	36.0	1.57	109.7	4.77
K^+	3.4	0.09	67.7	1.73
HCO_3^-	70.0	1.14	—	—
Cl^-	6.4	0.18	133.0	3.75
SO_4^{2-}	17.3	0.18	14.4	0.15
NO_3^-	6.4	0.10	141.1	2.28
F^-	1.4	0.07	1.5	0.08

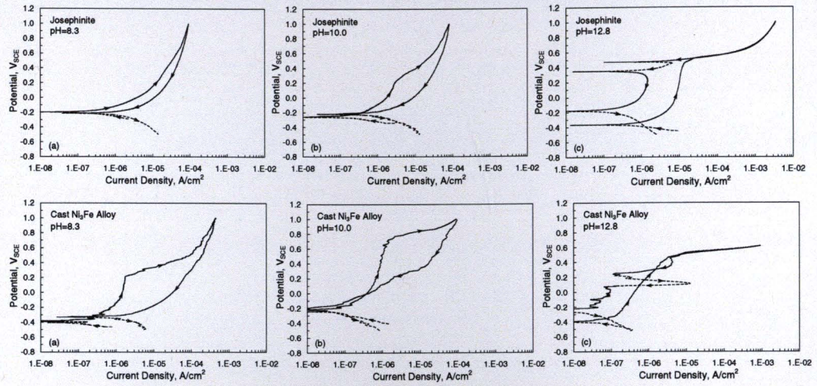

Figure 2. Cyclic potentiodynamic polarization curves of josephinite **(top)** and cast Ni_3Fe alloy **(bottom)** in simulated groundwater at pH values from 8.3 to 12.8

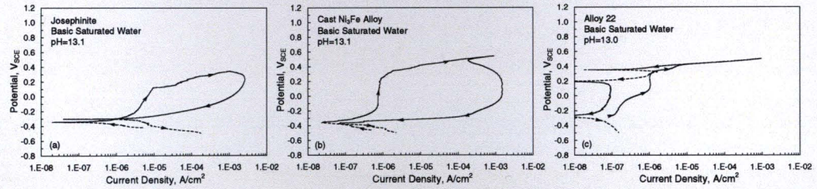

Figure 3. Cyclic potentiodynamic polarization curves of josephinite, cast Ni_3Fe alloy, and Alloy 22 in basic saturated water

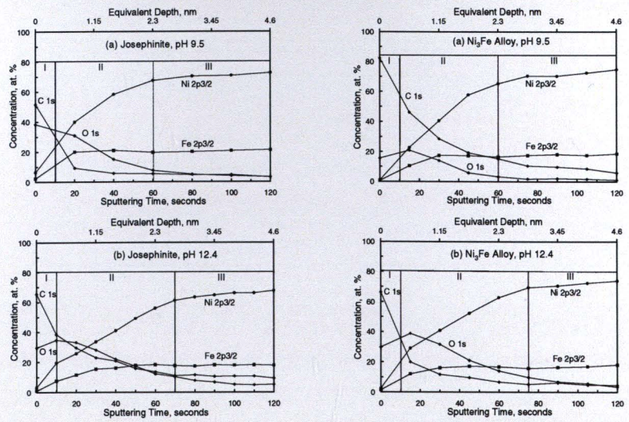

Figure 4. Concentration depth profiles of josephinite **(left)** and cast Ni_3Fe alloy **(right)** passivated in simulated groundwater with a potential of 0 V_{SCE} at pHs 9.5 and 12.4

RESULTS AND DISCUSSION

ELECTROCHEMICAL BEHAVIOR

- Josephinite exhibits an active anodic behavior in simulated groundwater at pHs 8.3 and 9.0, and a passive behavior at pH 10.0 and above.
- Localized corrosion occurs in josephinite above a critical potential at pH 10 to 12 but it is fully inhibited at pH 12.8 by the high $[OH^-]/[Cl^-]$ ratio in the test solution.
- Cast Ni_3Fe alloy exhibits a passive behavior in simulated groundwater at all the pH values. A lower $[OH^-]/[Cl^-]$ ratio is needed to inhibit localized corrosion.
- In basic saturated water, josephinite and cast Ni_3Fe alloy exhibit passivity breakdown and the occurrence of localized corrosion whereas Alloy 22 only exhibits a passive behavior preceding the onset of oxygen evolution.

PASSIVE FILM CHARACTERIZATION

- Three surface regions can be defined: (I) outer contaminated layer, (II) inner passive layer, and (III) base material.
- For both materials the thickness of the passive films formed at pH 12.4 is 2.3 nm, slightly thicker than the films formed at pH 9.5.
- The passive films have a duplex structure consisting of an Fe-rich hydroxide outer layer and a Ni-rich oxide inner layer.

VALIDITY OF JOSEPHINITE AS A NATURAL ANALOG

- Results from this study establish the environmental conditions leading to the passivity and localized corrosion of josephinite, and support the validity of the electrochemical concepts adopted in assessing the long-term waste package performance.
- Validity assessment confronts two main difficulties: lack of Cr in josephinite and no knowledge of the exposed geological environments.
- Differences in the environment and the precipitation of mineral deposits could be the reasons for a substantially lower corrosion rate than the one estimated from the potentiostatic measurements.
- The role of the alteration layers in preserving the stability of josephinite is essential for the long survival time of josephinite.

CONCLUSIONS

- The observed electrochemical behavior has established the environmental conditions leading to passivity and localized corrosion of josephinite.
- Josephinite exhibited passivity at a higher pH than did the cast Ni_3Fe alloy and was found to be slightly more susceptible to pitting corrosion.
- The passive films formed on josephinite and cast Ni_3Fe alloy have a duplex structure consisting of an Fe-rich hydroxide outer layer and a Ni-rich oxide inner layer.
- The relationship between the passive behavior and the formation of the alteration layers needs to be established for assessing the long-term survivability of josephinite.

ACKNOWLEDGMENTS

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