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Materials Research Society 2006 Fall Meeting  
November 27–December 1, 2006  
Boston, Massachusetts

## **EVOLUTION OF CHEMISTRY AND ITS EFFECTS ON THE CORROSION OF ENGINEERED BARRIER MATERIALS**

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### **ABSTRACT**

The evolution of environmental conditions within the emplacement drifts of a potential high-level waste repository at Yucca Mountain, Nevada, may be influenced by several factors, including the temperature and relative humidity within the emplacement drifts and the composition of seepage water. The performance of the waste package and the drip shield may be affected by the evolution of the environmental conditions within the emplacement drifts. In this study, tests evaluated the evolution of environmental conditions on the waste package surfaces and in the surrounding host rock. The tests were designed to (i) simulate the conditions expected within the emplacement drifts; (ii) measure the changes in near-field chemistry; and (iii) determine environmental influence on the performance of the engineered barrier materials. Results of tests conducted in this study indicate the solutions with high boiling points did not form from the evaporation of initially dilute simulated seepage waters. The composition of salt deposits was consistent with the initial dilute water chemistry. Salts and possibly concentrated calcium chloride brines may be more aggressive than either neutral or alkaline brines.

### **INTRODUCTION**

The U.S. Nuclear Regulatory Commission (NRC) is preparing to review a license application for a potential high-level radioactive waste repository. Waste packages for the potential repository will consist of an Alloy 22 (56Ni-22Cr-13.5Mo-3W-4Fe) outer container surrounding a Type 316 nuclear grade (NG) stainless steel (SS) inner container. The use of a corrosion-resistant waste package outer container material, the installation of a titanium alloy drip shield to protect the waste packages, and the location of the emplacement drifts in the unsaturated zone have been identified by the U.S. Department of Energy (DOE) as key attributes of the repository design that are expected to contribute to waste isolation [1,2].

Degradation of the Alloy 22 waste package outer containers may occur by uniform corrosion, pitting or crevice corrosion, and stress corrosion cracking. Work has been conducted by DOE and by NRC and the Center for Nuclear Waste Regulatory Analyses (CNWRA) to characterize the conditions under which the various degradation mechanisms may occur [3,4]. Uniform corrosion rates are typically less than  $10^{-4}$  mm/yr [ $4 \times 10^{-3}$  mpy] under conditions where the passive film on Alloy 22 is maintained. However, at temperatures above 120 °C [248 °F], accelerated uniform corrosion of Alloy 22 may be possible if the oxide film has poor stability. Previous studies [5,6] indicated that localized corrosion is possible only at elevated temperatures in oxidizing environments with high chloride concentrations and low concentration of inhibiting anions such as nitrate, carbonate, bicarbonate, and sulfate. Additional tests have shown that above a critical molar concentration ratio of corrosion-inhibiting anion to chloride,

localized corrosion does not occur [6,7]. Also, although bicarbonate may inhibit localized corrosion, stress corrosion cracking of Alloy 22 has been observed at high anodic potentials and in aqueous mixtures of chloride and bicarbonate [8-11].

The evolution of environmental conditions within the emplacement drifts may affect the performance of waste packages if the drip shields fail to function as designed. Factors that may affect the composition of water that contacts the waste packages under this scenario include the initial seepage chemistry, waste package temperature, and the humidity within the emplacement drifts. When the temperature is above the boiling point of any concentrated solution that may form as a result of evaporation, the waste package is expected to remain dry and not be subject to accelerated degradation mechanisms. However, some concentrated solutions have boiling points high enough such that accelerated uniform corrosion is a concern. For example, solutions containing dissolved sodium-potassium-chloride-nitrate salts may have boiling points up to 190 °C [374 °F] [12]. Whether or not such solutions will form has been the focus of work conducted by DOE [13] and CNWRA [14].

The objective of this study is to evaluate the evolution of environmental conditions on the engineered barrier surfaces and the effect of such conditions on the performance of the waste package outer container. The initial tests reported here focused on determining the composition of the salts that form due to evaporation and its dependence on the starting water chemistry. The results will be used to develop future tests to study the water chemistries and the environmental conditions that may lead to aggressive conditions within the emplacement drifts.

## METHODS

Thermodynamic calculations were conducted using the StreamAnalyzer Version 2.0 code to determine the range in water chemistries that could evolve through evaporation of seepage water. Of key interest were the concentration of aggressive species, such as chloride, and the concentration ratios of chloride to corrosion-inhibiting species. For the purpose of this study, the chemical compositions of pore water samples taken from the Yucca Mountain area and reported by the U.S. Geological Survey [15-17] were used as input in the evaporation simulations. This analysis assumes that seepage water will have characteristics similar to those sampled at Yucca Mountain under ambient conditions and neglects the potential effects of water interaction with natural and engineered materials in the near-field environment. Thirty-three pore water compositions were selected from the U.S. Geological Survey database—11 from each of 3 water types (neutral, alkaline, and calcium-chloride, according to the chemical divide concept of Hardie and Eugster [18]). These initially dilute waters were evaporated to equilibrium using StreamAnalyzer at a temperature of 110 °C [230 °F] and pressure of 0.86 kPa [0.85 atm], the approximate atmospheric pressure at Yucca Mountain.

The resulting ranges in ratio of corrosion-inhibiting species to chloride for the three water types are illustrated in Figure 1. These ranges were used to select 10 solution compositions for the experiments. For the calcium-chloride and neutral-type brines, the solution compositions selected for the tests included those with inhibiting anion to chloride ratios close to the 25<sup>th</sup>, 50<sup>th</sup> (median), and 75<sup>th</sup> percentile values indicated in Figure 1. For the alkaline-type brines, a solution composition with a inhibiting anion to chloride ratio near the median value was used because the initially dilute water chemistry was similar for the 25<sup>th</sup>, 50<sup>th</sup> and 75<sup>th</sup> percentile values. Using a spreadsheet, recipes were developed for synthesizing the 10 test solutions from reagent grade chloride, nitrate, sulfate, carbonate, and bicarbonate salts of sodium, potassium, calcium, and magnesium. The synthetic solutions are simpler than actual pore water compositions, which also contained silica, alumina, fluoride, and bromide species.

The tests were conducted using a test cell illustrated in Figure 2. An Alloy 22 disk-shaped specimen, which had a machined shallow depression in the center to contain the solution, was placed inside the cell. After heating the specimen and maintaining its temperature

at 110 °C [230 °F], water was slowly dripped onto the specimen with a typical drip rate of 200 mL/day [0.05 gal/day]. Upon hitting the specimen surface, the water rapidly boiled, and evaporated, leaving behind a solid salt deposit. After 2,000 mL [0.53 gal] of each test solution was dripped onto the specimen, the salt deposit was recovered with a glass rod and analyzed to determine the composition using a combination of inductively coupled plasma-atomic emission spectrometry, ion chromatography, and an elemental analyzer. The Alloy 22 specimen also was examined after each test for signs of corrosion.

## RESULTS AND DISCUSSION

The results of the evaporation simulations shown in Figure 1 indicate that most alkaline and neutral brines have corrosion inhibitor to chloride ratios unlikely to promote localized corrosion of Alloy 22, whereas some of the calcium chloride brines could cause localized corrosion of Alloy 22. The anion concentrations of the test solutions are shown in Figure 3. The calcium-chloride brines had the highest chloride concentrations, whereas the alkaline brines had the lowest chloride concentrations. Figure 4 shows the calculated molar ratios of corrosion-inhibiting anion to chloride. With the exception of the calcium-chloride brines, all solutions had individual inhibitor anion to chloride ratios sufficient to mitigate localized corrosion. Correspondingly, the ratio of the total inhibitor to chloride concentration ratio was lowest for the calcium-chloride brines and highest for the alkaline brines. All neutral brines tested had nitrate to chloride concentration ratios greater than 0.4, which is well above the ratio of 0.1 needed to inhibit localized corrosion of Alloy 22 according to previously published work [14].

During testing, all solutions were rapidly heated to boiling and evaporated upon contacting the Alloy 22 block. No aqueous solution persisted or appeared to be stable at 110° C [230 °F], even after salt deposits had formed, during the course of dripping and evaporating 2,000 mL [0.53 gal] of solution onto the specimen surface. The measured concentrations of the anions in the solid deposits are shown in Figure 5. The results shown here are based on single measurements for each salt deposit. Replicate measurements performed on a limited number of salt deposit samples were within 5 percent of the reported values. All of the solid deposits had appreciable chloride concentrations. The calcium-chloride and neutral brine deposits also had appreciable concentrations of sulfate salts, whereas the alkaline brine had high concentrations of carbonate and/or bicarbonate salts.

Figure 6 shows the concentration ratios of the corrosion-inhibiting anions to chloride in the salt deposits. All of the deposits had sufficiently high ratios of total inhibitor anion to chloride concentration to inhibit localized corrosion of Alloy 22. However, the solubility of the nitrate salts is known to be significantly greater than that of the sulfate, carbonate, and bicarbonate salts [7]. Low nitrate to chloride ratios were observed in the salt deposits from all brine types. In tests involving calcium-chloride-type waters, sulfate consistently was present in the salt deposits in sufficient concentrations to inhibit localized corrosion of Alloy 22, whereas in tests using neutral and alkaline waters, sulfate and carbonate/bicarbonate were present in high enough concentrations. Deposits from the calcium-chloride waters contained relatively low concentrations of carbonate or bicarbonate. The combination of chloride and bicarbonate under oxidizing conditions has been shown to promote stress corrosion cracking [8]. Although the salts deposited from the neutral and alkaline waters also had significant carbonate and/or bicarbonate concentrations, low pHs necessary to elevate the corrosion potential of Alloy 22 into regions where stress corrosion cracking has been observed are unlikely to form in the potential repository environment.

Tests using a laboratory-scale system to simulate the conditions expected within the emplacement drifts of the potential repository at Yucca Mountain are currently planned. A test system has been designed to determine the relative amount of water that penetrates the simulated drift as a function of infiltration rate and drift temperature. In addition to relative

humidity and temperature, corrosion sensors have been developed to monitor the evolution of environmental conditions within and adjacent to the simulated emplacement.

## CONCLUSIONS

Tests conducted in this study have used a wide range of solution compositions representative of calcium-chloride, neutral, or alkaline brines that can be produced through the evaporation and concentration of initially dilute seepage water at the potential repository at Yucca Mountain, Nevada. The formation of brines with boiling points greater than 110°C [230°F] was not observed with any of the solutions tested. The composition of the salts that formed was dependent on the composition of the initially dilute water chemistry. The measured salt compositions suggest that the deliquescence of the salt deposits will not result in brines that promote either localized corrosion or stress corrosion cracking of the Alloy 22 waste package outer barrier. A laboratory-scale system designed to measure the evolution of conditions within the emplacement drift will be used to verify the results of the tests reported in this study.

## DISCLAIMER

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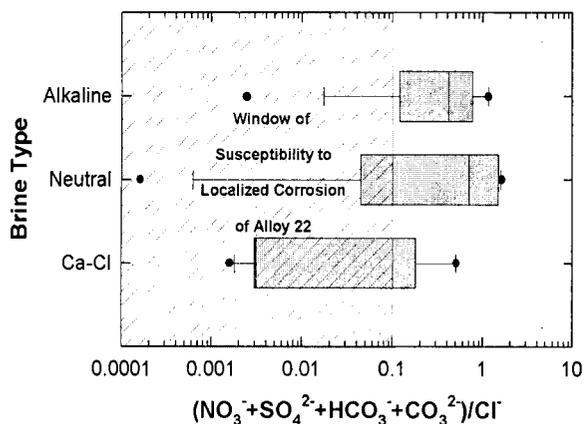
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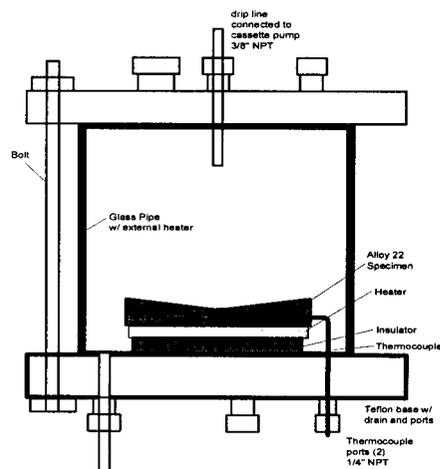
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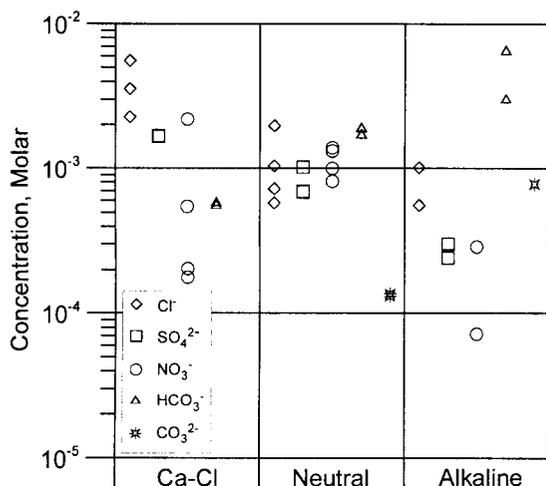
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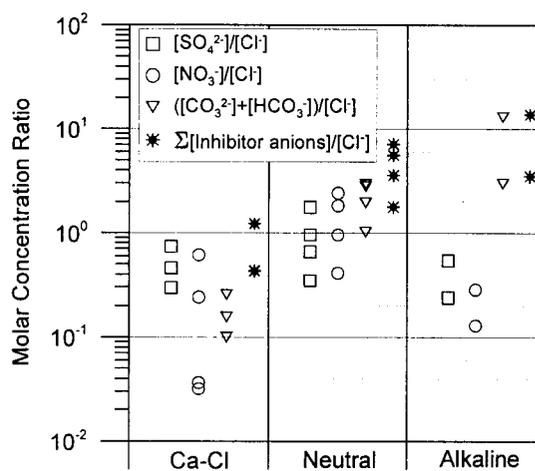
**Figure 1.** Ranges in calculated molar concentration ratio of corrosion-inhibiting ions to chloride for the three brine types. At ratios less than 0.1 Alloy 22 is considered susceptible to localized corrosion.



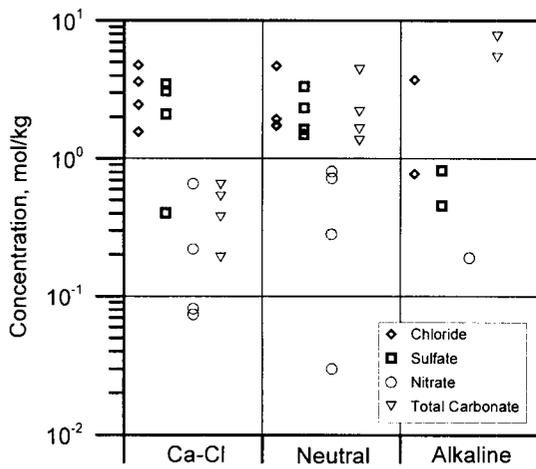
**Figure 2.** Schematic illustration of heated specimen test cell.



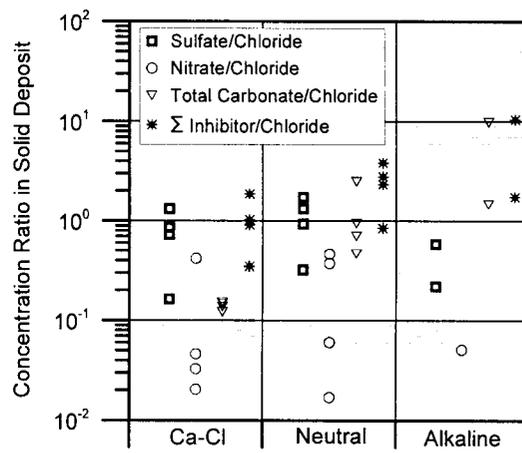
**Figure 3.** Calculated anion concentrations of the test solutions.



**Figure 4.** Calculated molar concentration ratios of the test solutions.



**Figure 5. Measured concentration of anionic species in salt deposits.**



**Figure 6. Molar ratios of corrosion-inhibiting anions to chloride in salt deposits.**