Thermodynamic Modeling of Brine Chemistry in the In-drift Environment of a Potential High-level Nuclear Waste Repository at Yucca Mountain, Nevada

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Background

Groundwater seeping into the underground drifts of the potential high-level nuclear waste repository at Yucca Mountain, Nevada, could undergo evaporative concentration resulting in brine formation. This process could lead to chemical conditions deleterious to the performance of the metallic components of the engineered barrier system, schematically shown in Figure 1. Because long-lived waste packages and drip shields are key factors in the safety strategy of the U.S. Department of Energy for the potential repository, it is important to evaluate the chemical evolution of in-drift waters that could contact and possibly degrade the engineered materials. Of particular importance in this evaluation are the concentrations of corrosive species (e.g., chloride and fluoride ions) and corrosion-inhibiting oxyanions (e.g., nitrate, sulfate, carbonate, and bicarbonate ions). The susceptibility to localized corrosion of Alloy 22, the material proposed for the outer container of the waste package, is strongly dependent on temperature and on the relative concentration of chloride ion and oxyanions (Dunn et al., 2003, 2004). Titanium alloy (Ti Grade 7), the material selected for the drip shields that would cover the waste packages, can become susceptible to accelerated corrosion if the fluoride ion concentration is greater than ~0.0005 molar (Brossia et al., 2001) and depending on the availability and rate of supply of fluoride ion to the metal surface.

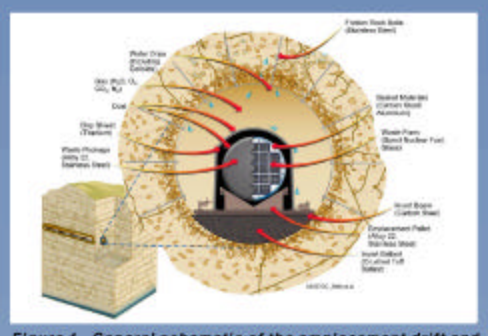

Figure 1. General schematic of the emplacement drift and engineered barrier system at the potential high-level nuclear waste repository at Yucca Mountain, Nevada. Figure taken from Andrews (2004).

Objective

Thermodynamic simulations of the chemical evolution of in-drift waters resulting from evaporation of seepage waters were conducted. The objective is to determine the types and the ranges in chemistry of brines that may form and contact the surfaces of drip shields, waste packages, and ground support materials. Such information will be useful for evaluating the potential degradation of those materials.

Technical Approach

- Measured chemical compositions of pore water and perched water from the unsaturated zone of Yucca Mountain were reported by Yang et al. (1996, 1998, 2003) and are plotted in Figure 2. For this study, the reported unsaturated zone water compositions were assumed to encompass the range in composition of water that could enter the repository drift.
- Thermodynamic simulations were conducted using LabAnalyzer and StreamAnalyzer (Versions 1.2), which are chemical equilibrium codes developed by OLI Systems, Inc. (Morris Plains, New Jersey, USA) for thermodynamic calculations in industrial and environmental applications. The codes allow evaluation of aqueous systems to 300 °C [572 °F], 1,500 bars [22,000 psi], and 30 molal.
- Twenty-nine Yucca Mountain pore water compositions selected from the Yang et al. (1996, 1998, 2003) database were used as input for the thermodynamic simulations of evaporation. The selected compositions represent the three brine types—calcium-chloride, neutral, and alkaline waters—according to the chemical divide concept of Hardie and Eugster (1970) (see Figure 3). Evaporation was simulated at different temperatures (95, 110, 125, and 140 °C [203, 230, 257, and 284 °F) and 0.85 bar [12 psi] (atmospheric pressure at Yucca Mountain).

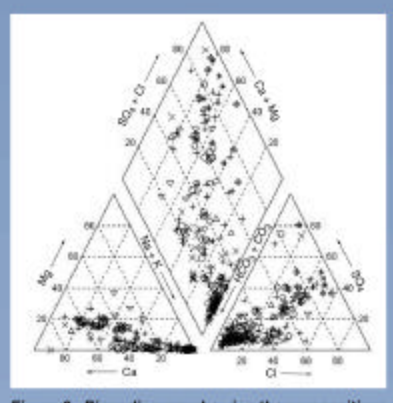

Figure 2. Piper diagram showing the compositions of 209 Yucca Mountain unsaturated zone groundwater samples reported by Yang et al. (1996, 1998, 2003).

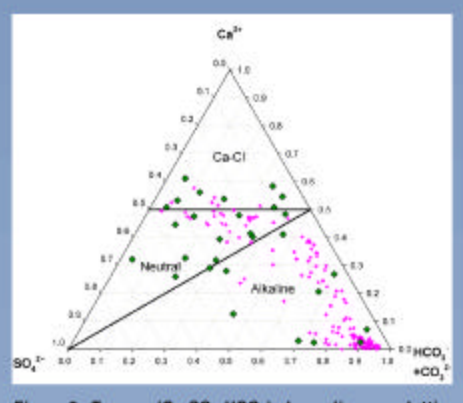

Figure 3. Ternary (Ca-SO_4-HCO_3) phase diagram plotting Yucca Mountain unsaturated zone groundwater compositions (●) shown in Fig. 2. "Chemical divide" lines separate the compositions into three brine types: (i) calcium-chloride, (ii) neutral, and (iii) alkaline (Hardie and Eugster, 1970). The compositions represented by the symbol ● were used as input to the thermodynamic simulations.

Results

- The ranges in brine compositions calculated for a temperature of 110 °C [230 °F] are shown as box plots in Figure 4. Median values of concentrations (moles/kg H_2O) of corrosive species (chloride and fluoride ions) and corrosion-inhibiting oxyanions (nitrate, sulfate, carbonate, and bicarbonate ions) are summarized below:
  - Alkaline waters
    - Corrosive species: $[Cl^-] - 5.6$; $[F^-] - 0.079$
    - Corrosion inhibitors: $[NO_3^-] - 0.34$; $[SO_4^{2-}] - 0.012$; $[HCO_3^- + HCO_3^{2-}] - 0.86$
  - Neutral waters
    - Corrosive species: $[Cl^-] - 7.0$; $[F^-] - 1.7 \times 10^{-4}$
    - Corrosion inhibitors: $[NO_3^-] - 2.8$; $[SO_4^{2-}] - 0.16$; $[HCO_3^- + HCO_3^{2-}] - 1.4 \times 10^{-5}$
  - Ca-Cl waters
    - Corrosive species: $[Cl^-] - 9.6$; $[F^-] - 1.1 \times 10^{-5}$
    - Corrosion inhibitors: $[NO_3^-] - 0.025$; $[SO_4^{2-}] - 2.8 \times 10^{-4}$; $[HCO_3^- + CO_3^{2-}] - 4.4 \times 10^{-8}$
- The range in the concentration ratios of chloride to oxyanions for the three brine types is shown in Figure 5. The "window of susceptibility" to localized corrosion of the Alloy 22 waste package material also is shown in the figure.
  - Most of the Yucca Mountain unsaturated zone waters would evolve, upon evaporation, to brines that are relatively benign to Alloy 22 due to sufficient concentrations of corrosion-inhibiting oxyanions
  - Calcium-chloride-type waters have high concentration ratios of chloride to oxyanions, which could enhance localized corrosion of Alloy 22
    - Concentration of NO_3^- ion is low due to the formation of $CaNO_3^+$ and $NaNO_3^\circ(aq)$ aqueous complexes, but there is uncertainty in the thermodynamic data for $CaNO_3^+$ and $NaNO_3^\circ(aq)$
  - Alkaline-type waters form brines, upon evaporation, with fluoride ion concentrations above the threshold for accelerated generalized corrosion of the titanium drip shield material.

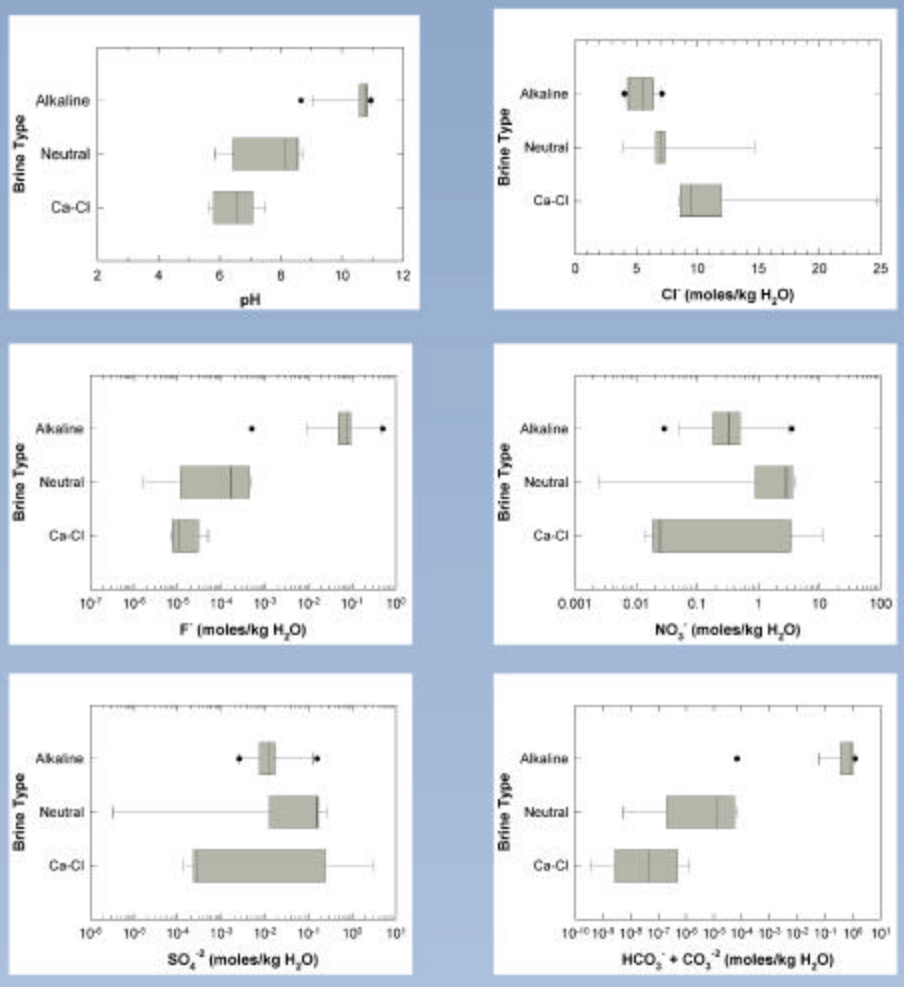

Figure 4. Box plots showing the range in pH and concentrations of chloride, fluoride, nitrate, sulfate and total carbonate of the three brine-types that could form by evaporation of the Yucca Mountain unsaturated zone waters plotted in Figs. 2 and 3. The left and right edges of the box are the 25th and 75th percentile values, respectively, and the line inside the box is the median value. The 10th and 90th percentile values are shown as whiskers, and outliers are represented by black dots. The results shown are for a temperature of 110 °C [230 °F].

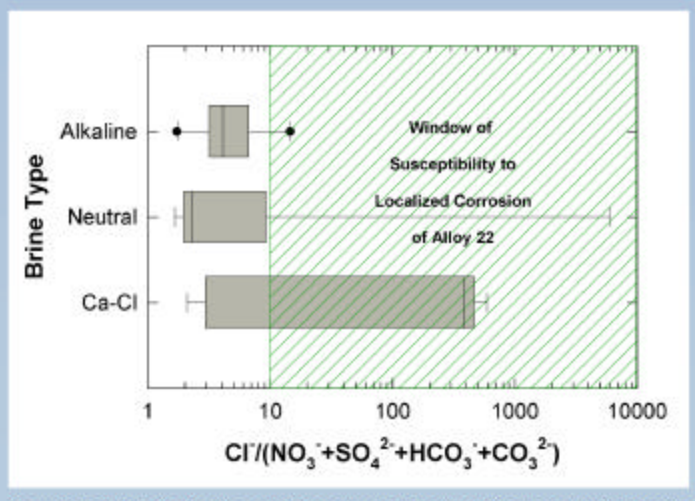

Figure 5. Box plots showing the range in the concentration ratio of chloride to oxyanions for the three brine-types that could form by evaporation of the Yucca Mountain unsaturated zone waters with compositions plotted in Figs. 2 and 3. Shown as a hatched area is the "window of susceptibility" to localized corrosion of the Alloy 22 waste package material, based on corrosion experiments conducted by Dunn et al. (2003,2004).

Conclusions

- Evaporation of seepage waters, with compositions similar to Yucca Mountain unsaturated zone pore waters, would form brines with elevated concentrations of corrosive species (chloride and fluoride ions) and corrosion-inhibiting oxyanions (nitrate, sulfate, bicarbonate, and carbonate ions). Chloride ions could be deleterious to the performance of the stainless steel ground support materials. Fluoride ions could enhance the general corrosion of the titanium drip shield, but its overall effect would depend on the total mass of fluoride present in evaporating seepage waters. Most brines formed by evaporation would not enhance the localized corrosion of the Alloy 22 waste package material due to sufficient concentrations of corrosion-inhibiting oxyanions.

References

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Acknowledgments

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