

Experimental approaches to predict the behavior of liquid films

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Introduction

The experimental techniques outlined here represent a new approach to understand the fundamental chemistry associated with the interaction of aqueous liquid films with metal oxide surfaces which might be susceptible to corrosion.

Discussion

The approaches taken in this initial stage of the project are as follows: (1) Gravimetric isopiestic analyses of solution compositions and phase changes for mixtures of soluble salts, including the precise measurement of the vapor pressure at elevated temperatures (<200°C) and detection of the deliquescence points of the dry mixtures. (2) The partitioning constants of volatile solutes (F^- , Cl^- , NO_3^- and SO_4^{2-} salts) are measured under equilibrium conditions as a function of temperature, pH, solution composition and concentration to help establish the fate of these anions in liquid films and the corresponding effects on the pH of the remaining film. (3) The continuous monitoring of the pH (as a function of time and temperature) of concentrated brines in contact with metal oxide coupons will help define the chemistry occurring on these surfaces. Identification of solid phases formed during the evolution of these experiments will also be carried. In all the above experiments, the effect of the presence of naturally occurring particulates and alloy coupons will be investigated. (4) Other techniques will probe the alloy and particulate surface layers to quantify the flux of species through these layers using state-of-the-art methods. The results of this research will be coordinated with other activities of the S&T program and will also be utilized in the development of a predictive localized corrosion code (OLI Systems, Inc.).

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Dust salts and deliquescence on waste packages in an unsaturated-zone repository

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Dust is expected to collect on waste packages emplaced in the unsaturated zone at Yucca Mountain, Nevada. During the repository cooldown phase, salts in the dust could initiate brine formation by deliquescence at "above-boiling" temperatures. The temperatures to which such brines can exist and the brine compositions are important factors in waste package corrosion. Sources of dust include tunneling, routine operations, and outside air ventilated through the repository prior to closure. Tunnel dusts are mostly rock flour with a few tenths percent of soluble salts. Atmospheric dusts, however, commonly contain 8-15% (or more) soluble salts.

Data on dust salt compositions have been collected and analyzed with thermodynamic modeling calculations, both to reconstruct equilibrium assemblages from leachate data, and to predict subsequent behavior under repository conditions. Previous studies based on tunnel dusts indicated that deliquescence would be controlled by the key assemblages NaCl-KNO₃, NaCl-KNO₃-NaNO₃, and NaCl-KNO₃-NaNO₃-Ca(NO₃)₂ (in decreasing order of abundance in dust samples). Such assemblages are highly deliquescent at elevated temperature, and the coexisting brine compositions have high NO₃/Cl ratios.

More complete data on the leachate chemistries of tunnel and outside dusts have recently been obtained. Ammonium (NH₄) is now recognized as present in the tunnel dusts; also, it is abundant in atmospheric dusts. NH₄ behaves somewhat analogously to K, suggesting that NaCl-KNO₃-NH₄NO₃ may be the most abundant key assemblage. The thermodynamic database (Pitzer-based) has been expanded to address NH₄, and new modeling calculations will be presented. The state of the thermodynamic modeling will be addressed, partly by comparison with experimental data (more extensively addressed by Carroll et al., this conference) and also by consideration of alternative thermodynamic data and models.