Reactive Transport Modeling of Acid Gas Generation and Condensation

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RESEARCH OBJECTIVES

Yucca Mountain, Nevada, is a proposed site for geologic storage of high-level nuclear waste. The safety case for the proposed repository greatly depends on the integrity of the engineered barrier system, especially where waste packages would be located. Of concern is the possible presence of corrosive brines or acid gases via evaporation of pore water on top of hot waste packages after seepage into waste emplacement tunnels. Pulvirenti et al. (2004) recently conducted a laboratory evaporation/condensation experiment on a synthetic solution of primarily calcium chloride. This solution represents one potential type of evaporated pore water at Yucca Mountain. These authors reported that boiling this solution to near dryness (a concentration factor >20,000 relative to actual pore waters) leads to the generation of acid condensate (pH <1.5), presumably due to volatilization of HCl (and minor HF and/or HNO_3). The objective of this study was to evaluate the experimental results of Pulvirenti et al. (2004), so as to better understand processes leading to acid gas generation and condensation, and their potential implications for Yucca Mountain.

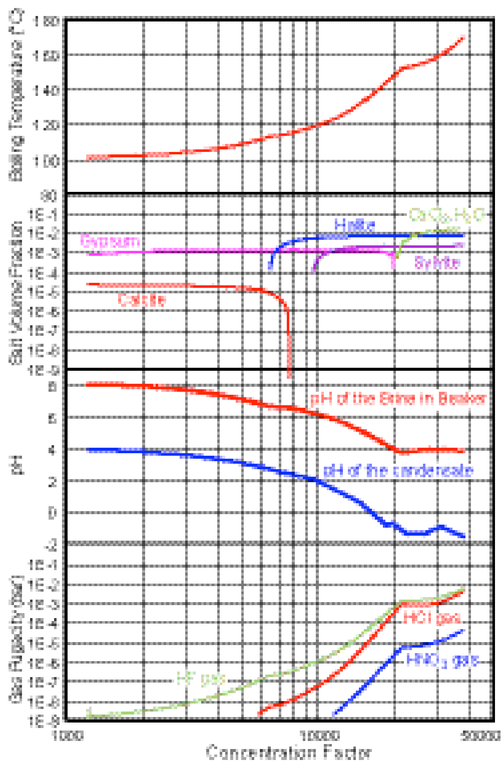

Figure 1. Simulated boiling temperature, salts volume fraction, pH, and fugacity

APPROACHES

The experiment of Pulverenti et al. (2004) was simulated with a multicomponent and multiphase reactive transport code (TOUGHREACT, Xu et al, 2004), including boiling, gas transport, and condensation. A Pitzer ion-interaction model was implemented into this simulator to allow calculations at high ionic strength. In addition, the code was modified to take into account vapor-pressure lowering caused by the increased salinity.

ACCOMPLISHMENT

The simulation of the experiment captures the observed increase in boiling temperature (up to 144°C and higher at ~1 bar) resulting from elevated concentrations of dissolved salts (up to 40 m ionic strength). The computed HCl fugacity (up to ~10^{-3} bars) generated by boiling under these conditions is not sufficient to lower the pH of the condensate (cooled to 80 and 25°C) down to observed values, unless the H_2O mass fraction in gas is reduced below ~2%. This is because the condensate becomes progressively diluted by H_2O gas condensation. However, when the system is modeled to remove water vapor, the computed pH of instantaneous condensates decreases to negative values (Figure 1), consistent with the Pulverenti experiment. The results also show that the HCl fugacity increases, and calcite, gypsum, halite, sylvite, and hydrated calcium chloride precipitate sequentially with increasing concentration factors.

SIGNIFICANCE OF FINDINGS

The acid gases generated from boiling Yucca Mountain unsaturated zone pore water lead to an acid condensate in the experiment, which was successfully simulated with the addition of a Pitzer ion-interaction model into TOUGHREACT. However, these experimental conditions—corresponding to equipment of ~15 m^3 of seepage water, and highly localized condensation within a closed system—are not anticipated in the drift environment at Yucca Mountain. Hence these extreme pH observations are irrelevant to the Yucca Mountain.

RELATED PUBLICATIONS

Pulvirenti, A.L., K.M. Needham, M.A. Adel-Hadadi, A. Barkatt, C.R. Marks, and J.A. Gorman, 2004, Multi-phase corrosion of engineered barrier materials. Corrosion 2004, NACE International, New Orleans, Louisiana, March 28–April 1, 2004.

Xu, T., E. Sonnenthal, N. Spycher and K Pruess, TOUGHREACT User's Guide: A simulation program for nonisothermal multiphase reactive geochemical transport in variably saturated geologic media. MOL.20050125.0172, 2004. Berkeley Lab Report LBNL-55460.

ACKNOWLEDGMENTS

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