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Intracrystalline Diffusion In Clinoptilolite: Implications For Radionuclide Isolation

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Summary

1.) Introduction. Experiments have been performed to measure the rate of exchange diffusion in the zeolite clinoptilolite (CL) for elements important to radionuclide isolation at Yucca Mountain, NV. Clinoptilolite is one of the major sorptive minerals in the tuffs at Yucca Mountain, and occurs both as a major component in zeolitized units (Calico Hills), and in fractures in non-zeolitized tuffs (Topopah Spring). Field evidence and numerical modeling[1] suggests that the movement of fluids through the tuff rocks adjacent to the potential repository may occur via episodic flow through fractures. Under conditions of rapid fracture flow the effective sorptive capacity of fracture-lining clinoptilolite may be controlled by exchange diffusion rather than exchange equilibrium.

2.) Description of work. Single crystals of clinoptilolite were oriented to a specific crystallographic face by mounting in epoxy and rendered nominally homoionic with respect to Na, K, and Ca by exchange with 1N NaCl, KCl, or $CaCl_2$ salt solutions. The homoionic crystals were then exposed to binary Cs/M or Sr/M (M = Na, K, Ca) solutions at different temperatures. The geochemical modeling code EQ3/6 was used to define binary solution compositions that would maintain a constant concentration boundary condition at the crystal surface and that would result in the inward diffusing cation occupying approximately 1% of the exchange sites (exchange data for Cs, K, Na, Ca, and Sr taken from Breck[2]) at the crystal/liquid boundary. The epoxy-mounted crystal was placed in the bottom of a Teflon erlenmeyer flask and 100 mL of the relevant binary solution was added to the flask. The sealed flasks were placed in an orbital shaker for the ambient temperature experiment (~30-32 °C); and a shaking water bath at 90 °C for the higher temperature

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experiment. After varying periods of contact, the crystals were removed from the diffusion solutions and concentration profiles of the inward diffusing cation normal to the exposed face were measured by secondary ion mass spectrometry (SIMS).

3.) Results. Results from the SIMS analyses showed clear diffusion profiles for both Cs and Sr at ambient and elevated temperatures. The shape of the concentration profile could not be fit using a single (constant) diffusion constant, so a binary interdiffusion model[3], in which the effective interdiffusion coefficient is dependent on the composition of the exchange sites, was used to model the ambient temperature diffusion of Cs and Sr into CL crystals. Preliminary data indicates that at 30 °C, Cs and Sr tracer diffusion coefficients are on the order of 10^{-13} and 10^{-18} cm^2s^{-1}, respectively. The diffusion of Cs into the Ca clinoptilolite at 90 °C was rapid enough to increase the Cs content several orders of magnitude above background to a depth of at least 35 μm (the maximum depth probed) over a 12 day exposure. Based on SIMS analysis of an unexposed nominally Ca clinoptilolite, it is apparent that the small concentrations of Na, K, and trace levels of Rb that are present are not constant with depth. It is possible that at least some of the observed diffusion of Cs may occur by preferential exchange with the residual monovalent cations in the Ca exchanged crystal.

4.) Conclusions. Analysis of Cs diffusion profiles into nominally Ca clinoptilolite for ambient and 90 °C experiments and for Sr diffusion into Ca clinoptilolite at ambient temperature reveals that using the binary interdiffusion model described in Doremus[3], and later in Viani et al.[4,5], the ambient temperature diffusion of Cs and Sr can be reasonably modeled. The tracer diffusion coefficients estimated from the Cs and Sr diffusion profiles in the ambient temperature experiments indicate diffusion coefficients on the order of 10^{-13} and 10^{-18} cm^2s^{-1} for Cs and Sr, respectively.

The experimental data and the parameters derived from them indicate that diffusion of Cs and Sr into clinoptilolite may not be rapid enough to allow the assumption of local cation-exchange equilibrium for situations in which groundwater flow is relatively rapid and clinoptilolite crystal size is relatively large. Therefore, applying equilibrium distribution coefficients obtained from batch adsorption experiments using fine grained clinoptilolites (1-2 μm) to predict adsorption during flow through fractured media may not be justifiable in certain cases.

5.) References.

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