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EFFECTS OF MINERALOGY, GRAIN SIZE, AND SOLUTION COMPOSITION ON LITHIUM SORPTION TO SATURATED ALLUVIUM SOUTH OF YUCCA MOUNTAIN, NEVADA

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Lithium is used frequently as a surrogate for cationic radionuclides such as NpO_2^+ in field and laboratory settings. Current plans include the use of Li⁺ as a reactive tracer in field tracer testing in the saturated alluvium south of Yucca Mountain, NV, site of a potential high-level nuclear waste. Characterization of the alluvial material for grain size, mineralogy, cation exchange capacity (CEC), and surface area yields data that is compared with lithium batch sorption as a first step in inferring radionuclide transport behavior. This research will be used to help assess performance of the potential repository.

Batch lithium sorption tests were performed on samples from 2 different wells, NC-EWPD-19P and -19D, located about 20 m apart at depth. Samples were wet sieved, dried, and divided into two size fraction ranges, from 75 to 500 μ m, and less than 75 μ m, prior to the equilibration. A range of lithium concentrations (1 mg/L to 300 mg/L) in filtered 19D water was equilibrated with the rock at a 1:4 solid:solution (g:ml) ratio for 24 hours. Equilibrium cation composition, including Na⁺, Ca²⁺, and K⁺ of the solutions also was measured. Total cation exchange capacities were measured using Cs⁺ alone and Li⁺ followed by Cs⁺ for the 75-500 μ m fraction samples. Surface areas were measured using the BET method.

Figure 1 shows a series of sorption isotherms for the two different size fractions at the same depth in 19P and 19D. Samples from 19P tended to have higher Li^+ sorption capacities than 19D samples, probably due to the difference in drilling method (air hammer for 19P versus water rotary for 19D) and, thus, the subsequent mineralogical distributions in the samples. X-ray diffraction data indicated a much higher percentage of smectite and clinoptilolite for the 19P samples than for the 19D samples. Figure 1 also shows that the Li^+ sorption isotherms tended to be nonlinear with the ratio of the amount sorbed (mmol/kg) to the amount in solution (mmol/L) [the often-cited K_d value (L/kg)], decreasing as solution concentrations increased. This sorption nonlinearity has important implications for field tracer tests where tracer injection concentrations often have to be very high to counteract the effects of dilution and dispersion and ensure quantifiable concentrations at observation wells.

Figure 2 shows how the $\text{Li}^+ K_d$ values measured at the lowest Li^+ concentrations vary with depth interval and size fraction at the 19D-19P site. These K_d values should be the most meaningful thermodynamically because they are measured closest to infinite dilution. Besides the tendency for greater K_d values onto 19P material relative to 19D material, it is apparent that the Li^+ sorption capacity of the alluvium tends to increase with depth and that the K_d values are consistently higher for the smaller of the two grain size fractions in any interval. Both of these observations can be related to the clay and zeolite content of the alluvium material. These minerals tend to be enriched as particle size decreases, and they also tend to increase with depth at the 19P-19D location.

Figure 3 shows how the $Li^+ K_d$ values of Figure 2 are correlated with smectite and clinoptilolite weight percentages in the alluvium samples. It is clear that the K_d values are much better correlated with clinoptilolite content than smectite content. In fact, multiple linear regression analyses indicated negligible benefit of adding smectite content as an independent variable to predict $Li^+ K_d$ values when clinoptilolite content was already included in the model. Additional statistical analyses indicated that $Li^+ K_d$ values were much better correlated with clinoptilolite content than either the specific surface area or CEC of the alluvium samples.

Figure 4 shows how the equilibrium solution concentrations of Li^+ , Na^+ , K^+ , and Ca^{++} from a set of batch sorption experiments at different starting Li^+ concentrations could be effectively fitted using a relatively simple cation exchange model. The model uses ion exchange coefficients and the CEC of the material as adjustable parameters. Fitted CEC values were in reasonably good agreement with measured CEC values. This multicomponent ion exchange modeling approach holds promise in being able to describe Li^+ transport much better than a "K_d-type" model in systems in which Li^+ comprises a large percentage of the cation equivalents in solution (e.g., in a field tracer test). Under these conditions, apparent sorption-desorption hysteresis and salinityfront effects often confound test interpretations using a K_d approach.



Adsorption of Li+ to Alluvium, Wells 19D and 19P, interval 420-425 ft bgs

Figure 1. Adsorption isotherms of Li^+ to alluvium plotted on log-log axes (75-500 µm and <75 µm fractions). The line with slope = 1 corresponds to a linear sorption isotherm, which makes it apparent that the relative amount of Li^+ sorption decreases as solution concentrations increase (i.e., lower apparent K_d values at higher concentrations).



Figure 2. $Li^+ K_d$ values measured at the lowest solution concentrations as a function of depth interval and grain size in boreholes 19P and 19D.



Figure 3. $\text{Li}^+ \text{K}_d$ values measured at the lowest solution concentrations as a function of weight percent smectite and clinoptilolite in alluvium material. The regression line is for clinoptilolite. The R² for the correlation of Li⁺ K_d with smectite content was only 0.16.





Figure 4. Measured and fitted Li^+ , Na^+ , K^+ , and Ca^{++} concentrations in solution as a function of Li^+ concentration for Li^+ sorption experiments onto alluvium material from 19D, 420-425 ft bgs, 75-500 μ m. Fitted values were obtained using a cation exchange model.