1 Laboratory Experiments to Characterize Cation-Exchanging Tracer Behavior for Fracture Surface
2 Area Estimation at Newberry Crater, OR

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9 Abstract

10 A series of column transport experiments ranging from 25°C to 275°C, as well as batch sorption
11 experiments at 25°C, were conducted to estimate cation exchange parameters for lithium and
12 cesium at the Newberry Crater Enhanced Geothermal System demonstration site.. The
13 experiments were designed to facilitate interpretation of single-well field tracer tests to
14 interrogate fracture surface area. Lithium column transport from 125°C to 275°C showed a
15 strong temperature dependence, with much greater cation exchange at higher temperatures
16 than in 25°C experiments. Cesium column transport at 225°C indicated a weaker temperature
17 dependence, and unlike Li^+ , its exchange decreased at higher temperatures.

18

19 1. Introduction

20 Newberry Volcano in central Oregon, USA is the site of an Enhanced Geothermal System (EGS)
21 Demonstration Project (AltaRock Energy, Inc., 2011), funded in part by the U. S. Department of
22 Energy. Single-well tracer tests involving lithium and cesium ions were originally planned as
23 part of the Demonstration Project to estimate fracture surface area generated during hydraulic
24 stimulations, or “hydroshearing”, to open and enlarge natural fractures. Surface area
25 estimation with these tracers is based on the concept that their adsorption onto fracture
26 surfaces by cation exchange should be proportional to the fracture surface area to volume ratio
27 (SA/V) seen by the injected tracer solution. Cation exchange is a rapid, reversible process in
28 which lithium and cesium ions (Li^+ and Cs^+) exchange with other cations present in the mineral

matrix, primarily sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+). The rapid and reversible adsorption behavior greatly simplifies the interpretation of tracer tests to estimate surface area. Lithium and cesium were chosen over other candidate cations primarily because of their relative lack of abundance in both water and rocks at the Newberry site, making it easy to distinguish them from naturally-occurring background, and also because of their availability in large quantities (which ruled out Rb^+). In a separate study, Li^+ exchange was found to be a robust method to estimate relative changes in surface area in an amphibolite schist material from Fenton Hill, NM under simulated geothermal reservoir conditions (Dean et al., 2012). Cation-exchanging alkali metal tracers such as Li^+ and Cs^+ also have advantages of being non-toxic, inexpensive, and highly soluble, making them well suited as adsorbing tracers for estimating fracture surface area in single-well tracer tests where tracer concentrations tend to remain relatively high. Their primary disadvantage is that they can have significant background concentrations in geothermal systems, which may limit their use to single-well tests because of the much larger dilution factors typically observed in interwell tracer tests. Large dilution factors can result in the tracer signals being obscured by background concentrations (Reimus et al., 2003).

Tracer injections were conducted at Newberry Crater in the fall of 2012 during sequential zonal stimulations in the same well, with Li^+ and Cs^+ being injected into different zones near the end of two different stimulation phases. Li^+ was injected near the bottom of the well where static temperatures were approximately 275°C, and Cs^+ was injected much shallower, where temperatures were approximately 225°C. Different conservative (nonsorbing) tracers were co-

50 injected with each cation so that when the well flows back, the adsorption of Li^+ and Cs^+ onto
51 fracture surfaces can be quantified by comparing the concentration vs. time histories
52 (breakthrough curves) of the cation tracers and the conservative tracers from each zone. As of
53 this writing, the flowback phase of these tests had not yet occurred.

54 In principle, relative changes in SA/V in the same flow system (for instance, before and after a
55 stimulation) can be estimated without direct knowledge of the dependence of cation exchange
56 on SA/V; i.e., a doubling of SA/V should correspond to a doubling of adsorption by cation
57 exchange. However, for estimating absolute surface areas, which is a goal at Newberry Crater,
58 the relationship between cation exchange and SA/V must be known. This relationship can only
59 be determined in laboratory experiments, preferably using site-specific water and rocks at site-
60 specific temperatures.

61 In this study, a series of laboratory experiments were conducted to quantify the cation
62 exchange behavior of Li^+ and Cs^+ in the Newberry Crater system to facilitate interpretations of
63 the single-well tracer tests. The temperature dependence of Li^+ and Cs^+ exchange was of
64 particular interest because such a dependence could be important in test interpretations and
65 also because we wanted to know whether high-temperature cation exchange parameters might
66 be estimated reasonably well from much simpler and less expensive low-temperature
67 experiments.

68 69 **2. Materials and Methods**

Lithium and cesium batch sorption experiments were conducted at room temperature using the individual minerals that make up the Newberry fracture mineralogy and a mineral mix comprised of equal mass fractions of the individual minerals. The mineral mix was used in laboratory scale column transport experiments under flowing conditions and over a range of reservoir temperatures and pressures using 1,5 naphthalene disulfonate (NDS), lithium bromide and cesium bromide as tracers in a synthetic groundwater. The semi-analytical model RELAP (Reimus et al., 2003; Williams et al., 2013) was used to fit the breakthroughs of the conservative NDS tracer to estimate column parameters. A multicomponent numerical transport model, MULTRAN (Sullivan et al., 2003; Williams et al., 2013), was used to describe lithium and cesium transport, including cation-exchange, through the columns. Details of the materials and methods used in this study are presented in Section 2.1 through Section 2.5.

2.1. Minerals

Minerals representing Newberry reservoir fracture surfaces and coatings were selected based on information contained in AltaRock Energy (2011) and also from personal communications with AltaRock staff and Nicholas Davatzes of Temple University, who was responsible for most of the mineralogic descriptions in AltaRock Energy (2011). A mineral assemblage consisting of albite, calcite, chlorite, epidote and quartz was chosen, with the minerals being purchased from commercial suppliers because sufficient quantities of fracture surfaces and coatings for our experiments were not available from core or cuttings. The minerals were crushed and sieved (250-500 μm), annealed (450°C for 48 hr) and mixed in roughly equal fractions (referred to as “mineral mix” or simply the “mix”) for use in batch and column experiments. The

annealing process was intended to decrease the surface energy of the newly-created mineral surfaces so that they might more closely approximate the reactivity of the fracture surfaces in the Newberry system. This process caused oxidation of Fe(II) in the chlorite, but it was later determined in batch sorption experiments with oxidized and re-reduced chlorite that the oxidation had negligible effect on Li^+ sorption.

Table 1 contains the chemical formulas, fraction of each mineral contained in the mix, mineral surface areas (multipoint BET method with krypton as sorbent) (Brunauer, 1938), and lithium and cesium cation-exchange capacity (CEC) measurements (method reported in Section 2.3).

Also included are BET surface area and CEC measurements of the mix as well as a calculation of the combined mass-weighted surface area and CEC of the mix, referred to as the “fractional” surface area/CEC (sum of the products of mineral mass fractions and specific surface areas/CECs of the individual minerals). The calculated fractional surface area of the mix is twice the directly-measured value for the mix. The calculated fractional Li CEC is 13% lower than that measured in the mix and the fractional Cs CEC is 8% higher than the measured CEC of the mix. These inconsistencies between calculated and measured parameters in the mineral mix are attributed to sample heterogeneity. Qualitative X-ray diffraction analysis of a 1.3 g grab sample of the mix contained the mineral mass fractions listed in Table 2. Given that the mass fractions of each mineral listed in Table 1 are considered highly representative of the bulk mix used in this study, the QXRD-measured mass fractions of the bulk mix sample (1.3 grams) clearly demonstrate how non-representative a small grab sample can be. Table 2 also lists the calculated fractional surface area and CEC of the minerals and mix according to the QXRD-

determined mass fractions. Interestingly, the QXRD-based fractional surface area agrees quite well with the measured surface area of the mix sample, which may reflect that the 4.1 g Kr-BET mix sample had similar biases in relative mineral representation as the smaller QXRD sample (most notably an under-representation of chlorite, which has an order-of-magnitude higher specific surface area than any of the other minerals in the mix). CEC values for the mix exhibit much better agreement between fractional and measured values, which we attribute to (1) the smaller range and greater uniformity of mineral-specific CEC values compared to the surface area values, and (2) the fact that the two minerals with the highest CEC values, albite and chlorite, tended to offset each other in that albite was the most over-represented and chlorite the most under-represented in the QXRD mass fractions (and presumably also the CEC samples). We conclude that the calculated fractional surface area and CEC values using the weighed-out mass fractions (Table 1) provide the best representation of the bulk mix properties, although we recognize that the surface areas may only be accurate in representing the bulk mix to within 30-50% and the CECs only accurate to within 10-30%.

Table 1

Table 2

2.2. Synthetic Groundwater

A synthetic groundwater was created from the chemical composition of a shallow groundwater aquifer at the Newberry demonstration site (from Pad 29) that will be used as the stimulation fluid. A second synthetic groundwater was created in which all the calcium and magnesium salts in the Newberry water composition were substituted with potassium salts. The recipe for the two synthetic waters, designated N (original Newberry groundwater composition) and K (potassium substituted for divalent cations), are listed in Table 3. The K- water was used in all high-temperature flow-through experiments described in Section 2.3 because calcite (CaCO_3) and magnesite (MgCO_3) were predicted by PHREEQC (Parkhurst and Appelo, 2013) to be significantly supersaturated at the higher temperatures (Figure 1) using the Lawrence Livermore National Laboratory (LLNL) thermodynamic database of inorganic aqueous species and minerals (Johnson, 2010). There was a concern that such precipitation could interfere with lithium and cesium transport via co-precipitation reactions and also that it could significantly decrease the permeability of the reactor, possibly leading to plugging.

Table 3

Figure 1

2.3. Room Temperature Batch Experiments

Room temperature lithium and cesium batch sorption experiments were conducted in triplicate in 50-ml polycarbonate Oakridge (OR) tubes. 5 grams of dry material was weighed into the

centrifuge tubes and equilibrated with 10 ml of tracer-free synthetic water followed by centrifugation and sequential replacement of the supernatant with tracer solutions of 1 mg/L, 5 mg/L, 25 mg/L and 6,941 mg/L (1 molar) Li^+ (as lithium chloride). The solution volume in each case was 10 ml, yielding a solution/solid ratio of 2 ml/g. The Li was then desorbed from the material by replacing the supernatant with tracer-free water. Once the Li was desorbed, the supernatant was replaced sequentially with 10 ml of solutions of 1 mg/L, 5 mg/L, 25 mg/L and 132,905 mg/L (1 molar) Cs^+ (as cesium chloride). Aliquots of the supernatants after each sequential addition were analyzed for Li^+ and/or Cs^+ , aluminum (Al), Ca, iron (Fe), Mg, K, Na and silica (Si) by either ICP-OES or ICP-MS. The Li^+ and Cs^+ cation-exchange capacity (CEC) was determined for each mineral and the mix by measuring the displacement of cations in the 1M Li/Cs batch experiments.

Each of the five individual minerals plus the mix were tested using the N-water, whereas only the mix and calcite were tested with the K-water. The N-water was emphasized because this water was used as the stimulation water (to which tracers were added) in the field experiments. The experiments with the K-water were conducted to evaluate whether Li or Cs sorption was significantly different in the water that was used in the column experiments. Calcite was tested with the K-water because of the concern that sorption onto this mineral might be suppressed if it were slowly dissolving in the Ca-free water. Room temperature batch experimental results are reported in Section 3.1.

2.4. Column Transport Experiments

Lithium and cesium column transport experiments were conducted at both Los Alamos National Laboratory (LANL) and the Energy and Geoscience Institute (EGI) at the University of Utah. Table 4 shows the experimental matrix for the columns, with the experiments greater than 200°C being conducted at LANL and those less than 200°C being conducted at EGI. The experiments at LANL were conducted in a specially designed high-pressure, high-temperature flow-through system that simulates reservoir conditions. Figure 2 is a simplified schematic of the experimental apparatus. A titanium pressure vessel (approximate volume of 540 ml) was filled with the mineral mix and flushed with de-ionized water to remove any mineral fines that might later result in clogging. After insertion into a resistance-heated furnace to provide temperature control, the vessel was saturated by applying vacuum at the outlet side of the vessel and flowing K-water through the vessel. Tracer breakthrough curve analysis suggested a flowing pore volume of approximately 215 ml. The vessel was slowly heated to 225°C and pressurized to 1000 PSI (pressure was maintained above the boiling point of the aqueous phase during heating) and allowed to equilibrate for several days. The three LANL experiments were conducted at LANL at 20 ml/hr, yielding an approximate mean residence time of 10.5 hours for a conservative tracer. Separate column testing of lithium cation exchange on an amphibolite schist material from Fenton Hill, NM indicated that there were insignificant differences in cation exchange behavior at 10 ml/hr and 20 ml/hr in a similar-sized column (Dean et al., 2012), so only one flow rate was used in this study. The first two experiments involved the injection of a solution of LiBr and 1,5 NDS that was approximately 10 mg/L Li. These experiments were conducted at 225°C and 275°C, respectively. The third experiment was conducted at 225°C and

involved the injection of a solution of CsBr and 1,5 NDS that was ~170 mg/L Cs. For the first two experiments (with LiBr) the tracer was loaded into a sample loop attached to a valve that would allow for approximately 50 ml of degassed tracer to be pulse injected into the system without flow interruption. For the third experiment (with CsBr), approximately 50 ml of tracer solution was injected by switching the pump feed reservoir to a flask containing degassed tracer. Starting immediately after injection in all experiments, samples were collected at regular intervals in a fraction collector downstream of a back pressure regulator. Aqueous samples were analyzed for NDS by fluorescence detection, Li by ICP-OES and Cs by ICP-MS.

Table 4

Figure 2

The EGI experimental apparatus was similar to that of Figure 2, although the column was about half the volume of the LANL reactor (~260 ml), and it was oriented vertically instead of horizontally with heating coils and insulation used instead of a furnace for temperature control. The column was filled with the mineral mix (which was a split of the mix prepared at LANL) and flushed with de-ionized water to remove any mineral fines that might later result in clogging. The vessel was saturated by applying vacuum at the outlet side and flowing K-water through it. An approximate pore volume of 95 ml was calculated by subtracting the volume of material from the total volume of the vessel. The vessel was slowly heated to 125°C and pressurized to

1000-1100 psi to maintain the aqueous phase above the boiling point during heating and then allowed to equilibrate for several days. Three tracer experiments were conducted at temperatures of 125°C, 150°C, and 175°C. The flow rate in the 125°C experiment was about 13 ml/hr, corresponding to a mean residence time of ~7.7 hr in the column, and the flow rates in the other two experiments were ~30 ml/hr, corresponding to a mean residence time of ~3 hr. Each experiment involved the injection of a solution of 1,5 NDS and LiBr with the Li concentration approximately 9-10 mg/L. Starting immediately after injection, samples were collected at regular intervals in a fraction collector downstream of a back pressure regulator. Aqueous samples collected from the reactor were analyzed for NDS by fluorescence detection and Li by HPLC/conductivity detection.

At the conclusion of the above column experiments, it was apparent that lithium transport in the columns was highly temperature dependent and, in all cases, quite different from what would have been predicted from the room temperature batch experiments (see Results section). Thus, it was decided to conduct an additional 20 ml/hr Li column experiment at LANL at room temperature and pressure to determine whether column transport could be predicted reasonably well from the batch results obtained under the same conditions. This column experiment was conducted in the column still packed with the same mineral mix that was used in the high temperature experiments so that a direct comparison could be made to the high-temperature results. This experiment was then followed with a room temperature cesium transport experiment at 20 ml/hr in the same column to do the same evaluation for cesium.

2.5. Model Interpretations

To estimate transport parameters in the column experiments, the semi-analytical transport model RELAP, described in detail in Reimus et al (2003), Appendix A, was used to fit the 1,5 NDS breakthrough curves. The RELAP model simulates flow through either a single- or a dual-porosity medium by solving the 1-D advection dispersion equation. In the case of a dual-porosity system, 1-D diffusion is assumed to occur between the primary or flowing porosity (e.g., the fracture porosity in fractured media or a high-permeability layer in a porous medium) and adjacent secondary or nonflowing porosity (the porous matrix in fractured media or a low permeability layer in a porous medium). For the column experiments, a single-porosity system was assumed (all porosity was assumed to flow), and the only fitted parameters were the mean column residence time (τ) and the Peclet number (Pe), a dimensionless parameter given by the length of the column divided by the longitudinal dispersivity. These estimated parameters were then carried over to the computer model MULTRAN (Sullivan et al., 2003; Williams et al., 2013) to simulate the transport of the cation exchanging tracers. Cation transport was simulated by simultaneously solving the transport equations for the primary and secondary porosity, equations (1) and (2), respectively, using an implicit finite-difference method for all anionic and cationic species subject to the mass-action expressions in Equation (3), which represent the cation exchange reactions of Equation (4) (Gaines-Thomas convention (Gaines and Henry, 1955)).

257 Equation (1)

258 Transport in Primary Porosity: $R_f \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} - D_L \frac{\partial^2 C}{\partial x^2} - \frac{\phi}{b} D_m \frac{\partial C}{\partial y} \Big|_{y=b} + Rx = 0$

259 Equation (2)

260 Transport in Secondary Porosity: $R_m \frac{\partial C}{\partial t} - D_m \frac{\partial^2 C}{\partial y^2} + Rx = 0$, for $b < y < L$

261 Equation (3)

$$K_{Na/Cat} = \frac{[NaX][Cat^{i+}]^{1/i}}{[Na^+][CatX_i]^{1/i}}$$

262 Equation (4)

264

265 A Newton-Raphson iterative method was employed at each time step to solve equations (3) for

266 all cations while maintaining surface and solution charge balance according to Equations (5) and

267 (6); equations (3) and (5) effectively constitute the Rx terms in equations (1) and (2).

268

269 Equation (5)

270 Surface Charge Balance: $CEC = \frac{\phi}{\rho_B} \sum_{all\ cats} [CatX_i]$

271 Equation (6)

272 Solution Charge Balance: $\sum_{all\ cats} [Cat^{i+}] = \sum_{all\ A} [A^{i-}]$

273

274 Each time step involved a mass transport calculation followed by a reaction calculation (i.e.,
275 transport and reaction operator splitting), and solution accuracy was assured by decreasing the
276 time step size until there was no sensitivity observed in the model results. The temperature
277 dependence of tracer diffusion coefficients was accounted for using equation (7) (Perry and
278 Chilton, 1973).

279

280 Equation (7)

$$\frac{D_{T_2}}{D_{T_1}} = \frac{T_2 \mu_{T_1}}{T_1 \mu_{T_2}}$$

281

282 The temperature dependence of the viscosity of water in equation (7) was approximated using
283 equation (8) (Likhachev, 2003).

284

285 Equation (8)

$$\frac{\mu_{T_2}}{\mu_{T_1}} = \frac{10^{\frac{247.8}{T_1-240}}}{10^{\frac{247.8}{T_2-240}}}$$

286

287 Equations (1) and (2) are written for fractured media, with the primary porosity being parallel-
288 plate fractures with aperture 2b and the secondary porosity being the matrix surrounding the

fractures (the same equations are used in RELAP). However, these equations can be reduced to a single-porosity system by setting the matrix porosity in equation (3) equal to zero, or they can be used to simulate transport through a granular medium with porous grains (as a secondary porosity) by using a small domain size (small value of L in equation (2)) for the secondary porosity. In the latter case, we take advantage of the fact that the half-aperture of a parallel-plate fracture (b) is equivalent to the flowing pore volume divided by the flow-wetted surface area (Moreno and Neretnieks, 1993), which can be applied to any generalized flow geometry. The strategy for fitting the cation breakthrough curves was to initially assume a single-porosity system (which was found to be adequate to fit the conservative tracer breakthrough curves) and adjust the CEC and selectivity coefficients of the media grains to achieve a match to the data, using the experimentally measured CEC value as a rough constraint. However, it very quickly became apparent that it was necessary to assume dual-porosity behavior to fit the cation breakthrough curves, particularly at the higher temperatures. Because the media was nominally a granular system consisting of crushed and sieved mineral grains, the dual-porosity behavior was interpreted as being indicative of a thin boundary layer or “rim zone” on the grain surfaces into which the cations could diffuse and adsorb. Such a rim zone has been implicated in fractured media with very low porosity matrices (Andersson et al., 2002; Cvetkovic, 2010) and it seems logical that it should apply to granular media as well. The column modeling results are discussed in Section 3.2.

3. Results

3.1. Room Temperature Batch Experiments

The equilibrium partitioning of lithium and cesium between the mineral mix and the K- and N-waters at room temperature is shown in Figure 3a for lithium and Figure 3b for cesium. The Li data has poorly-defined trends, which is consistent with weak sorption that is partially obscured by analytical and experimental errors. A representative Li partition coefficient, or K_d value (the ratio of sorbed concentration in mg/g to solution concentration in mg/ml at equilibrium, or C^*/C_{equil}), was estimated for each water by averaging the partition coefficients associated with each data point of Figure 3a, resulting in an estimate of 0.22 ml/g for the K water and 0.13 ml/g for the N water. Statistical t-tests (Choi, 1978) indicated that these values could be considered different only at the 50% confidence level and that they could be considered distinguishable from zero only at the 90% confidence level.

Figure 3

Figure 3b shows that the Cs partitioning data have much tighter trends than the Li data and that Cs sorption appears to follow a Freundlich isotherm ($C^* = K_f * (C_{\text{equil}})^n$) (Langmuir, 1997), with both waters having essentially the same K_f value but with an exponent n of 0.51 for the N-water and 0.60 for the K-water. Given the large R^2 values of the power-law curve fits, the differences between the two Freundlich isotherms are statistically significant at virtually any confidence level, with Cs sorption being consistently stronger in the N-water than the K-water. This result suggests that potassium (K) competes with Cs for exchange sites more strongly than

magnesium (Mg) and calcium (Ca) (Barrer and Munday, 1971; Carroll et al., 2001; Appelo and Postma, 2005).

The black squares and lines in Figures 3a and 3b show the Li and Cs partitioning predicted using the cation exchange parameters that provided good matches to the room temperature column experimental data using the MULTRAN transport model, discussed in the next section. The cation exchange model provides reasonable matches to the batch sorption data. However, the Freundlich isotherm behavior of the Cs is not well reproduced in Figure 3b. This result can probably be attributed to the fact that the room temperature column experiments were conducted after the column had been tested at elevated temperatures, so the mineral assemblage was likely altered and behaved differently than in the batch experiments, which used minerals that had not been exposed to high temperature hydrothermal conditions.

The Li and Cs K_d values, averaged over each experiment on the individual minerals using the N-water, are shown in Figure 4a and 4b, respectively, along with the surface area and CEC measurements. Note that the y-axis for Cs in Figure 4b has a logarithmic scale to better capture the wide range of Cs K_d values. Although Cs partitioning clearly followed Freundlich isotherm behavior for the mineral mix (Figure 3b), this behavior was not observed for all the individual minerals. Thus, to allow a consistent comparison across all minerals and between Li and Cs, the K_d values in Figures 4a and 4b were calculated as simple averages of the values associated with each measurement for each mineral.

Figure 4

352

353 It is apparent in Figures 4a and 4b that for both Li and Cs, chlorite has the largest K_d values, CEC
354 and specific surface area of all the minerals contained in the mix, followed by albite, epidote,
355 calcite and quartz. It is noteworthy that the K_d values for Li in Figure 4a are more uniform
356 between the different minerals than the K_d values for Cs in Figure 4b, which suggests that Li
357 may be a better cation for estimating overall surface area. Cs tends to adsorb much more
358 preferentially to chlorite, thus making it much more sensitive to minor variations in chlorite
359 than Li. However, the Li adsorption results are more uncertain than Cs because of the low
360 levels of adsorption of Li to all the minerals, and this uncertainty may be masking a similar
361 dependence of Li sorption to the different minerals as Cs. Similarities between Li and Cs might
362 also be expected to increase at higher temperatures where Li adsorption was comparable to or
363 greater than Cs in column transport experiments (Section 3.2).

364

365 One of the objectives of this study was to evaluate batch sorption as a method of estimating
366 cation retardation factors under flowing, geothermal conditions. To simplify this process, the
367 average cation partition coefficients in the batch experiments were used as K_d values (partition
368 coefficients that do not vary with concentration) in equation (9) to estimate retardation factors
369 for lithium and cesium in the column experiments. We recognize that this is an approximation
370 given the nonlinearity of the isotherms of Figure 3, but it serves as a reasonable starting point
371 for an evaluation.

372

Equation (9)

$$R = 1 + \frac{\rho_B}{\phi} K_d$$

The average batch K_d values of Li and Cs on the mix in the K-water were used in equation (9) because the K-water was used in all the column experiments. The average Li K_d value was 0.22 ml/g (Standard Deviation = .13 mg/L), and the average Cs K_d value was 5.2 ml/g, although the average Cs K_d value for the two higher starting concentrations in the batch experiments was 3.1 ml/g, which is considered to be more representative of the columns because of the higher Cs injection concentrations in the column experiments.

3.2. Column Transport Experiments

Figure 5 shows the breakthrough curves of Li relative to NDS in each of the higher temperature column experiments involving Li. The normalized NDS breakthrough in Figures 5a, 5b and 5c for the EGI intermediate temperature column experiments are consistent, indicating that the flow properties of the column did not change significantly between runs. As the temperature was increased, the Li breakthrough became more delayed relative to the NDS and the Li peak concentration was lower. The tracer breakthrough curves in the higher temperature experiments performed at LANL are shown in Figures 5d and 5e. It is apparent that the LANL experiments were performed with much smaller tracer injection pulse volumes relative to the column volume than the EGI experiments. The Li breaks through at approximately the same

time in the two LANL experiments, and the peak normalized concentration is lower in the higher temperature experiment. The decrease in Li recovery at higher temperatures in both the EGI and LANL experiments and the fact that recoveries are much lower in the higher temperature LANL experiments indicates a strong temperature dependence of Li cation exchange.

Figure 5

The NDS model curves shown in Figure 5 were generated by RELAP and the Li model curves by MULTRAN. The RELAP and MULTRAN parameters used to generate the model curves are listed in Table 5. The NDS curves represent least-squares fit to the data in each individual experiment, whereas the Li curves reflect a qualitative compromise to achieve reasonable fits to the data at each temperature by adjusting only the selectivity coefficient, $K_{Na/Li}$, as a function of temperature while keeping all other cation exchange parameters constant across all experiments. As stated previously, despite the fact that a single-porosity fit to the NDS breakthrough curves provided an adequate match to the data, it was necessary to assume dual-porosity behavior in the columns to achieve a reasonable match to the higher temperature Li data. This same observation was made in high-temperature column experiments using crushed material from the former Fenton Hill EGS site (Dean et al., 2012), so dual-porosity behavior at high temperatures is not unique to the Newberry mineral system. Single-porosity models consistently over-predicted the peak Li concentration when the peak timing was matched or

predicted much later breakthroughs when the peak concentration was matched; it was possible to match both observations only with a dual-porosity model. However, one of the constraints of the dual-porosity model was that the model parameters had to be such that the predicted NDS transport behavior was basically unchanged from the single-porosity RELAP fits. This constraint requires that the volume of the secondary porosity be only a small fraction of the primary (flowing) porosity volume and that the length scale for diffusion into the secondary porosity (L) be relatively short.

Table 5

The dual-porosity parameters of Table 5 imply a low-porosity diffusive/sorptive boundary layer extending a short distance into the grains that provides considerable cation exchange capacity. The value of b in Table 5 is small for a fractured system, but it is believed to be a reasonable estimate of the volume to surface area ratio in the column experiments (see Section 4, Discussion and Conclusions). For a given set of cation exchange parameters, the model results are sensitive primarily to the ratio b/L and to the value of $\sqrt{\tau D_m}/L$, so if b and L are both changed but these ratios are preserved, the predicted results will be the same (this was verified with MULTRAN simulations). The rim zone thickness and porosity might be better constrained by detailed microscopic examinations of the grain surfaces, and the CEC values might be better

constrained if rim zone material were isolated for CEC measurements, but these activities were beyond the scope of this study.

It should be emphasized that the parameters of Table 5 are not a unique or optimized set of values; no attempt was made to evaluate the uniqueness or sensitivity of the model curves to the parameters. Given the number of parameters involved, and the fact that there were five Li data sets to simultaneously fit, such an exercise would be quite involved and was considered beyond the scope of this paper. The model curves of Figure 5 match the data sets remarkably well, especially considering that the only adjustable parameter was the selectivity coefficient for Li exchange with Na, ($K_{Na/Li}$ in equation (3)). In reality, all of the selectivity coefficients for the different cations exchanging with Na ($K_{Na/C}$ in equation (3)) would be expected to have a temperature dependence (Gaines 1955; Kraus and Raridon 1959), but because we were concerned only with Li transport behavior, we allowed only $K_{Na/Li}$ to be adjusted. The remaining cations were assigned selectivity coefficients in accordance with the values reported in Appelo and Postma (2005), which are for a typical soil matrix at 25°C ($K_{Na/Ca} = 0.4$, $K_{Na/Mg} = 0.5$, $K_{Na/K} = 0.2$). Each of the experiments involved analyzing the column effluent solutions for all of the major cations (Na, K, Ca, Mg) in addition to Li, so data are available to make simultaneous adjustments to all the selectivity coefficients to capture the exchange behavior of all the cations if this is desired for model refinement. However, by capturing the Li behavior, we achieved the necessary objectives for interpreting single-well tracer tests at Newberry crater.

The magnitude of the deduced temperature dependence of $K_{Na/Li}$ (Table 5) was somewhat surprising and is tentatively attributed to a decrease in the number of waters of hydration associated with Li^+ ion in aqueous solution as temperatures increase (Egorov et al., 2003). Being the monovalent cation with the highest charge density because of its small ionic size, Li^+ is known to be more hydrated (i.e., has more water molecules strongly associated with it) than other monovalent cations at low to moderate temperatures, which effectively increases its size and decreases its reactivity and diffusivity relative to the other monovalent cations. However, as temperatures increase, thermal energy causes the waters of hydration to be disrupted, giving Li^+ a smaller hydrodynamic radius and making it more reactive and more diffusive. We believe that this behavior is being reflected in the observed temperature dependence of $K_{Na/Li}$. Figure 6 gives a practical appreciation for the temperature dependence of the Li cation exchange behavior. In this figure, the model curves for the two highest temperature experiments, conducted at LANL, are plotted along with hypothetical curves for the three lower-temperature experiments, conducted at EGI. The latter three curves were calculated using the experimentally-observed Li cation-exchange parameters while assuming the column parameters and injection pulse volumes in the LANL experiments. A sixth curve is also shown in Figure 6 in which the Li transport behavior at room temperature (25°C) is predicted in the LANL column using the room-temperature batch experimental data. It is clear from this figure that Li transport at room temperature or even at moderate temperatures is significantly different than Li transport observed at the highest temperatures, which fall within the temperature range expected at Newberry crater.

Figure 6

Figure 7 shows the results of the Cs transport experiment conducted at 225°C in the same column used to conduct the LANL Li transport experiments. The breakthrough curve of Li at 225°C is also shown in Figure 7. Although it is well known that Cs exchanges much more strongly with most minerals than Li at low temperatures (as verified by the batch sorption data, Section 3.1), Cs is actually more weakly attenuated than Li in the column at 225°C. The parameters used to obtain the MULTRAN Cs model curve shown in Figure 7 were the same as those used for the Li model curve at the same temperature except that the CEC value on the grain surfaces was increased from 0.0011 to 0.0025 eq/kg and the CEC value in the rim zone was increased from 0.046 to 0.056 eq/kg. The Cs selectivity coefficient ($K_{Na/Cs}$) was assumed to be 0.15, which is somewhat larger than literature values at lower temperatures (Appelo and Postma, 2005).

Figure 7

As with the Li modeling, the Cs model results should not be considered unique or optimized fits to the Cs data. However, it is encouraging that qualitative matches between the model and experimental data were obtained using model parameters very similar to those used to simulate the Li experiments. The increases in the CEC values on the grain surfaces and in the

rim zone were modest adjustments that are reasonable in light of the mineral alteration that likely occurred in the column at 275°C in the Li experiment immediately preceding the Cs experiment and also considering that larger CEC values were measured for Cs than for Li in the batch experiments.

The increase in the Cs concentration at around 80 hours into the Cs column experiment (Figure 7) was caused by an inadvertent increase in the ionic strength of the injection solution into the column at that time. This increase was the result of adding NaOH to a newly-prepared batch of synthetic K-substituted groundwater to raise its pH to match that of the previously-prepared batches. This adjustment increased the concentration of Na in the water enough to promote desorption of Cs (due to increased competition for cation exchange sites from Na), an effect that was captured by the MULTAN model. Thus, although unintended, the introduction of extra Na provided an additional test of the robustness of the MULTRAN model.

Although not originally planned, the dramatic temperature dependence of Li transport observed in the column experiments prompted an additional Li column experiment at LANL to evaluate low-temperature transport in the same column used for the high-temperature experiments. An additional Cs experiment was also conducted in this column at room temperature. Both experiments were conducted with the K-substituted water at 20 ml/hr to be consistent with the higher-temperature experiments.

Figures 8a and 8b show the Li and Cs breakthrough curves, respectively, in the room-temperature column experiments along with the corresponding NDS breakthrough curves. These figures also include a NDS breakthrough curve from one of the higher temperature experiments (all the high-temperature NDS breakthrough curves were very similar). It is apparent that there was a significant increase in the column residence time and decrease in dispersion at room temperature despite the fact that all experiments were conducted at approximately the same flow rate. This residence time increase reflects a significant increase in column porosity (from approximately 0.4 to 0.63), which we believe was caused by partial dissolution of silicates at the higher temperatures (increased silicon concentrations were observed in the column effluent of the high temperature experiments) as well as some calcite dissolution that occurred as the reactor was cooled and flushed with K-water, which is significantly undersaturated with respect to calcite at lower temperatures.

Figure 8

Figures 8a and 8b also show RELAP and MULTRAN model curves for Li and Cs, with the RELAP curves being single-porosity fits to the data obtained by adjusting the Li or Cs retardation factor and the MULTRAN curves being dual-porosity fits using the parameters of Table 5 but allowing the value of $K_{Na/Li}$ or $K_{Na/Cs}$ to be adjusted for the lower temperature. The retardation factors obtained with RELAP were 1.19 and 8 for Li and Cs, respectively, which correspond to K_d values of 0.12 ml/g for Li and 4.5 ml/g for Cs. The column retardation factors estimated from the

room temperature batch sorption experiments with the K-substituted water, as calculated from equation (9) using the increased porosity in the room temperature column experiments, were 1.34 and 5.8 for Li and Cs, respectively, (the retardation factors prior to the increase in porosity would have been 1.87 and 13.3, respectively). The agreement between the fitted retardation factors and the retardation factors predicted from the batch sorption experimental data is reasonably good, especially considering the uncertainty in the batch K_d values for Li and the mineral alteration that likely occurred in the columns at the higher temperatures before the room-temperature experiments were run. The MULTRAN curves in Figures 8a and 8b were generated using a $K_{Na/Li}$ value of 1.1 and a $K_{Na/Cs}$ value of 0.03. These values were used, along with the other cation exchange parameters of Table 5, to generate the predicted batch partitioning curves of Figures 3a and 3b, which match the observed batch data reasonably well.

4. Discussion and Conclusions

The results of this study underscore the importance of evaluating tracer transport behavior at target geothermal system temperatures rather than relying on laboratory data obtained at lower temperatures. The room temperature experiments on the individual minerals and the mineral assemblage significantly under-predicted lithium cation exchange and slightly overpredicted cesium cation exchange in column transport experiments conducted under simulated reservoir conditions. Also, the relative retardation of lithium and cesium in the high-temperature column experiments was unexpected in that the retardation of lithium was greater than that of cesium despite the fact that cesium is much more strongly retarded than

lithium at lower temperatures. We hypothesize that the change in hydration characteristics of lithium ion as a function of temperature were responsible for the dramatic differences seen in lithium transport behavior over the range of temperatures studied.

Another unexpected result of this study was that the transport behavior of both lithium and cesium at high temperatures exhibited dual-porosity behavior despite the fact that the laboratory columns were set up as single-porosity flow systems (i.e., classical granular porous media). Single-porosity transport behavior of the cations was in fact observed in the room temperature column experiments, as demonstrated by the good prediction of the column breakthrough curves using the room-temperature batch results in a single-porosity model. The dual-porosity transport behavior at higher temperatures is tentatively attributed to the temperature dependence of tracer diffusion coefficients coupled with a low-porosity, high-tortuosity, and strongly adsorbing rim zone on the grain surfaces. At low temperatures, tracer diffusion occurs only very slowly into this rim zone, so the secondary porosity has only a minor impact on the tracer breakthrough curves, resulting in what appears to be single-porosity behavior. However, at higher temperatures, tracer diffusion occurs more rapidly into the rim zone, so the secondary porosity plays a greater role in transport, and dual-porosity behavior is observed.

As mentioned previously, the model matches to the cation breakthrough curves in the column experiments should not be considered unique or optimized fits to the data. The CEC values and

selectivity coefficients can be adjusted in tandem (decreasing or increasing both of them at the same time) to yield similar results for a given cation. There are similar correlations between other model parameters (e.g., the aforementioned simultaneous adjustments of b , L and D_m that can yield the same results). Also, it was observed that the model results were quite sensitive to different assumed initial cation distributions on exchange sites in the columns, which likely varied in the experiments because of the sequential injections of tracer solutions in the same columns and the different periods of flushing between experiments. We assumed the same initial cation distribution in all experiments (consistent with equilibrium partitioning to the K-water).

Our goal was to explain the data sets obtained at different temperatures with as few adjustable parameters as possible, and we accomplished this by matching all the lithium data sets quite well by adjusting only the value of $K_{Na/Li}$ as a function of temperature and by matching the cesium data by adjusting only $K_{Na/Cs}$ with temperature and decreasing the rim-zone porosity slightly from what was assumed for lithium. The value of $K_{Na/Li}$ varied over a range of a factor of 14 between 25°C and 225°C and a factor of 22 between 25°C and 275°C (with smaller values at higher temperatures), while the value of $K_{Na/Cs}$ varied by less than a factor of 4 between 25°C and 225°C (larger values at higher temperatures). Thus, lithium cation exchange had a greater temperature dependence than cesium cation exchange, although the cesium dependence was based on experiments conducted at only two temperatures. We did not attempt to adjust the values of the selectivity coefficients of the other cations as a function of temperature, which

would have had an effect on the deduced temperature dependence of both $K_{Na/Li}$ and $K_{Na/Cs}$. The model-deduced values of $K_{Na/Li}$ and $K_{Na/Cs}$ in all of the column experiments, including the room-temperature experiments, are plotted as a function of temperature in Figure 9. Note that the temperature dependence of $K_{Na/Li}$ largely disappears as temperatures decrease below 125°C, which may indicate that the disruption of the waters of hydration surrounding Li^+ does not occur until temperatures exceed 100-125°C.

Figure 9

It must be emphasized that the BET surface areas measured in this study represent a significant overestimation of the surface area available for heat transfer, or the flow-wetted surface area, which is the surface area of interest for evaluating reservoir stimulations. The difference between the two surface areas is depicted schematically for a fractured system in Figure 10, where the BET surface area is referred to as the sorption surface area because it is also presumably the surface area that cationic tracers will interrogate. Because thermal diffusion is rapid (three to five orders of magnitude faster than mass diffusion), heat transfer is blind to small-scale fracture surface roughness features, and the interfacial area across which heat is transferred from the hot rock to the flowing water is thus defined by the interface between flowing water and either stagnant water along the rock walls or the rock walls themselves (the flow-wetted surface area in Figure 10). However, the interfacial area interrogated by cations is

all of the rock surface area accessible by tracers (the red surface in the lower diagram of Figure 10). The flow-wetted surface area to volume ratio in flowing fractures is given by $1/b$.

Figure 10

In principle, there should be a proportionality between the BET or tracer surface area and the flow-wetted or heat transfer surface area in a given system, although this proportionality may vary from mineral to mineral and from system to system. The equivalent heat transfer surface area in the column experiments of this study is given by the geometric surface area of the grains used to pack the columns, and the equivalent value of b in the columns is the total pore volume of the columns divided by the total geometric surface area of the grains. Based on the sieve size range of the material used to pack the columns (250-500 μm) and assuming an average mineral density of 2.65 g/cm^3 , the geometric surface area to mass ratio of the column grains can be bounded at about $0.0045 \text{ m}^2/\text{g}$ to $0.009 \text{ m}^2/\text{g}$ (assuming both rectangular and spherical shaped grains), which is a factor of about 15 to 60 less than the BET surface area of the mineral mix, depending whether one uses the measured BET surface area of $0.14 \text{ m}^2/\text{g}$ or the calculated fractional surface area of $0.28 \text{ m}^2/\text{g}$. Using $0.0045 \text{ m}^2/\text{g}$ to $0.009 \text{ m}^2/\text{g}$ as the geometric surface area to mass ratio of the grains, the surface area to fluid volume ratio in the columns is calculated to fall within the range of 180 to 360 cm^{-1} , which is equivalent to a b value ranging from 0.0028 to 0.0056 cm . The b value assumed in the modeling described in Section 3.2 was 0.005 cm , which falls within this range.

Knowledge of the ratio of flow-wetted surface area to BET surface area would be crucial for estimating heat transfer surface area in a single-porosity fracture system (i.e., a fracture system in which there is little or no tracer diffusion into the fracture walls) because in this case tracers will interact with the BET surface area (or some substantial fraction of this surface area), which will have to be adjusted downward (using the ratio) to obtain an estimate of heat transfer surface area. However, in this study we observed dual-porosity behavior in the column experiments at high temperatures, and similar dual-porosity behavior can be expected in a fractured field reservoir at high temperatures.

The key to estimating the heat transfer surface area in a dual-porosity system will be to use reasonable estimates of rim-zone properties in the interpretive model so that reasonable estimates of b can be obtained. It was previously pointed out that dual-porosity model results are sensitive to b/L and $\sqrt{\tau D_m}/L$, so if the values of the rim-zone parameters L and D_m are poorly constrained, it will be impossible to obtain well-constrained estimates of b . As a first approximation, we suggest using the values of L and D_m listed in Table 5 for field test interpretations at Newberry Crater, but these values should be considered lower bounds because we expect them to be larger for fracture surfaces in a reservoir than for the individual grains used in the laboratory experiments. We also suggest using the cation exchange parameters of Table 5 as a first approximation, although it is important to recognize that these parameters may be different in the field because the actual Newberry mineral assemblage on

fracture surfaces may not be exactly the same as the assemblage used in this study (particularly the relative proportions of each mineral phase). Because the properties of the rim zone are so important for translating cation transport behavior into fracture surface area estimates, future work on the use of cations to estimate fracture surface area should include more detailed examination of both the physical and chemical characteristics of the rim zone, which are likely to be system specific. Given that both the physical and chemical differences between the field and laboratory systems will be very difficult to quantify, the field experiment interpretations will necessarily have uncertainties associated with them, and these uncertainties should be addressed by conducting model sensitivity studies to estimate uncertainty bounds for the critical parameter b . Note that in single-well tracer tests, the volume of injected tracer solution plus any “chase” water will be known, as will the volume of water that is flowed back, so the volume portion of b , the volume to geometric surface area ratio, should be known reasonably well.

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741

742 **List of Symbols:**

743 $C = \text{tracer or solute concentration, } \frac{\text{mol}}{L} \text{ or } \frac{\text{mg}}{L}$

744 $x = \text{distance in flow direction, cm}$

745 $y = \text{distance in matrix or secondary porosity perpendicular to flow, cm}$

746 $t = \text{time, sec or hr}$

747 $v = \text{flow velocity, } \frac{\text{cm}}{\text{sec}}$

748 $D_L = \text{longitudinal dispersion coefficient, } \frac{\text{cm}^2}{\text{sec}}$

749 $D_m = \text{matrix diffusion coefficient, } \frac{\text{cm}^2}{\text{sec}}$

750 $b = \text{fracture half aperture, cm}$

$\phi = \text{matrix porosity}$

751 $L = \text{diffusion distance into matrix or grains, cm}$

752 $Rx = \text{generic reaction}$

$K_d = \text{partition or distribution coefficient, } \frac{\text{ml}}{\text{g}}$

$R = \text{retardation factor}$

753 $R_f = \text{retardation factor in fractures or primary porosity}$

$R_m = \text{retardation factor in matrix or secondary porosity}$

754 $T = \text{temperature, degrees C or K}$

755 $D_{T_x} = \text{diffusion coefficient at temperature } T_x, \frac{\text{cm}^2}{\text{sec}}$

756 $\mu = \text{viscosity, } \frac{\text{g}}{\text{cm-sec}}$

- 757 $\mu_{T_x} = \text{viscosity at temperature } T_x, \frac{g}{cm-sec}$
- 758 $X = \text{generic cation exchange site with charge of } -1$
- 759 $i = \text{absolute value of charge on cation or anion}$
- 760 $Cat^{i+} = \text{generic cation with charge of } +i$
- 761 $A^{i-} = \text{generic anion with charge of } -i$
- 762 $CatX_i = \text{cation exchange site occupied by generic cation of charge } +i$
- 763 $\tau = \text{mean residence time, sec or hr}$
- 764 $Pe = \text{Peclet number} = \text{transport distance divided by longitudinal dispersivity}$

Table 1: Material Properties

Mineral	Chemical Formula	Added Mineral Mass Fraction in Mix	Meas'd Specific SA ² (m ² /g)	Calc'd Fractional Specific SA (m ² /g)	Measured		Calculated Fractional	
					Li CEC (meq/Kg)	Cs CEC (meq/Kg)	Li CEC (meq/Kg)	Cs CEC (meq/Kg)
Albite	NaAlSi ₃ O ₈	0.21	0.12	0.0252	6.46	6.41	1.36	1.35
Calcite	CaCO ₃	0.21	0.02	0.0042	1.56	1.60	0.33	0.34
Chlorite	(Mg,Fe ²⁺) ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	0.21	1.17	0.2457	7.16	13.62	1.50	2.86
Epidote	Ca ₂ (Fe ³⁺ ,Al) ₃ (SiO ₄) ₃ (OH)	0.18	0.02	0.0036	1.69	0.95	0.30	0.17
Quartz	SiO ₂	0.21	0.02	0.0042	1.21	1.02	0.25	0.21
Mix	---	---	0.14	0.2829	4.29	4.53	3.75	4.93

Table 2: QXRD-determined mineral fractions and fractionally calculated mineral properties

Mineral	QXRD Mineral Fraction in Mix	Fractional Specific SA (m ² /g)	Fractional	
			Li CEC (meq/Kg)	Cs CEC (meq/Kg)
Albite	0.40	0.048	2.58	2.56
Calcite	0.20	0.004	0.31	0.32
Chlorite	0.09	0.1053	0.65	1.23
Epidote	0.02	0.0004	0.03	0.02
Quartz	0.29	0.0058	0.35	0.30
Mix	---	0.1635	3.93	4.42

Table 3: Synthetic water recipes

Newberry Crater Synthetic Water (N)		K-Substituted Synthetic Water (K)	
Chemical	(mg/L)	Chemical	(mg/L)
MgSO ₄	3.13	K ₂ SO ₄	4.53
CaCl ₂	5.55	KCl	7.46
KHCO ₃	13.01	KHCO ₃	13.01
Mg(HCO ₃) ₂	146.74	KHCO ₃	200.80
Ca(HCO ₃) ₂	68.72	KHCO ₃	84.89
NaHCO ₃	160.75	NaHCO ₃	160.75
H ₄ SiO ₄	96.00	H ₄ SiO ₄	96.00
pH	8.01	pH	8.01

Table 4: Column Transport Experiments at Elevated Temperatures

Column Experiment	Flow Rate (ml/hr)	Tracer Pulse Duration (hr)	Temperature °C	Tracers	Concentration of Li or Cs (M)
1	12.9	22	125	LiCl+NDS	0.00145
2	30.3	8.5	150	LiCl+NDS	0.00145
3	31.5	7	175	LiCl+NDS	0.00145
4	20	2.5	225	LiBr+LiCl+NDS	0.00145
5	20	2.5	275	LiBr+LiCl+NDS	0.00145
6	20	2.5	225	CsBr+NDS	0.0013

Table 5: RELAP (τ and Pe) and MULTRAN Column Transport Parameters for model curves of Figures 5 and 7 (Elevated Temperature Experiments).

Column- or Experiment-Independent Parameters	
Half-Aperture (Volume to Surface Area Ratio)	0.005 cm
Column Porosity	0.4 (40%)
CEC on Grain Surfaces for Li experiments	0.0011 eq/kg
CEC on Grain Surfaces for Cs experiment	0.0025 eq/kg
Thickness of "Rim Zone" Layer on Grains	0.004 cm
Porosity in Rim Zone	0.0022
Cation Exchange Capacity in Rim Zone for Li	0.046 eq/kg
Cation Exchange Capacity in Rim Zone for Cs	0.056 eq/kg
Tracer Diffusion Coefficients in Rim Zone at 25°C (adjusted using equations 7 and 8 for higher temperatures)	$8 \times 10^{-10} \text{ cm}^2/\text{s}$ for bromide $2 \times 10^{-10} \text{ cm}^2/\text{s}$ for NDS $5.4 \times 10^{-10} \text{ cm}^2/\text{s}$ for Li $6.4 \times 10^{-10} \text{ cm}^2/\text{s}$ for Cs
Rock and Water Properties (density and thermal)	Corresponding to Quartz or Basalt and Dilute Water

Column- or Experiment-Dependent Parameters			
Column Experiment	Res. Time (hr)	Pe	$K_{Na/Li}$
1	7.7	71	1.0
2	3.1	100	0.63
3	3.0	120	0.4
4	10.5	7	0.08
5	10.5	7	0.05
6	10.5	7	0.15*

* $K_{Na/Cs}$ for Experiment 6.

Figure 1: PHREEQC geochemical modeling of calcite and magnesite saturation index as a function of temperature for the Newberry Crater stimulation water. A saturation index greater than one indicates that the mineral will precipitate.

Figure 2: Simplified schematic of LANL experimental apparatus used for 225°C and 275°C experiments.

Figure 3: Log-log plots of batch experiment results of (a) Li and (b) Cs sorption onto mineral mix in N- and K-waters at starting concentrations of ~1ppm, ~5ppm and ~25ppm. Black points/lines are predictions using MULTRAN cation exchange model with parameters that provided good matches to the column experimental data. Results of Freundlich isotherm fits to Cs data are shown in (b).

Figure 4: Average Li (a) and Cs (b) K_d values on each of the minerals in the Newberry mix with the synthetic N water. Specific surface areas and CEC values are also shown for each mineral. Note the change to log scale in Figure b.

Figure 5: Experimental data and RELAP/MULTRAN modeling for Li column transport at (a) 125°C, (b) 150°C, (c) 175°C, (d) 225°C, and (e) 275°C. Note the change to a log concentration scale in figures d and e. Model parameters are listed in Table 5.

Figure 6: Simulated Li breakthrough curves at different temperatures using the cation exchange parameters of Table 5 and assuming a mean residence time of 10.5 hrs, a Peclet number of 7, a tracer pulse duration of 2.5 hrs, and a column pore volume of 215 ml, corresponding to the LANL columns. The 25°C curve was generated using the average K_d value from Li/mix/K-water batch experiments.

Figure 7: Experimental data and RELAP/MULTRAN modeling for Cs column transport at 225°C. Li data and model at 225°C are also shown. Model parameters are listed in Table 5.

Figure 8. Experimental data and RELAP/MULTRAN modeling for Li (a) and Cs (b) column transport at 25°C (room temperature). NDS breakthrough curve at 225°C is also shown in each plot to illustrate how dramatically the transport characteristics of the column changed after lowering the column temperature. Model parameters are listed in the legends and discussed in the text. The mean residence time in (a) was 16.5 hrs, and the Peclet number was 80.

Figure 9: Li and Cs selectivity coefficients as a function of temperature used to model cation transport in the column experiments.

Figure 10. Schematic showing the difference between flow-wetted surface area available for heat transfer and BET surface area.