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EVALUATION OF A CATION EXCHANGING TRACER TO INTERROGATE FRACTURE SURFACE AREA IN EGS SYSTEMS

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ABSTRACT

Laboratory tracer experiments were conducted to evaluate the potential use of lithium ion as a cation-exchanging tracer to interrogate relative changes in fracture surface area in EGS reservoirs. Tracer experiments were conducted at two different temperatures (225C and 300C) in high-pressure columns packed with crushed amphibolite schist from Fenton Hill, NM using a synthetic brine solution as the working fluid. Lithium transport through the columns was compared to that of bromide and 1,5 naphthalenedisulfonate (two conservative tracers with diffusion coefficients that vary by a factor of 3-4) to extract surface area estimates. Lithium as a tracer has the advantages that it does not thermally decay, and it adsorbs weakly according to a simple reversible process (cation-exchange), which simplifies test interpretations. The use of lithium as a tracer may be very well suited to single-well tracer tests where return concentrations are much higher than in interwell tests (thus avoiding limitations imposed by lithium background concentrations in reservoir water), and it could be especially useful for interrogating additional surface area created by a stimulation procedure. Information on additional surface area could in principle be deduced from relative lithium responses before and after stimulation without having detailed knowledge of lithium sorption behavior onto fracture surfaces (which would be required to obtain absolute estimates of surface area). Cesium ion is discussed as a potential alternative to lithium that would have lower background concentrations and stronger sorption behavior, making it more suitable to interrogating systems with low surface-area-to-volume ratios.

INTRODUCTION

The use of tracers in geothermal applications was first suggested by model simulations by Los Alamos National Laboratory during the Fenton Hill Hot Dry Rock geothermal project (Robinson et al., 1988). LANL has subsequently used adsorbing tracers and conservative tracers with different diffusion coefficients to estimate surface area-to-volume (SA/V) ratios and distinguish between matrix and free water diffusion in fractured rock groundwater systems (Reimus and Callahan, 2007; Reimus et al., 2003). The lithium ion has been used as a surrogate for radionuclides species in both laboratory and field scale reactive transport experiments (Anghel et al., 2002; Reimus et al., 2003; Sullivan et al., 2003a; Sullivan et al., 2003b). Several characteristics make lithium an ideal tracer; it is weakly sorbing, non-toxic, inexpensive and lithium has a relatively low background concentration in most rock-water systems. Additionally, lithium's thermal stability makes it appropriate for use in geothermal systems. Additional motivation came from the work of Andersson et al. (2002) in Figure 1, which is a set of breakthrough curves from a granite field system with a matrix porosity of ~1%, very relevant to EGS. The results of this field experiment, which was intended to evaluate radionuclide transport in a Swedish granite waste repository, clearly show that interpretable breakthrough curves can be obtained in an EGS-like system for many cation-exchanging tracers. In this paper, we present the preliminary results of experiments designed to evaluate the potential use of lithium as a cation exchanging tracer to interrogate relative changes in surface area in single-phase aqueous geothermal systems under varying flow and temperature conditions.

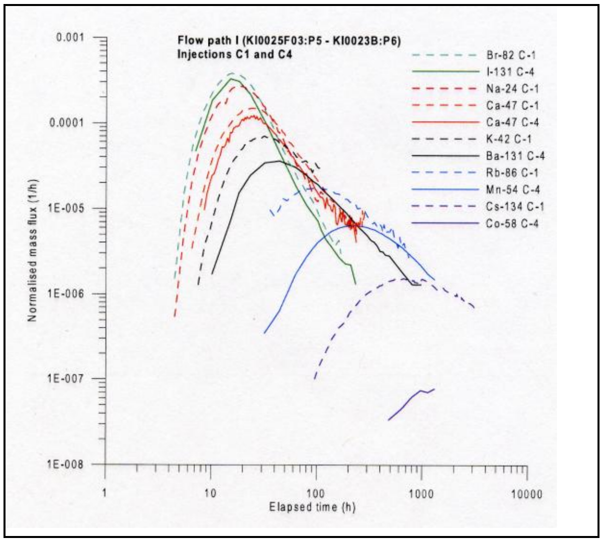

Figure 1: Breakthrough curves of several cations relative to conservative tracers (Br and I) in fractured Swedish granite. (Taken from Andersson et al., 2002, Fig. 6-11).

Cation-exchange is a simple, reversible process by which an exchanger exchanges with other cations present in the host rock. Lithium is a monovalent cation tracer that exchanges with both monovalent and divalent cations by the following reactions:

Cation-exchange reactions:

$$A + BX \rightarrow AX + B \qquad (1a)$$

$$2A + CX_2 \rightarrow 2AX + C \qquad (1b)$$

$$2B + CX_2 \rightarrow 2BX + C \qquad (1c)$$

Where A (in this case lithium) and B are monovalent cations and C is a divalent cation and X is a negatively charged surface site. In Sullivan et al. (2003a) the linearized Freundlich isotherms (K_{lin}) for lithium in volcanic tuff samples with varying mineralogy was found to be positively correlated to surface area, albeit the percent clinoptilolite in the material was found to be a better predictor of K_{lin}. Nevertheless, comparing relative differences in lithium breakthrough before and after reservoir stimulation (and assuming reservoir flow and mineral properties are heterogeneous) can provide evidence of an increase in fracture surface area with little knowledge of the tracer sorption properties or Cation-Exchange Capacity of the host rock.

Cation exchanging tracers have advantages over diffusive tracers because they do not rely on matrix diffusion processes. This allows for surface area estimates in host rocks with low matrix porosities where little dependence on diffusion coefficients is observed in tracer breakthrough. In systems with significant matrix diffusion the use of tracers that react in various ways with the host rock (such as lithium) has the effect of enhancing the diffusion coefficient of that tracer by a factor equal to its partition coefficient (Williams et al., 2010):

$$\text{nonreactive tracer: } \frac{\phi}{b}\sqrt{D_m} \qquad (2a)$$

$$\text{reactive tracer: } \frac{\phi}{b}\sqrt{D_m R_m} \qquad (2b)$$

Where b is the volume to surface area ratio (SA/V), D_m is the matrix diffusion coefficient and R_m is the tracer partition coefficient.

We also summarize in this paper the use of the Multicomponent Transport (MULTRAN) computer model (Sullivan et al., 2003b) to predict breakthrough concentrations of diffusive and reactive tracers in a single-well test to interrogate surface area. The same model is used to fit the experimental data.

EXPERIMENTAL METHODS

The lithium tracer experiments were conducted at Los Alamos National Laboratory in a specially designed high-pressure high-temperature flow through system that simulates reservoir conditions. A titanium pressure vessel (approximate volume of 500 ml) was filled with crushed amphibolite schist (1-2 mm) from Fenton Hill, NM using a synthetic brine solution as the working fluid. The pressure vessel was inserted into a resistance-heated furnace to provide temperature control. Figure 2 is a simplified schematic of the experimental apparatus. Three experiments were conducted with a 10 mg/L lithium, bromide and 1,5 naphthalenedisulfonate (NDS) solution (tracer solution) in a synthetic geothermal brine, two at 225C and 20 ml/hr (1st experiment) and 10 ml/hr (2nd experiment) and at 300C and 20 ml/hr (3rd experiment), all in the same vessel with the same material. The synthetic brine recipe and amphibolite schist composition (by Quantitative X-ray Diffraction, QXRD) are listed in Tables 1 and 2, respectively.

The vessel was filled with the amphibolite schist material and sealed. The material was saturated by applying vacuum at the outlet side of the vessel while injecting CO_2 into the inlet side and subsequently flowing the brine solution through the vessel. The approximate pore volume of 221 ml was calculated by subtracting the volume of material from the total volume of the vessel. The experiment was slowly heated to 225C and pressurized to 1500 PSI (pressure was maintained above the boiling point of the aqueous phase during heating) and allowed to equilibrate for several days. The tracer was loaded into a sample loop attached to a valve that would allow for approximately 50 ml of tracer to be pulse injected into the system without flow interruption. Immediately after injection samples were collected at regular intervals in a fraction collector through a back pressure regulator.

After approximately 9 months at 225C, the reactor temperature was raised to 300C for the remaining experiment. The duration of the experiments varied between 2 and 5 days, depending on flow rate and tracer breakthrough.

Aqueous samples collected from the reactor were analyzed for NDS by fluorescence, Li by ICP-OES and Br by ion chromatography. Microscope examination of the amphibolite schist material both pre- and post-experiment revealed hydrothermal alteration of mineral phases had occurred. BET surface area measurement (multipoint method with krypton) and X-ray Diffraction analysis was used to compare the pre- and post-experimental material. The results of these analyses are reported below in results and discussion.

Table 1: Synthetic brine recipe (all masses are per 1000 g of deionized water).

Chemical	**Mass (g)**
NaH_2PO_4	0.665
Na_2HPO_4	0.755
$NaHCO_3$	1.498
KCl	0.415
NaCl	3.481
H_4SiO_4	0.105
Na_2SO_4	0.053
Total Dissolved Solids	6.617
Ionic Strength (M)	0.092 M
pH (adjusted with HCl)	6.5

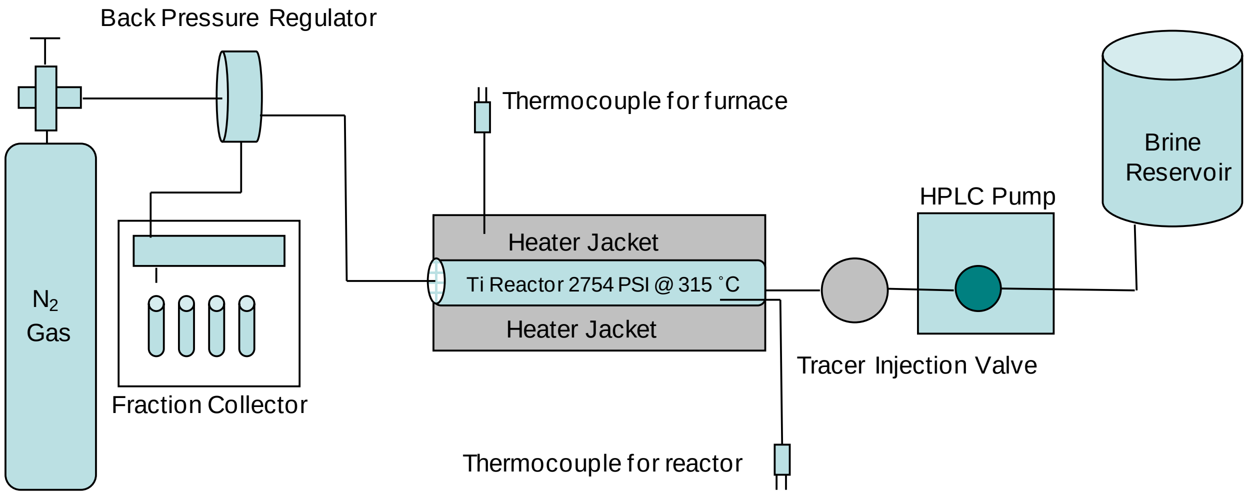

Figure 2: Simplified schematic of experimental apparatus used for the lithium tracer experiments.

Table 2: QXRD and surface area of amphibolite schist.

Mineral	**Wt. %**
Amphibole (hornblende)	64.9
Plagioclase	27.1
Mica (phlogopite, biotite)	8.0
Surface Area (m^2/g)	0.036

MODELING METHODS

Prior to conducting laboratory experiments the MULTRAN computer model was employed to simulate transport of a cation-exchanging tracer in sing-well tracer tests to evaluate the potential use of such tracers to interrogate surface area in EGS reservoirs. MULTRAN simulates the transport of cation exchanging tracers by solving mass action equations (3a), (3b) and (3c) for cation-exchange equilibria simultaneously with the surface cation balance (4) and the transport equations (5) and (6). For the simulations in this paper, a simple three-component system represented by the reactions (1a), (1b) and (1c) was simulated involving a monovalent cation tracer that exchanges with both a monovalent and a divalent cation present in the ambient reservoir.

Mass-action expressions corresponding to Reactions (1a), (1b) and (1c), respectively:

$$Q_1 = \frac{[AX][B]}{[A][BX]} \tag{3a}$$

$$Q_2 = \frac{[AX]^2[C]}{[A]^2[CX_2]} \qquad (3b)$$

$$Q_3 = \frac{[BX]^2[C]}{[B]^2[CX_2]} \qquad (3c)$$

[Note that $Q_3 = Q_2/Q_1^2$, so it is not an independent parameter]

Surface cation balance:

$$CEC = \frac{\phi}{\rho_b}\left([AX]+[BX]+2[CX_2]\right) \qquad (4)$$

Where, [i] = concentration of species i, moles/L of solution, Q_i = ion exchange constant, CEC = cation-exchange capacity, eq/Kg and ρ_b = bulk density of rock, kg/L of bulk rock. Note that the Q_i values are not equilibrium constants because absolute concentrations of species, not species activities, are used.

Mass transport:

Fractures:

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} - D\frac{\partial^2 C}{\partial x^2} - \frac{\phi_m}{b}D_m\left.\frac{\partial C_m}{\partial y}\right|_{y=b} = 0 \qquad (5)$$

Matrix:

$$\frac{\partial C}{\partial t} - D_m\frac{\partial^2 C_m}{\partial y^2} = 0 \qquad (6)$$

where, C = tracer concentration (g/cm^3), v = flow velocity in fractures (cm/s), D = tracer dispersion coefficient (cm^2/s), D_m = tracer diffusion coefficient in matrix (cm^2/s), ϕ = matrix porosity, b = fracture half aperture (cm) with the subscript m referring to matrix. One of the advantages of using a simple cation-exchange model like MULTRAN (i.e. no interacting species and requirement for steady state flow conditions) allows the simulation of flow interruption and flow reversals associated with single-well tracer tests.

EXPERIMENTAL RESULTS

The results shown in Figure 3 clearly reflect little difference in the breakthrough of bromide and NDS in each experiment, despite their factor of 3 to 4 difference in diffusion coefficient. The cation exchanging tracer, lithium, shows a discernible difference in breakthrough from the conservative tracers in each experiment, with the greatest difference being in the 300C experiment. Interestingly, the peak lithium breakthrough concentrations occur at roughly the same pore volume as the peak conservative tracer concentrations, but the peaks are much lower and the tails longer than for the conservative tracers. These responses suggest dual-porosity behavior, wherein lithium sorption occurs only after diffusion into stagnant porosity within the system. However, the lack of any separation in the conservative tracer breakthrough curves, and the very low matrix porosity of the amphibolite schist argue for a relatively small volume of stagnant porosity that is likely confined to a thin layer of roughness at the grain surfaces and perhaps includes some dead-end pore spaces between grains. The fact that the lithium breakthrough curves did not exhibit a notable delay in arrival relative to the conservative tracers, as would be expected for a classic porous medium, was quite surprising. Post-experimental analysis of the amphibolite schist from the vessel revealed that the surface area of the material had increased to 0.073 m^2/g, twice the pre-experimental value. The images in Figure 3 suggest that the material went through hydrothermal alteration, although the XRD results in Table 3 indicate that the mineral phases in the pre- and post-experimental material are the same. The change in color and texture shown in the images and the two fold increase in surface area are most likely a result of iron dissolution and re-precipitation as iron oxide coatings on mineral grains. Quantitative XRD is planned for the fractionated material to identify trace minerals such as iron and manganese oxides.

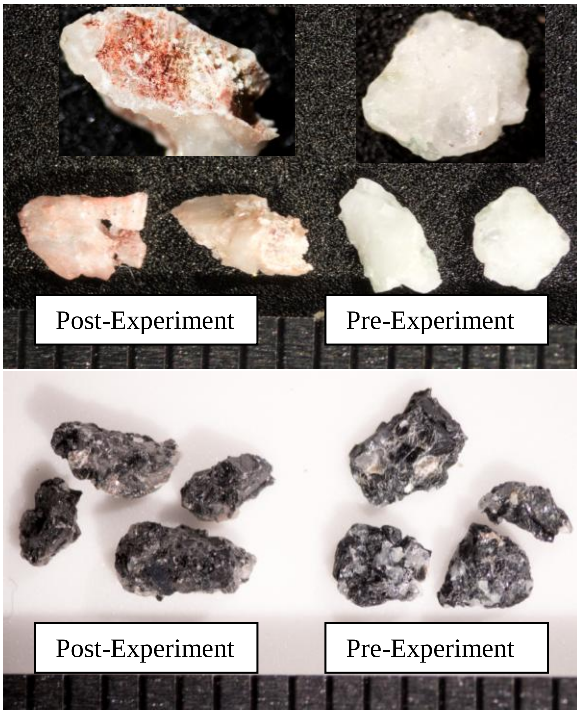

Figure 3: Plagioclase (top) and hornblende (bottom) separated from the amphibolite schist material. Scale marks are in mm.

Table 3: XRD and surface area of amphibolite schist material.

Sample	**Minerals Present**				
	Plagioclase	**Quartz**	**Mica**	**Hornblende**	**Kaolinite**
Plagioclase fraction-pre experiment	X	X	X	X	
Plagioclase fraction-post experiment	X	X	X	X	
Hornblende fraction-pre experiment	X		X	X	X
Hornblende fraction-post experiment	X		X	X	X
Post Experimental Surface Area (m^2/g)	0.073				

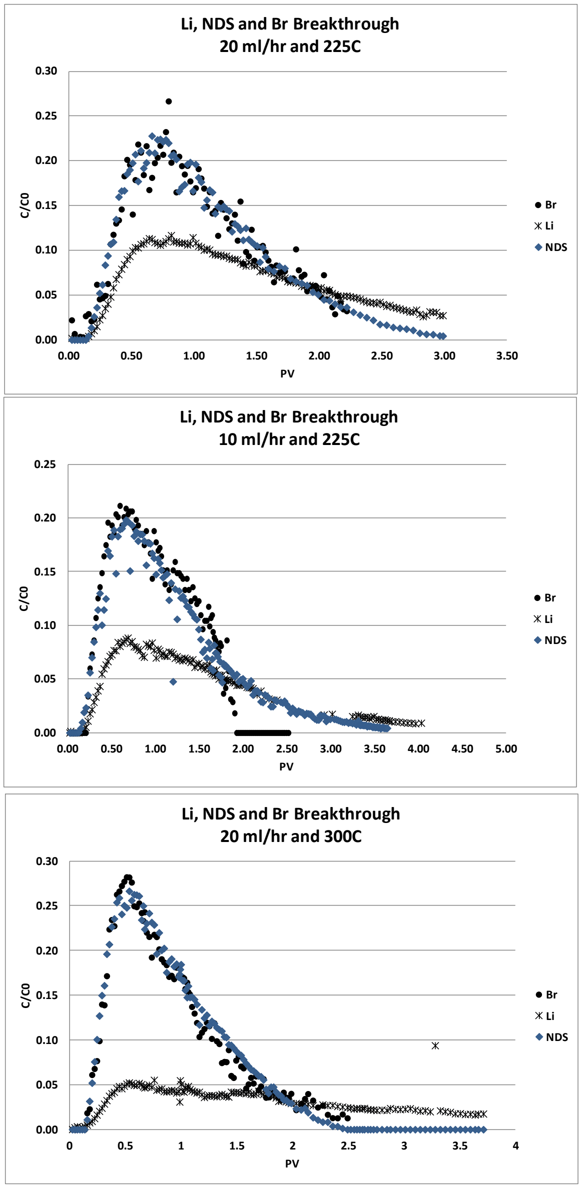

Figure 3: Breakthrough (normalized concentration as a function of pore volume) of Li, NDS and Br at 20 ml/hr and 225C (1st experiment, top), 10 ml/h and 225C (2nd experiment, middle) and 20 ml/hr and 300C (3rd experiment, bottom).

MODELING RESULTS

Modeling of experimental data

The three column transport experiments were interpreted by first using the semi-analytical RELAP model (Reimus et al., 2003) to match the 1,5-NDS and bromide normalized breakthrough curves shown in Figure 3. The matching was accomplished by adjusting the mean residence time and Peclet number (column length divided by dispersivity) in the column without assuming any diffusion into secondary porosity. Once a good match was achieved, the tracer mean residence times were arbitrarily decreased by 17% (corresponding to a 17% decrease in flowing porosity) and a secondary porosity equal to 20% of the new flowing porosity was introduced. These adjustments provided a small amount of diffusion into secondary porosity (though not enough to result in significant differences in the breakthrough curves of the conservative tracers) while keeping the overall column pore volume constant. The pore volumes estimated by multiplying the calculated mean residence times of the conservative tracers by the experimental flow rates were 255 ml, 240 ml, and 204 ml for the three experiments. These volumes compare well with the gravimetrically-estimated column pore volume (221 ml), and the decrease with time is consistent with alteration of the amphibolite schist in the column over time. The greatest amount of alteration would be expected to occur at the higher temperature.

The best-fitting parameters from the RELAP simulations were then used in MULTRAN to simulate both the conservative tracer and lithium breakthrough curves. It was first verified that MULTRAN reproduced the conservative tracer breakthrough curves simulated by RELAP, and then the lithium ion exchange parameters were adjusted to obtain reasonable matches to the lithium data. The resulting matches to both the conservative tracer and lithium breakthrough curves are shown in Figure 4.

In the following discussion, it is important to recognize that the goal is to use the lithium cation-exchange method to estimate the surface area that dictates heat transfer in a geothermal system, which is the *flow-wetted surface area*. However, the exchange reactions actually interrogate molecular-scale surface area, not flow-wetted surface area. For a dual-porosity system, the flow-wetted surface area appears in expressions (2a) or (2b) as part of the parameter b, which is the flowing pore volume of the system divided by the flow-wetted surface area. The molecular-scale surface area, on the other hand, is reflected in the parameter R_m in expression (2b). In this study, we lacked the information needed to independently estimate each of the individual parameters in expression (2b), so constant values were initially assumed for ϕ_m, D_m and b (equal to the values yielding good matches to the conservative tracer data in RELAP) and then the CEC value, which R_m is directly proportional to, was adjusted in MULTRAN to match the lithium breakthrough curves. The values of Q_1 and Q_2 were fixed to be 0.83 and 0.13, respectively, based on typical values of selectivity coefficients for lithium exchange with sodium and calcium (Appelo and Postma, 1994).

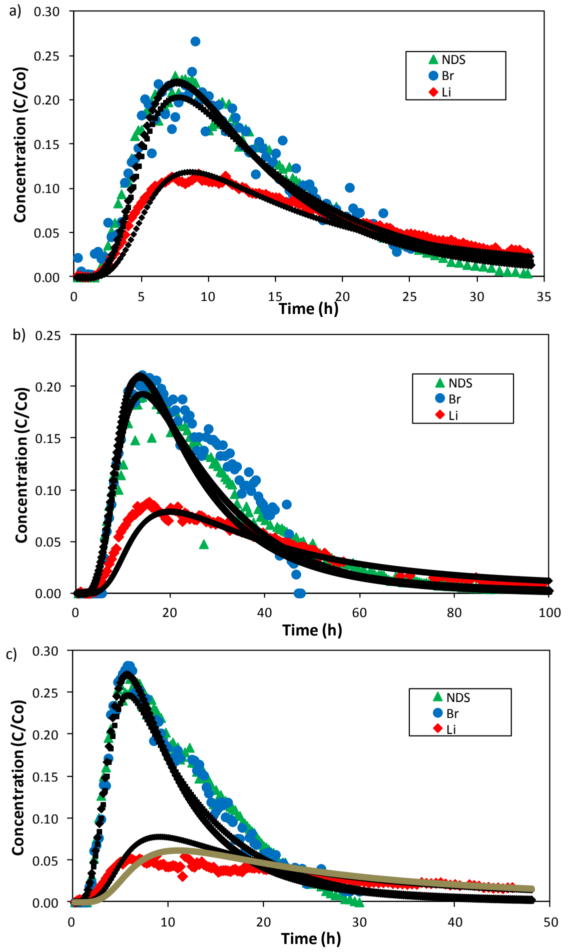

Figure 4: MULTRAN matches to tracer breakthrough curves for (a) 225C, 20 ml/h, (b) 225C, 10 ml/h, and (c) 300C, 20 ml/h. Grey line in (c) is match obtained to Li breakthrough curve when the parameter b was adjusted from a 20% decrease to a 30% decrease relative to the value of b in experiments (a) and (b) (see text).

After obtaining a CEC value that provided a reasonable match to the lithium data in the 20 ml/h experiment at 225C (Figure 4a), the same values of ϕ_m, D_m b, and CEC were used to simulate the 10 ml/h experiment at 225C, with the result shown in Figure 4b. The rationale for keeping the parameters the same was that little mineral alteration was believed to occur at 225C, as suggested by the very minor change in flowing pore volume (and also dispersivity) estimated from the conservative tracer responses in the two experiments. Also, no change in D_m or CEC would be expected if the temperature remained the same. The cation-exchange reaction rates were assumed to be fast relative to mass transport rates in both experiments (i.e., local cation-exchange equilibrium was assumed).

The fact that the same parameters provided good matches to the breakthrough curves at the two different flow rates implies the flow-wetted surface area estimate was approximately the same in the two experiments. This result also indicates good method reproducibility and no apparent kinetic effects, both of which are desirable for surface area estimation. However, the result does not yield an absolute value of the estimated surface area because this would require accurate estimates of all the other parameters in expression (2b), which was beyond the scope of this study. Rather, the result confirms that the method accurately reproduces the same surface area estimate at the same temperature and different flow rates.

When using MULTRAN to match the lithium breakthrough curve obtained at 300C, the following adjustments were made in advance to the parameter values: (1) the diffusion coefficients of all tracers were increased of a factor of 1.5 to account for the temperature and viscosity dependence of diffusion coefficients (the temperature dependence of viscosity must be factored into this calculation), (2) the CEC was increased by a factor of 2 to account for the doubling of molecular scale surface area of the amphibolite schist after the experiments relative to the pre-test material (this assumes that the increase occurred mainly after the higher temperature was reached), and (3) a decrease of 20% in the value of b based on the decrease of 20% in the flowing pore volume estimated from the conservative tracers in the 300C test. The last adjustment assumes that the flow-wetted surface area was not significantly changed by the mineral alteration, and the second adjustment assumes that the CEC does not have a temperature dependence (only a specific surface area dependence).

The resulting match to the 300C data is shown in Figure 4c. This match is remarkably good considering the uncertainties associated with the parameter adjustments described above. A second model simulation with the same parameter adjustments but a 30% decrease in the value of b instead of a 20% decrease is shown in Figure 4c to yield an improved match to the data. This result implies that after accounting for all the other known changes occurring in the system, the flow-wetted surface area estimate obtained from matching the lithium breakthrough curve at 300C would be within 10-15% of the estimate obtained at 225C. Again, we cannot compare absolute estimates, but we can state that the estimates at the two temperatures would be the same to within 15%. Although not shown, an increase of an additional 20% in the CEC value (to a factor of 2.4 times the value at 225C) while keeping b fixed at a value corresponding to the flow-wetted surface area determined at 225C also yielded a good match to the lithium data. This result is reasonable given that the mineralogic alteration of the amphibolite schist could be expected to result in increases to the effective CEC value because some alteration minerals (e.g., iron oxide coatings) have inherently greater CEC values per unit surface area than their parent minerals.

Several potential changes to parameter values resulting from the hydrothermal alteration at 300C were ignored due to lack of information. For instance, the alteration would be expected to change the porosity, tortuosity, and thickness of the surface layer in which diffusion and sorption were assumed to occur. Also, the effective CEC value per unit surface area likely had a temperature dependence that was not accounted for. All these things considered, the consistency in flow-wetted surface area estimates between the experiments suggest that the cation-exchange method is reasonably robust for estimating surface area (or more specifically, volume to surface area ratio) provided that temperature effects and molecular-scale surface area changes resulting from hydrothermal alteration can be reasonably accounted for. Although more detailed characterization would be needed in any given system to obtain absolute flow-wetted surface area estimates, the results of this study clearly suggest that it should be possible to obtain reasonable estimates of relative surface area changes before and after stimulation treatments or after dilations of fracture apertures due to temperature or pressure changes.

Simulation of single-well testing with conservative and cation exchanging tracers

We demonstrate here the use of cation-exchanging tracers in single-well tests because single-well tests have advantages over multi-well tests in that a second well need not be drilled to determine reservoir characteristics and effectiveness of EGS stimulation in generating fracture surface area. Figure 6 shows shows results of using MULTRAN to simulate a cation-exchanging tracer (in this case Rb^+ exchanging with Na^+ and Ca^{2+}) (Williams et al., 2010). The average fracture aperture in the system is assumed to 0.05 cm with a fracture spacing of 10 cm. The fluid and rock thermal properties correspond to water and basalt. The simulation assumes 10 hours of water injection, followed by 20 hours of "shut-in," and finally, withdrawal of water/tracers starting at 32 hours. Some key points for the single-well simulation are (Williams et al., 2010):

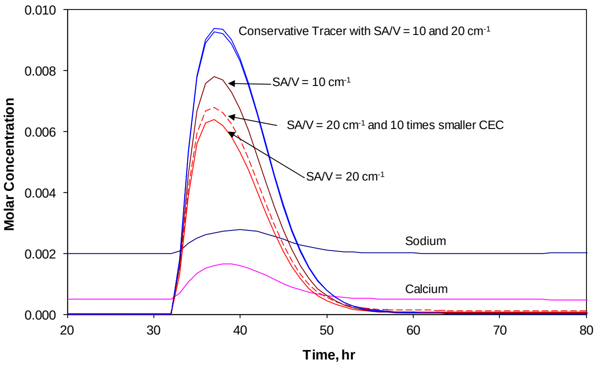

Figure 5: Simulated Differences in Conservative and Cation-Exchanging Tracer Breakthrough Curves for SA/V Value of 10 cm^{-1} and 20 10 cm^{-1}(solid brown and red curves) in a single-well test .

- Breakthrough of the cation-exchanging tracer is sensitive enough to the SA/V ratio that relative changes in surface area can be evaluated using only the cation-exchanging tracer response before and after stimulation.
- Breakthrough of the cation-exchanging tracer is not sensitive to changes in CEC value therefore prior knowledge of reservoir CEC would not be necessary.
- The differences in breakthrough of conservative tracers with different diffusion coefficients in these systems are too small to be distinguished and could not be used effectively to determine changes in SA/V ratios.

DISCUSSION AND CONCLUSIONS

The results of this study indicate that lithium cation-exchange is reproducible with no apparent kinetic effects in the amphibolite schist material under simulated geothermal reservoir conditions. This, along with other advantages (non-toxic, inexpensive, low background concentration), would make the lithium ion an ideal tracer for estimates of relative surface area changes before and after reservoir stimulation. Other cation-exchanging tracers could be considered as well depending on the cation-exchange capacity in an EGS system. For example, lithium could be used to interrogate surface area in high CEC systems because it is a relatively weak cation-exchanger and strongly exchanging cations such as cesium and rubidium could serve as exchangers in systems with low CEC values.

To further evaluate the sensitivity of cation-exchanging tracer breakthrough curves to cation-exchange capacity and SA/V ratios, future experiments are planned using the amphibolite schist material with different (larger) grain sizes at 225C (avoiding hydrothermal alteration). The experiments will be repeated with quartz sand to demonstrate applicability to a different and simpler, unaltered system.

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