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Laboratory experiments to characterize cation-exchanging tracer behavior for fracture surface area estimation at Newberry Crater, OR

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ABSTRACT

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

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1. Introduction

Newberry Volcano in central Oregon, USA is the site of an Enhanced Geothermal System (EGS) Demonstration Project (AltaRock Energy Inc., 2011), funded in part by the U.S. Department of Energy. Single-well tracer tests involving lithium and cesium ions were originally planned as part of the Demonstration Project to estimate fracture surface area generated during hydraulic stimulations, or "hydroshearing", to open and enlarge natural fractures. Surface area estimation with these tracers is based on the concept that their adsorption onto fracture surfaces by cation exchange should be proportional to the fracture surface area to volume ratio (SA/V) seen by the injected tracer solution. Cation exchange is a rapid, reversible process in 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-injected with each cation so that when the well flows back, the adsorption of Li^+ and Cs^+ onto fracture surfaces can be quantified by comparing the concentration vs. time histories (breakthrough curves) of the cation tracers and the conservative tracers from each

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Table 1
Material properties.

Mineral	Chemical formula	Added mineral mass fraction in mix	Meas'd specific SA (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	$NaAlSi_3O_8$	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	$(Mg,Fe^{2+})_5Al_2Si_3O_{10}(OH)_8$	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

zone. As of this writing, the flowback phase of these tests had not yet occurred.

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

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

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 Sections 2.1–2.5.

2.1. *Minerals*

Minerals representing Newberry reservoir fracture surfaces and coatings were selected based on information contained in AltaRock Energy Inc. (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 Inc. (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 h) 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 et al., 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

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