Geothermics 71 (2018) 12–23

Contents lists available at ScienceDirect

Geothermics

journal homepage: www.elsevier.com/locate/geothermics

Evaluation of a cation-exchanging tracer to interrogate fracture surface area in enhanced geothermal systems

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ARTICLE INFO

Keywords:
Tracers
Surface area
Cation exchange

ABSTRACT

Column transport experiments were conducted at 225 °C and 300 °C using a crushed amphibolite schist from Fenton Hill, NM to evaluate lithium ion as a cation-exchanging tracer to interrogate fracture surface area in enhanced geothermal systems. Lithium exchange proceeded to equilibrium rapidly, and Li^+ selectivity doubled from 225 °C to 300 °C, with the selectivity at both temperatures being much greater than at room temperature. Also, cation exchange was deduced to be occurring primarily in a thin "rim zone" (< 0.05 mm) on the rock surfaces. These results are all encouraging for using lithium ion to interrogate fracture surface area in enhanced geothermal systems.

1. Introduction

Cation exchange is a simple, reversible process by which a cation in solution exchanges with other cations present on rock surfaces; e.g.,

$$A + BX \rightarrow AX + B \quad (1)$$

$$2A + CX_2 \rightarrow 2AX + C \quad (2)$$

$$2B + CX_2 \rightarrow 2BX + C \quad (3)$$

where A and B are monovalent cations, C is a divalent cation and X is a negatively charged surface site. Several characteristics make alkali metals and alkaline earth metals (monovalent and divalent cations in the first two columns of the periodic table) good potential surface-area-interrogating tracers for Enhanced Geothermal System (EGS) applications; they have a wide range of sorption strengths, are generally non-toxic and inexpensive, and some (for example, lithium, cesium, rubidium, barium) have relatively low background concentrations in most rock-water systems. Their thermal stability also makes them suitable for use in geothermal systems.

The use of tracers in geothermal applications was first suggested in model simulations by Los Alamos National Laboratory (LANL) during the Fenton Hill Hot Dry Rock geothermal project (Robinson et al., 1988), although tracers for interrogating fracture surface area were not explicitly considered. LANL has subsequently used lithium ion (Li^+) as a reactive tracer in conjunction with conservative tracers to interrogate fractured media properties, including surface area to volume (SA/V) ratios, in both laboratory and field-scale transport experiments (Anghel et al., 2002; Reimus et al., 2003; Sullivan et al., 2003). In Sullivan et al. (2003), lithium sorption to volcanic tuff samples of varying composition was found to be positively correlated with surface area, although there were also correlations with mineralogy. More relevant to enhanced geothermal systems (EGS), Andersson et al. (2002) showed that cation-exchanging tracers transported in a manner consistent with their relative sorption strengths in a fractured Swedish granite, with the tracers deduced to be diffusing into a thin "rim zone" on the fracture surfaces (matrix porosity of ~1%) before adsorbing to minerals in the rim zone. They further showed that in addition to the diffusion and sorption properties of the rim zone, the cation breakthrough curves were dependent on the fracture surface area to volume ratio (flow-wetted surface area) in the fracture network (Andersson et al., 2002). Based on these previous efforts, we hypothesized that the differences between the breakthrough curves of cation-exchanging tracers and conservative tracers could potentially provide estimates of fracture surface area to volume ratios in EGS.

Using this line of reasoning, the monovalent cations Li^+ and Cs^+ were co-injected with conservative tracers in two single-well stimulations at the Newberry Crater, OR EGS demonstration project, with the expectation that tracer concentration histories in the return flow could provide fracture surface area estimates. To support this effort, we conducted a laboratory study of the transport behavior of these cations at elevated temperatures in a mineral assemblage representative of the

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http://dx.doi.org/10.1016/j.geothermics.2017.08.002
Received 23 June 2016; Received in revised form 21 July 2017; Accepted 2 August 2017
Available online 21 August 2017
0375-6505/

fracture mineralogy at Newberry Crater (Dean et al., 2015). Although the water used in the field stimulations never flowed back to allow for tracer analyses, the results of the laboratory study indicated that (1) both Li^+ and Cs^+ exhibited dual-porosity behavior that was consistent with a "rim zone" at the higher temperatures (suggesting cation exchange *after* a diffusion step) even though the experiments were conducted in granular porous media, and (2) Li^+ cation exchange increased in strength and Cs^+ decreased in strength as temperatures increased. Both of these results were considered positive for the use of cation-exchanging tracers to interrogate fracture surface area because (1) dual-porosity behavior allows for better-constrained estimates of surface area in fractured systems, and observing this behavior in granular materials of low intragranular porosity suggests a robustness of the method, and (2) there was concern that Li^+ may be too weakly exchanging and Cs^+ too strongly exchanging to be useful as tracers (based on their behavior at low temperatures), so the stronger Li^+ exchange and weaker Cs^+ exchange at elevated temperatures were welcome results.

In this paper, we present the results of a second set of laboratory experiments (mentioned in Dean et al., 2015 and partially reported in Dean et al., 2012) that were conducted to further evaluate the method of using cation-exchanging tracers to interrogate surface area in EGS. Rather than using a representative (but artificial) mineral assemblage, as in the Newberry Crater experiments (Dean et al., 2015), the experiments reported here were conducted using crushed core from Fenton Hill, New Mexico, the site of the world's first EGS demonstration. This core material was considered to be representative of a deep EGS site in which tensile fractures are created in a competent basement rock, whereas Newberry Crater is a site where fractures were expected to be created by shearing of pre-existing semi-closed fractures. Also, the mineralogy of the materials at the two sites is significantly different, which was considered desirable to provide a robust test of the applicability of the cation exchange method in two very different settings. The Fenton Hill experiments had the added objective of evaluating potential sorption kinetics effects on cation tracer transport, which was accomplished by conducting experiments at different flow rates in the same column and at the same temperature.

A batch sorption experiment at elevated temperatures was also conducted to allow a comparison of cation exchange parameters deduced from high-temperature batch and column transport experiments (only room temperature batch experiments were conducted for the Newberry study). Additionally, more detailed mineralogical characterizations of the pre- and post-test materials were conducted for the Fenton Hill study to try to better understand some of the experimental observations, and a set of column experiments were conducted at elevated temperature using a silica sand with virtually no cation exchange capacity to verify that processes other than cation exchange were not responsible for the attenuation of lithium in the Fenton Hill columns. The Fenton Hill study scaled back on the number of cations evaluated relative to the Newberry study (only one, Li^+, was evaluated, as opposed to two, Li^+ and Cs^+, for the Newberry study) and also the range of temperatures evaluated was narrower for the Fenton Hill study (225 °C to 300 °C, as opposed to 25 °C to 275 °C).

This paper also provides an overview, through the use of models, of how cation-exchanging tracers can be used in single-well EGS stimulations to provide estimates of fracture surface area. While it is beyond the scope of this paper to address all the variations in test design and the potential uncertainties associated with the cation exchange method, it is useful to summarize the method to gain an appreciation of its advantages and potential limitations. This summary is provided in the next section before the experimental results are presented.

2. Cation-exchanging tracers in single-well EGS stimulations

The multicomponent cation exchange transport model MULTRAN (Sullivan et al., 2003), which was used in the interpretation of the Newberry Crater laboratory column experiments (Dean et al., 2015), is used here to illustrate how cation tracer breakthrough curves are expected to depend on fracture apertures in single-well EGS stimulations. The reader is referred to Dean et al. (2015) for a description of the model features, but briefly, MULTRAN can account for up to 10 cations simultaneously exchanging with each other over a range of concentrations extending well beyond the normal range of adsorption linearity for cation-exchanging tracers. When tracer concentrations vary by several orders of magnitude, as they often do in field tracer tests, a simple linear partition coefficient is not sufficient to describe the sorption process, so a model like MULTRAN is needed to more accurately estimate fracture surface area to volume ratios from cation exchanging tracer responses.

We focus on single-well tracer tests because EGS stimulations are inherently single-well operations in which it is relatively easy to add tracers and observe responses during a flow back phase. Also, single-well tracer tests typically have much higher tracer recoveries and return concentrations than interwell tracer tests, which is advantageous when using cations that may have nonzero background concentrations and relatively high detection limits compared to other tracers. In principle, single-well tracer tests are also quite easy to repeat, and such repeated tests might allow interrogation of *relative* changes in surface area resulting from repeat stimulations even if there is considerable uncertainty in absolute surface area estimates because of uncertainties in site-specific cation exchange and mass transfer parameters.

To maintain relevance to EGS, the model simulations presented here use the parameters deduced for the Newberry Crater mineral assemblage (Dean et al., 2015), which reflect the strong influence of a low-porosity rim zone on grain surfaces. A reservoir temperature of 225 °C was assumed in all cases. Fig. 1 shows the results of a set of model simulations for average fracture apertures of 1, 3 and 10 mm, corresponding to fracture volume to surface area ratios of 0.05, 0.15, and 0.5 cm, respectively. In these simulations it was assumed that a single-well injection for the purposes of creating reservoir fractures (i.e., a stimulation) was conducted for 50 h, with conservative tracers and a cation-exchanging tracer (Li^+ in this case) being injected for 5 h starting 42 h into the stimulation. During the last 3 h of the stimulation (between h 47 and 50) the tracers were "chased" into the reservoir by injecting tracer-free water, and the system was then "shut-in" for 2 h before being allowed to flow back at approximately the rate of injection. In reality, most EGS stimulations and shut-in periods are likely to last considerably longer, but these times are sufficient for demonstrating single-well tracer responses. The tracer injection near the end of the stimulation period reflects the expectation that only a fraction of the injected water will flow back when the wellhead pressure is

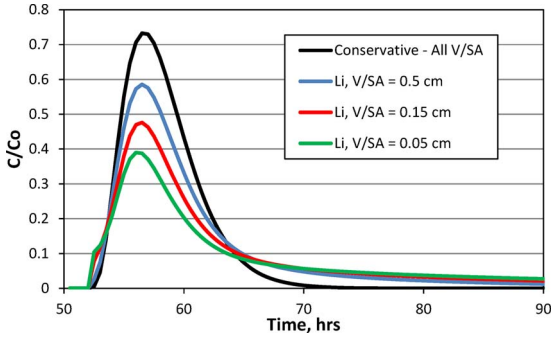

Fig. 1. Simulated single-well tracer test breakthrough curves of two conservative tracers with different diffusion coefficients (identical curves) and lithium ion for three different fracture volume to surface area ratios (V/SA) using the rim-zone cation-exchange properties deduced from the experiments of Dean et al. (2015). Return flow begins at 52 h; tracers injected from 42 to 47 h after start of injection (time zero); and shut-in/no-flow from 50 to 52 h. Concentrations are normalized to injection concentration (C/Co, where Co is injection concentration). (This figure is better viewed in color; the reader is referred to the web version of this article to see the color.)