The Use of Reversibly Adsorbing Tracers for Characterizing Reservoir Fracture Surface Area in Engineered Geothermal Systems

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ABSTRACT

Conservative tracers can be used to characterize flow processes between injection and production wells, since, by definition, they react neither with the aqueous medium nor with fracture surfaces as they are advected through a geothermal formation. In contrast, reversibly adsorbing tracers interact electrostatically with the fracture-rock surface and this interaction serves to retard slightly their arrivals at a production well relative to those of conservative tracers. In combination with numerical simulation modeling, this slight retardation can be used to constrain the adsorptive-surface area, which is related to the surface area for heat transfer—a critical parameter for predicting reservoir performance. We examine a range of molecular and colloidal candidates for use as reversibly adsorbing tracers in Engineered Geothermal Systems (EGS), including fluorescent organic anions and cations, Group 1A metals, and fluorescent nanoparticles.

1. INTRODUCTION

Chemical tracing in EGS reservoirs involves the tracking of fluids using chemical compounds that are typically injected into injection wells, advected through the reservoir, and then produced at production wells, where their concentrations are measured. Tracers can be characterized as belonging to either of two broad categories—conservative or reactive. Conservative tracers are those that do not engage with the reservoir rock and/or the solvent as they are advected through the formation; their flow is therefore indistinguishable from that of the solvent molecules. Such tracers are used to measure interwell travel times, flow patterns, pore volumes, and reservoir dispersivity (Rose et al., 2004; Shook et al., 2005). In contrast to conservative tracers, reversibly adsorbing tracers are slightly attracted to the rock, retarding their passage through the reservoir. If a reversibly adsorbing tracer is co-injected and then co-produced with a conservative tracer, a measure of the relative retardation of the reversibly adsorbing tracer provides an independent variable that can serve to measure the tracer-contacted fracture surface area, which is a critical parameter for constraining geothermal reservoir performance and sustainability.

In addition to possessing good thermal stability, geothermal tracers must also be very detectable, environmentally benign, nontoxic, available in bulk and affordable. One family of conservative tracers that meets these requirements and that has been used extensively in geothermal reservoirs is the naphthalene sulfonates (Rose et al., 2001). Their polyaromatic backbone and their strongly bonded sulfonate groups imbue these molecules with excellent thermal stability. Likewise, they possess excellent detectability by High Performance Liquid Chromatography/fluorescence since the polyaromatic backbone provides a large cross-section for uv-absorption and subsequent fluorescence emission. In addition, a low detection limit means that lower quantities are required for fullscale applications, thereby enhancing affordability. These compounds are nontoxic, environmentally benign (Greim et al., 1994) and available in bulk. And since there are several, they are useful for tracing multiple flow pathways simultaneously. The naphthalene sulfonates have been shown to exhibit excellent resistance to thermal degradation in laboratory studies under conditions that simulate the reducing environment of a geothermal field (Rose et al., 2001). These laboratory results have been confirmed in numerous field tests (Rose et al., 2002a; Rose et al. 2002b; Rose et al., 2003). However, in a series of laboratory experiments that exposed the naphthalene sulfonate tracers to mineral surfaces and temperatures found in some of the world's hottest (>300°C) geothermal reservoirs, they were shown to isomerize and/or degrade— especially when exposed to these high temperatures for long residence times (Sajkowski, L., 2020).

2. THE SEARCH FOR REVERSIBLY ADSORBING TRACERS

Tracers interact with geothermal fracture surfaces primarily through electrostatic London/van der Walls forces. Since geothermal-reservoir rock possesses a negative surface charge, negatively charged tracer molecules, including the fluorescent naphthalene sulfonates and other organic anions, resist adsorption. In contrast, a positively charged or even amphoteric fluorescent molecule will be slightly attracted to negatively charged rock fracture surfaces, slowing its advection through the reservoir relative to that of a conservative tracer.

A similar mechanism involves cation exchange. Through this process, small metallic cations such as Li^+ , Cs^+ or Rb^+ naturally exchange with Na⁺ or K⁺ at the fracture surface. This replacement process is reversible, with solute Na⁺ or K⁺ instantly displacing the newly installed Li^+ , Cs^+ or Rb^+ . The passage of these small metal cations is thereby slightly retarded relative to a conservative tracer, and the degree of retardation is dependent on the surface area for cation exchange.

A third category of candidate reversibly adsorbing tracers are fluorescent nanoparticles, including quantum dots (Rose et al., 2010). These colloidal nanocrystals are shown to fluoresce brightly within the visible range according to particle size. Furthermore, we showed that surface ligands could be attached to the CdS surface of the quantum dots, allowing these particles either to resist sorption or to be reversibly

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adsorptive on fractures possessing a negative surface charge. Recently, Spitzmüller et al. (2023, 2024a, 2024b) investigated the use of mesoporous silica nanoparticles as conservative geothermal tracers. As with the quantum dots, the surfaces of these nanoparticles can be coated with ligands possessing a positive charge, allowing them to potentially be reversibly adsorptive under geothermal reservoir conditions.

2.1 Fluorescent organic molecules

Reversibly adsorbing tracers must meet the requirements of conventional tracers. They must be thermally stable, very detectable, affordable, available in bulk, environmentally benign and, generally, multiple. An additional requirement is that they must also adsorb slightly with the fracture surface. Since so few known compounds meet even all of the requirements of conservative tracers, it makes sense to search for reversibly-adsorbing tracer candidates among the families of aqueous tracers—either geothermal, groundwater or waterflood petroleum—that have already been characterized for commercial applications. Given that virtually all conventional geothermal tracers and all aqueous-phase petroleum tracers are anions (negatively charged), it seems unlikely that any of these compounds would be good candidates for use as reversibly adsorbing tracers in geothermal reservoirs. However, one of the naphthalene sulfonates—2-naphthalene sulfonate—was shown to reversibly sorb in a field test at a 150 °C Dilly Creek shale-gas reservoir in British Columbia, Canada. Likewise, 1,3,6,8-pyrene tetrasulfonate (PTSA) reversibly adsorbed on Dilly Creek shale drill cuttings under reservoir-simulated laboratory conditions. Many of the petroleum waterflood tracers—the halogenated benzoates—were shown to reversibly adsorb on Austin Chalk (shale) drill cuttings in flow experiments at 160 °C.

If the fractured shales in the tracing experiments at Dilly Creek and in the Austin Chalk were able to retard the flow of some of the anionic naphthalene sulfonates and halogenated benzoates relative to a conservative tracer, could newly fractured, clay-containing rocks in an EGS reservoir likewise retard the flow of these compounds? We were given the opportunity to screen candidate tracer for reversible adsorption during a circulation test at the FORGE EGS site near Milford, Utah in August, 2024. Since little was known about the *in situ* surface charges of these newly fractured granitic rocks, this tracer screening test would provide insights for subsequent laboratory studies.

The candidates included 1,3,6,8-pyrene tetrasulfonate, Tinopal CBS-X (a fluorescent whitening agent), and three halogenated benzoates— 2,5-dichlorobenzoate, 3,4-dichlorobenzoate, and 4-chloro-3-fluorobenzoate. One kg of each was mixed in about 200 gal of water along with 1 kg of 1,5-naphthalene disulfonate, which was known to behave conservatively under geothermal reservoir conditions as well as those at the Dilly Creek and Austin Chalk reservoirs. The solution was injected as a slug into FORGE injection well 16A-32. Samples were subsequently taken at regular intervals at the neighboring subparallel production well 16B-32. Figure 1 shows that although many of the candidates had adsorbed on shales at 150-160 °C, none of the candidates showed any adsorption on the granitic rocks at FORGE at 225 °C; all of the compounds either co-eluted with the conservative tracer or were thermally degraded. The three halogenated benzoates all showed some degree of thermal degradation, whereas PTSA showed significant decay. The compound Tinopal CBS-X either completely degraded or irreversibly adsorbed in the reservoir.



Figure 1. Return curves of candidate compounds that were tested for their use as adsorbing tracers as part of the August, 2024 circulation test. One kg of each was mixed in solution and then injected as a slug into well 16A-32. Water from production well 16B-32 was subsequently sampled and analyzed. None of the candidates showed any reversible adsorption.

Since none of the anionic compounds tested in the FORGE 2024 circulation test showed any tendency for adsorption, we next considered cationic fluorescent compounds, which possess the excellent detectability of anionic fluorescents but possess opposite charge to that of the assumed negatively charged fracture surfaces within the FORGE reservoir. Safranin T (3,7-diamino-2,8-dimethyl-5-

(1)

phenylphenazinium chloride), which is positively charged in solution and hence cationic, was studied in a benchtop flow reactor and subsequently in a field experiment at the Soda Lake geothermal reservoir (Rose et al., 2012).

The adsorptivity of a reversibly adsorbing tracer can be measured in the laboratory under conditions that simulate a geothermal reservoir. Using a column reactor filled with drill cuttings, a candidate reversibly adsorbing tracer is co-injected in solution with a conservative tracer at one end of the column and produced at the other, where the two tracers can be sampled and analyzed. Figure 1 shows plots of a conservative tracer, 1,5-naphthalene disulfonate (1,5-nds), and a reversibly adsorbing tracer, Safranin T, that had flowed through a sand-packed column reactor at a constant temperature of 160 $^{\circ}$ C.



Figure 2: Measured concentrations of a conservative tracer, 1,5-nds, and a reversibly adsorbing tracer, Safranin T, in the effluent of a flow experiment using a sand-packed column at 160 °C.

The tracers' measured response was used to characterize Safranin T's advection relative to that of a conservative tracer. This response is the relative retardation, which is related to the adsorption equilibrium constant K_d by equation 1:

$$K_d = (RF - 1) * N_e/P_b$$

where RF is the retardation factor as measured from a plot such as in Figure 2, N_e is the effective porosity of the medium (pore volume divided by total column volume) and P_b is the bulk density of the porous medium (mass of shale cuttings in column divided by total column volume). Once K_d for a reactive tracer has been determined, it can be used to constrain the tracer-contacted, fracture surface area, which is proportional to the surface area for heat transfer (Pruess et al., 2005; Fayer et al., 2009; Reimus et al., 2012; Rose et al., 2012).

Shown in Figure 3 are plots of a conservative tracer, 1,6-naphthalene disulfonate that was co-injected with Safranin T and then produced at a nearby production well. Unfortunately, like most textile dyes, Safranin T possesses poor thermal stability at geothermal reservoir temperatures and was severely thermally degraded. But after correcting for thermal decay, we were able to produce plots of the conservative tracer 1,6-naphthalene disulfonate and the temperature corrected, reversibly adsorbing, Safranin T. The tracer-contacted, interwell fracture surface area was subsequently determined (Reimus et al. 2012). But since Safranin T was severely thermally degraded, only about 3% of its original mass was produced.

Since the mean residence time for the interwell flow process was only about 5 days and since the reservoir temperature was only about 190 °C, Safranin T's thermal stability was considered to be inadequate as a reversibly adsorbing tracer for most geothermal applications. Nevertheless, the project was a success as the first documented experiment to constrain the tracer-contacted fracture surface-area-to-volume ratio in a geothermal reservoir using a reversibly adsorbing tracer.

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Figure 3. Return curves for an interwell tracer test using a conservative tracer (1,6-naphthalene disulfonate) and a reversibly adsorbing tracer (Safranin T) at the Soda Lake geothermal reservoir. Safranin T was severely thermally decayed, but since we had measured its decay kinetics, we were able to correct for thermal decay and reconstruct a portion of its undecayed return curve, as shown in blue in the figure.

2.2 Group 1A metals

Another group of reversibly adsorbing cations that meets most of the long list of candidate requirements is the Group 1A metals. Dean et al (2015) showed in laboratory flow experiments that cations from this group, e.g., lithium (Li⁺) and cesium (Cs⁺) rapidly exchange with other cations at the geothermal-fracture surface, primarily Na⁺, K⁺, Ca⁺⁺ and Mg⁺⁺. As with the fluorescent cations, this rapid exchange results in the retardation of these ions relative to a conservatively (e.g. negatively charged) advected tracer. The Group 1A metals possess most of the qualities required of reversibly adsorbing EGS tracers in that they possess excellent thermal stability, good availability and affordability. In addition, they are nontoxic and environmentally benign. But, unfortunately, they lack the property of multiplicity since there are only two that are commonly available, Li⁺ and Cs⁺.

Shown in Figure 4 are the simulated breakthrough curves for a non-adsorbing naphthalene sulfonate tracer that was co-injected into a laboratory flow reactor with reversibly adsorbing Li+ and Cs+ at 225 °C. Rock properties, adsorption data and other parameters for this simulation were adapted from Reimus et al., (2003), Reimus et al., (2020); Dean et al., (2015). The partition coefficient values for lithium and cesium were 0.22 ml/g and 5.2 ml/g respectively. Mean residence time of 7.7 hr, Peclet number of 71, and fracture half aperture of 0.005 cm were used as input in a single porosity finite system assuming a completely open planar fracture (fracture porosity equals 100% in a 1D flow direction). The simulated experiment involved the injection of a tracer pulse for 22 hr such that the tracer injection concentration is 10 mg/L Li⁺ (or Cs⁺) yielding a lithium and cesium fracture retardation factors of 3.5 and 6.7 respectively.

Shown in Figure 5 are the simulated breakthrough curves for a tracer experiment like the one conducted during the August, 2024 circulation test at the FORGE EGS site, using a model calibrated from the laboratory experiment described above. Similar rock properties and adsorption parameters were adopted for this simulation. The field simulation results were obtained by assuming a dual porosity semiinfinite system with a mean residence time of 168 hr, Peclet number of 7, matrix porosity of 1% and a recirculation ratio of 0.265 (0 = no recirculation, 1 = full recirculation). The lithium and cesium fracture retardation factors observed were 3.5 and 6.7 respectively, and the matrix retardation factors were 4 and 8 for lithium and cesium respectively.



Figure 4: Typical measured concentrations of a conservative tracer, 1,5-nds, and reversibly adsorbing tracers, Li and Cs, in a short flow experiment in a single porosity finite matrix domain at 225 °C.



Figure 5: Simulated concentrations of a conservative tracer, 1,5-nds, and reversibly adsorbing tracers, Li and Cs, in a long flow experiment at 225 °C using a dual porosity semi-infinite matrix domain with tracer recirculation.

2.3 Fluorescent nanoparticles

A third category of candidate reversibly adsorbing tracers for geothermal tracing is fluorescent colloids, including quantum dots and silica nanoparticles. But whereas these colloids potentially address all the issues of thermally stability, detectability, affordability, nontoxicity and, especially, multiplicity, they risk being filtered to some extent by the tiny pore spaces and narrow channels in geothermal reservoirs since they are orders of magnitude larger than molecular tracers. Therefore, resistance to filtration is an additional hurdle to be cleared in the design of colloidal geothermal tracers.

2.3.1 Quantum dots

Fluorescent colloidal nanocrystals (quantum dots) are very small crystallites of semiconductors in the size range of about 5 to 15 nm that are composed of a few hundred atoms. As a result of quantum size effects and strongly confined excitons, quantum dots display unique size and shape-related electronic and optical properties. In particular, they can be made to fluoresce brightly over a wide range, including the visible and near infrared (NIR) regions of light – regions where geothermal and EGS reservoir waters possess very little interference (Rose et al., 2010). Whereas the inorganic semiconducting nanocrystal core delivers tunable emission colors, the surface chemistry of colloidal quantum dots can independently be adjusted by the choice of ligands to optimize their interaction with the sensing environment (e.g., hydrophilic/hydrophobic, chemically functional groups, positively/negatively charged surface, etc.). They could then be used to interrogate interwell fracture-surface area in EGS reservoirs in a manner similar to that of the reversibly adsorbing solute molecules described above. As with all colloidal tracers, questions remain regarding the problem of filtering within dual porosity geothermal reservoirs, resulting in the possibility of permanent nanoparticle trapping.



Figure 6. Photoluminescence images and UV-vis absorption spectra of a range of CdSe quantum dot samples (Rose et al., 2010).

2.3.2 Silica nanoparticle tracers

Silica nanoparticle tracers consist of tiny spheres of mesoporous silica filled with thermally stable molecules that fluoresce in the visible (Spitzmüller et al., 2023). The particles are coated with a thin layer of an appropriate, pore-blocking material (e.g., titanium oxide) that prevents the fluorescent molecules from leaking away. As with the quantum dots, the surfaces of such anatase-coated silica nanoparticles can be modified by bonding charged ligands that can render them either resistant or conducive to adsorption onto negatively charged, geothermal fracture surfaces. This offers a powerful tool for tuning the degree of adsorption beyond what is available for solute tracers.

Silica nanoparticle tracers offer potential advantages over quantum dot tracers in that they have been much more thoroughly studied for the effects of straining, dispersion, diffusion, coagulation, gravity and adsorption in fractured and porous media (Spitzmüller et al., 2025). However, an advantage that quantum dots possess over silica nanoparticles is that they offer a very large number of distinct tracer colors. Since the wavelength at which quantum dots fluoresce is dependent only on the diameter of the crystalline CdSe core, the number of tracers becomes a practical challenge of synthesizing cores with distinct diameters. But since the visible/IR spectrum is quite wide, there are potentially dozens of distinct quantum dot tracers that could be synthesized. In contrast, conventional silica nanoparticle tracers are limited by the very few thermally stable fluorescent molecules available for filling the pores in their cores. This means that they fail the requirement of multiplicity. Perhaps the best approach is to combine the best of both worlds by replacing the porous-silica-nanoparticle core with a quantum dot core. This would overcome the silica nanoparticle limitations of dissolution and multiplicity, while maintaining their other advantages. The silica nanoparticle tracers would then become the only category of candidate reversibly adsorbing tracers to potentially satisfy all of the requirements of thermal stability, detectability, nontoxicity, affordability and multiplicity.

3. SUMMARY AND CONCLUSIONS

The use of reversibly adsorbing tracers in combination with conservative tracers can serve to measure the interwell surface area of EGS reservoirs; this tracer-contacted surface area is related to the surface area for heat transfer, which is a very important parameter for measuring reservoir performance and sustainability. Various families of tracer candidates were screened for their potential use as reversibly adsorbing compounds in Engineered Geothermal Systems. In order to pass the screening test for suitability, each candidate had to possess all of the properties of the conservative geothermal tracers—thermal stability, excellent detectability, nontoxicity, affordability and multiplicity—in addition to being reversibly adsorbing on geothermal reservoir rock.

The three families of tracers considered were anionic fluorescent molecules, cationic exchanging Group 1A metals, and fluorescent nanoparticles. None of the anionic geothermal tracers showed any propensity to adsorb on freshly fractured granites at the FORGE Utah EGS site, in spite of some having been shown to reversibly adsorb on high temperature petroleum shale reservoirs. The Group 1A metals satisfied most of the conditions, but failed the detectability and multiplicity tests. The fluorescent nanoparticles showed promise for satisfying all of the conditions with the exception of affordability, since they are not yet available in bulk and must be synthesized by a laborious laboratory batch process.

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