LABORATORY TESTING AND MODELING TO EVALUATE PERFLUOROCARBON COMPOUNDS AS TRACERS IN GEOTHERMAL SYSTEMS

Paul W. Reimus[1], Thomas Watson[2], Vince Vermeul[3], Dennis Newell[1], and Mark Williams[3]

[1]Los Alamos National Laboratory, P.O. Box 1663, MS J966, Los Alamos, NM 87545
[2]Brookhaven National Laboratory, 75 Rutherford Dr., Upton, NY 11973
[3]Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99352

e-mail: preimus@lanl.gov

ABSTRACT

The thermal stability and adsorption characteristics of three perfluorinated hydrocarbon compounds were evaluated under geothermal conditions to determine the potential to use these compounds as conservative or thermally-degrading tracers in Engineered (or Enhanced) Geothermal Systems (EGS). The three compounds tested were perfluorodimethyl-cyclobutane (PDCB), perfluoromethylcyclohexane (PMCH), and perfluorotrimethylcyclohexane (PTCH), which are collectively referred to as perfluorinated tracers, or PFTs. Two sets of duplicate tests were conducted in batch mode in gold-bag reactors, with one pair of reactors charged with a synthetic geothermal brine containing the PFTs and a second pair was charged with the brine-PFT mixture plus a mineral assemblage chosen to be representative of activated fractures in an EGS reservoir. A fifth reactor was charged with deionized water containing the three PFTs. The experiments were conducted at ~100 bar, with temperatures ranging from 230C to 300C.

Semi-analytical and numerical modeling was also conducted to show how the PFTs could be used in conjunction with other tracers to interrogate surface area to volume ratios and temperature profiles in EGS reservoirs. Both single-well and cross-hole tracer tests are simulated to illustrate how different suites of tracers could be used to accomplish these objectives. The single-well tests are especially attractive for EGS applications because they allow the effectiveness of a stimulation to be evaluated without drilling a second well.

INTRODUCTION

Perfluorinated hydrocarbons have previously been used as vapor-phase tracers in geothermal reservoirs (Sugandhi et al., 2009; Bloomfield and Moore, 2003). Their thermal stability in the gas phase and low solubility in water make them well suited to trace the vapor/steam phase in two-phase geothermal systems. In this paper, we present the preliminary results of experiments designed to evaluate the potential use of perfluorinated hydrocarbons as tracers in single-phase aqueous geothermal systems. Despite their low solubility in water (on the order of 1-10 ppm), the perfluorinated tracers, or PFTs, can still serve as effective aqueous-phase tracers because of the ability to quantify them at parts-per-quadrillion levels using analytical methods developed at Brookhaven National Laboratory. These methods have been perfected over many years for atmospheric dispersion tests and detection of gas leaks (Draxler et al., 1991, Senum et al, 1997).

To our knowledge, the thermal stability of PFTs has not previously been evaluated in the aqueous phase under geothermal conditions. Our principle objective in this study was to address this information gap. To do this, we conducted thermal stability experiments with three different PFTs that span nearly the full range of molecular weights and boiling points of PFTs that are commonly used as gas-phase tracers: perfluorodimethylcyclobutane (PDCB, bp = 45C), perfluoromethylcyclohexane (PMCH, bp = 76C), and perfluorotrimethylcyclohexane (PTCH, bp = 125C). If the thermal stability of these compounds could be demonstrated, thermal stability of other commonly-used PFTs could be confidently inferred. Additionally, the experiments were intended to evaluate the potential adsorption of PFTs to mineral phases that may be present in geothermal systems. Such sorption is not expected for these nonpolar compounds, but if it did occur, it would greatly complicate and possibly preclude the use of the PFTs as aqueous-phase geothermal tracers.

We recognize that the practical use of PFTs in aqueous-dominated geothermal systems depends not only on a knowledge of their thermal stability, but also on the ability to introduce the tracers and collect water/brine samples without inadvertently losing them by volatilization to any gas phase present. The PFTs will partition very strongly and rapidly to any

gas phase they encounter. Such partitioning could also occur in the subsurface if vapor/steam pockets develop in an otherwise liquid-dominated system.

The aqueous partitioning of the PFTs at low concentrations can be determined by the Henry's Law, $p_a = x_a K$, where p_a = partial pressure of the PFT, x_a = mole fraction of the PFT in solution, and K = Henry's Law constant. The Henry's Law constant for the PFT PDCB is 2.4 x 10^3 atm/weight%. Using this relationship it can be shown that about 98% of the PFT in a solution will be transferred to the headspace whenever the aqueous solution comes in contact with a significant volume of gas phase whether in sample handling or in a geothermal environment.

In recognition of these potential difficulties, we are pursuing the development of microencapsulated PFTs as sub-micron-sized particle tracers. With this concept, the PFTs will remain encapsulated and thus not be detected in geothermal production fluids unless the particles encounter a temperature-time history that causes their shells to breach. Shell materials are being developed and tested that will thermally degrade under different temperature-time conditions so that the detection of PFTs in production fluids can be related to specific reservoir temperature conditions. The extremely low detection limits of the PFTs should make this method very sensitive for interrogating temperature profiles in reservoirs.

We also summarize in this paper the modeling of both cross-hole and single-well tracer tests to illustrate the potential uses of PFTs as thermally-degrading tracers (either by direct degradation as aqueous-phase tracers or by degradation of particle shells to release encapsulated PFTs). A semi-analytical model was developed to efficiently simulate simultaneous heat and mass transfer in cross-hole tracer tests. This model was used to evaluate optimal Arrhenius decay parameters as a function of reservoir temperatures and tracer residence times in cross-hole tests. A numerical model was implemented to simulate heat and mass transfer in single-well tests, illustrating how the PFTs might be used in these types of tests.

EXPERIMENTAL METHODS

The thermal stability experiments were conducted at Los Alamos National Laboratory in flexible gold bag reactors that were placed inside stainless steel pressure vessels filled with deionized water that served as a pressurizing fluid. The pressure vessels were inserted into resistance-heated furnaces to provide temperature control. Figure 1 is a schematic of the experimental apparatus. Two duplicate experiments were conducted with PFTs in a synthetic geothermal brine, two with PFTs in the synthetic

brine plus a crushed mineral assemblage (0.5-2 mm size range) considered representative of activated fractures in a geothermal reservoir, and one experiment was conducted with PFTs in deionized water. The synthetic brine recipe and mineral assemblage are listed in Tables 1 and 2, respectively.

Each gold reaction bag was charged first with the aqueous solutions and minerals, and then approximately 1 ml of a nearly saturated solution of the 3 PFTs in deionized water was injected as far below the liquid surface as possible in the reactors using a long syringe needle to minimize PFT losses to volatilization. The reactors were then sealed (with a titanium flange/cap equipped with a sampling tube) and inserted into the stainless steel pressure vessels. Once inside the pressure vessels, the reactors were purged of air, and a sample of the aqueous phase was collected to allow measurement of the initial PFT concentrations. After leak testing, the vessels were pressurized to 100 bar and then inserted into furnaces to be brought up to 230C where they were maintained for anywhere from 21 to 28 days. Duplicate aqueous samples (~1 ml each) were collected from each reactor at regular intervals by slowly opening a needle valve at the end of the sampling tube and allowing liquid to be forced out of the bags into gas-tight syringes. Each time a sample was taken, the bags collapsed slightly under the confining pressure of the deionized water inside the pressure vessels (but outside the bags). The confining pressure was always
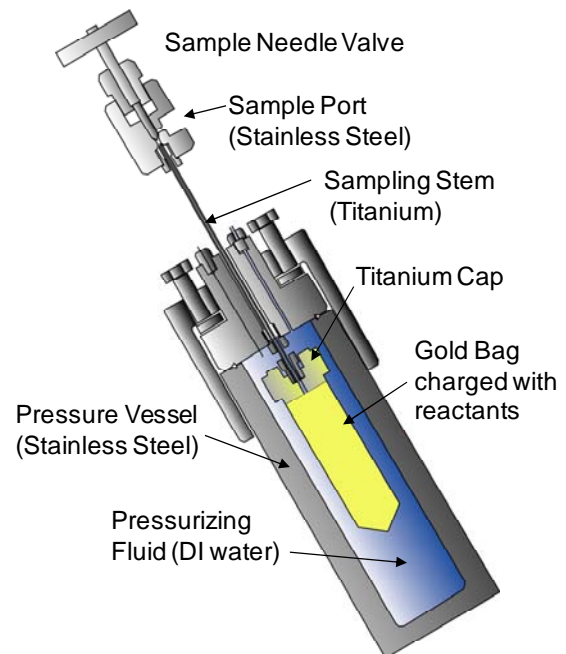

Figure 1: Schematic of experimental apparatus used for the tracer thermal stability experiments.

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	0.400
$NaHCO_3$	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

Table 2: *Mineral assemblage added to the two reactors containing minerals.*

Mineral	Mass (g)
Analcime	4.0
Anhydrite	4.0
Chlorite	4.0
Epidote	4.0
Hematite	4.0
Illite*	4.0
Microcline	4.0
Montmorillonite*	1.0
Muscovite*	2.0
Olivine Basalt	4.0
Pyrite	4.0
Quartz	4.0

*These minerals included material that was < 0.5 mm or >2 mm in the case of muscovite.

maintained above the boiling point of the aqueous phase during the sampling events.

After 21 to 28 days at 230C, the reactor temperatures were raised to 300C for the remainder of the experiments. The reactors were still being maintained at 300C at the time this paper was written. Sampling is planned to continue until the bags are collapsed to about half their original volume, which is the minimum volume that still allows reliable recovery and reuse of the bags.

Aqueous samples collected from the reactors were injected through septa into gas-tight vials that had been pre-purged with high-purity nitrogen. These were sent to Brookhaven National Laboratory for analysis. Based on previous experience, it was known that the PFTs would partition entirely to the headspace gas in the vials. Samples of the headspace gas were analyzed using a highly optimized gas chromatography process involving catalytic reaction steps to eliminate potential interfering compounds and culminating in electron capture detection, which is highly sensitive to halogenated compounds like the PFTs. Samples were also periodically collected from the reactors containing brine and brine plus minerals for major ion analysis and pH measurements. The brine chemistry was observed to change with time in the reactors with minerals because of hydrothermal alteration of the mineral phases. The results of these analyses are not reported here.

MODELING METHODS

A semi-analytical model was developed to conduct rapid scoping calculations of responses of thermally degrading and diffusing tracers in cross-hole tracer tests in geothermal systems. The model is based on an existing Laplace transform inversion model for solute transport in dual-porosity media (Reimus et al., 2003). The heat- and mass-transfer calculations are decoupled and conducted sequentially, taking advantage of the fact that heat transfer between fractures and the rock matrix is much more rapid than mass transfer and therefore mass transfer will effectively occur in a locally isothermal system (although the system will be nonisothermal along fracture flow pathways, which is accounted for by discretizing the flow pathways into multiple segments that have different temperature histories). The model takes advantage of the analogies between mass and heat transfer, solving essentially the same governing equations (see Figure 2 for the assumed model geometry):

Mass Transport:

Fractures:
$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - gC - q \qquad (1)$$

Matrix:
$$\frac{\partial C}{\partial t} = D_m\frac{\partial^2 C}{\partial y^2} - gC \qquad (2)$$

F-M Interaction Term:
$$q = -\left[\frac{\phi D_m}{b}\frac{\partial C}{\partial y}\right]_{y=b} \qquad (3)$$

Matrix B.C.:
$$\frac{\partial C}{\partial y} = 0 \; at \; y = \frac{L}{2} \qquad (4)$$

Heat Transport:

Fractures:
$$\frac{\partial T}{\partial t} = -v\frac{\partial T}{\partial x} + D\frac{\partial^2 T}{\partial x^2} - q_T \qquad (5)$$

Matrix:
$$\frac{\partial T}{\partial t} = \frac{k_m}{(\rho C_p)_m}\frac{\partial^2 T}{\partial y^2} = \alpha_m\frac{\partial^2 T}{\partial y^2} \qquad (6)$$

F-M Interaction Term:
$$q_T = -\left[\frac{\alpha_m}{b(\rho C_p)_w}\frac{\partial T}{\partial y}\right]_{y=b} \qquad (7)$$

Matrix B.C.:
$$\frac{\partial T}{\partial y} = 0 \; at \; y = \frac{L}{2} \qquad (8)$$

where, C = tracer concentration (g/cm^3), T = temperature (C or K), v = flow velocity in fractures
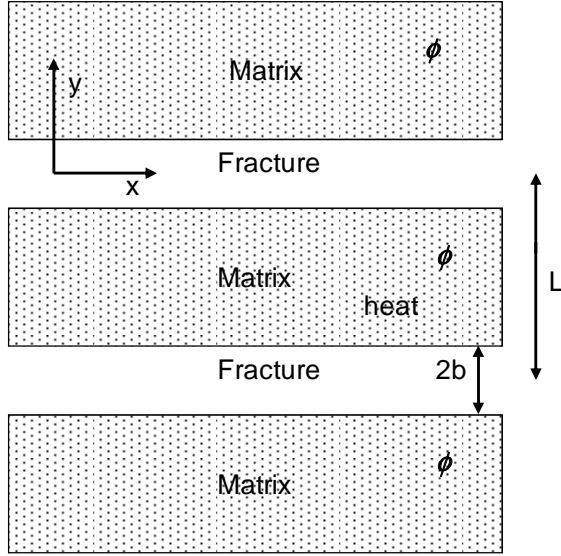
Figure 2: Assumed model geometry.

(cm/s), D = tracer dispersion coefficient (cm^2/s), g = first-order thermal decay rate constant (s^{-1}), D_m = tracer diffusion coefficient in matrix (cm^2/s), ϕ = matrix porosity, b = fracture half aperture (cm), L distance between fractures (cm), k = thermal conductivity (cal/cm-s-K), ρ = density (g/cm^3), C_p = heat capacity at constant pressure (cal/g-K), and α = thermal diffusivity, with the subscripts w and m referring to water and matrix, respectively. With the exception of the thermal decay term in the mass transport equations, the equations for mass and heat transfer are identical, with $k_m/(\rho C_p)_w$ being substituted for ϕD_m in the equation for fracture heat transport and $k_m/(\rho C_p)_m$ being substituting for D_m in the equation for matrix heat transport. A significant advantage of the model is that it executes in a fraction of second on a single-CPU personal computer, making it very amenable for parameter estimation algorithms that involve repeated runs to find global minima.

One of limitations of the semi-analytical model is that the Laplace transform solution method can only accommodate steady-state flow conditions, so it cannot be used to simulate single-well injection-backflow tests. To simulate single-well tests, a numerical model was employed that assumes the same geometry as Figure 2 and implements equations (1) through (8). This model is a version of an existing mass transport numerical model (Reimus 2002; Sullivan et al., 2003) that has been modified to simultaneously solve for heat and mass transport.

Both models were exercised to evaluate responses of PFTs that could be expected in the two types of tracer tests relative to other tracers. The semi-analytical model was also used to conduct a general investigation of the optimal Arrhenius decay parameters for thermally-decaying tracers as a function of reservoir temperature and tracer residence times in cross-hole tracer tests. According to Arrhenius theory, the thermal decay rate constant, g, varies with temperature as:

$$g = Ae^{-\frac{E_a}{RT}} \qquad (9)$$

where A = pre-exponential factor (s^{-1}), E_a = activation energy (cal/mol), and R = gas constant (cal/K-mol). In an analysis presented in the Results section, it is shown how PFTs encapsulated in thermally-decaying shells could significantly increase the range of Arrhenius parameters that could be used to interrogate temperature profiles in geothermal reservoirs.

EXPERIMENTAL RESULTS

The experimental results clearly reflected the difficulties in working with sparingly soluble tracers that have a strong tendency to partition to the gas phase. The concentrations of PFTs in the samples taken from the reactors were much lower and more scattered than anticipated, and even samples of the stock solutions taken prior to injection into the reactors (at room temperature) had orders of magnitude lower PFT concentrations than samples of the same stock solutions that were collected and analyzed at Brookhaven prior to shipment to Los Alamos. Also, the concentration ratios of the high volatility and low volatility PFTs were the opposite of what was expected in some cases. These results, especially for the stock solution samples, cannot be attributed to thermal decay. Rather it seems that one or a combination of the following must have occurred:

- The PFTs somehow escaped from the stock solution vials before the solutions were injected into the reactors (note that the stock solutions were shipped in vials containing little to no headspace gas).
- The PFTs escaped from the reactor solutions before the reactors could be sealed (which took only a few minutes after stock solution injection).
- The PFTs partitioned to the small amount of air that remained in each reactor after sealing and then escaped when this air was bled from the reactors prior to reactor pressurization.
- The PFTs escaped from the sample vials during the long time period (up to 5 weeks) between sample collection and analysis. Pressure changes during transportation from New Mexico to New York may have been a contributing factor.
- The syringes used to collect the samples allowed the PFTs to escape during the sampling process.
- The PFTs absorbed significantly to internal syringe components during the sampling process.

- Gas pockets formed in the reactors, and the vast majority of the PFT mass in the reactors partitioned to these gas pockets, which were not sampled.

Given previous experience with PFT handling and sample vial usage at Brookhaven, none of these explanations seem entirely consistent with the very low and variable concentrations measured in all the samples.

Although the intent was to collect strictly liquid samples, it was observed that variable amounts of gas were collected in the syringes used to sample the reactors, and the PFTs could have partitioned to this gas phase before the liquid portion of the sample was injected into a sample vial. Whenever gas was present in a syringe, as much of it as possible was injected into a sample vial along with the liquid portion of the sample. Thus, even if PFTs partitioned to the gas phase in the sample syringes, the majority of the PFT mass in each sample should have made it into a sample vial. Also, the samples of the stock solutions collected prior to injecting the tracers into the reactors were collected as liquid-only samples in gas-tight syringes that were different (glass rather than plastic) than the syringes used to collect the reactor samples.

A satisfactory explanation for the low and variable PFT concentrations would require significantly more investigation, but these results make it apparent that the use of PFTs as aqueous-phase tracers in geothermal systems would be extremely challenging in a field setting. If the PFTs could not be adequately introduced or sampled in a controlled laboratory environment, then the situation could hardly be expected to improve in the field. Significant method development involving more complicated sampling protocols will be required if the use of PFTs as aqueous-phase tracers is to be pursued further.

Based on these results, we are now exclusively pursuing the encapsulation of PFTs in sub-micron-sized particles that have shells that are either stable with respect to temperature decay or degrade at different rates as a function of temperature. The motivation for developing these particle tracers is discussed in the next section.

MODELING RESULTS

Cross-hole testing with thermally-decaying tracers

Figure 3 shows results of using the semi-analytical model to simulate the temperature drawdown in a geothermal reservoir that is initially at 250C with water being injected continuously under steady-flow conditions at 150C. The fluid residence time in the system is assumed to be 300 hr, with average fracture
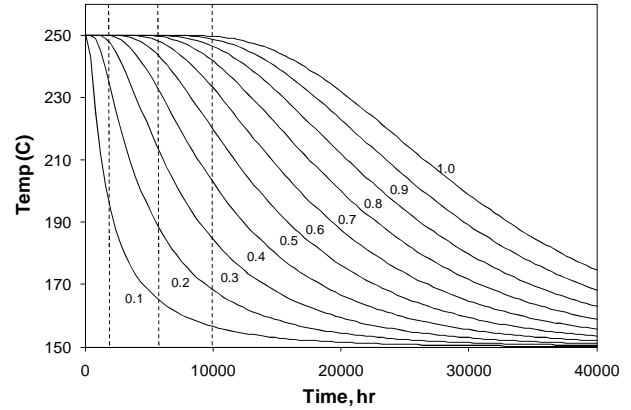

Figure 3: Temperature vs. time at different fractional distances (numbers next to curves) between an injection well and production well in a 250C reservoir that is injected with 150C water. Dashed vertical lines are times of simulated tracer tests shown in Figure 4.

apertures of 0.05 cm and a fracture spacing of 20 cm. The fluid and rock thermal properties correspond to water and basalt. Each curve in Figure 3 corresponds to the temperature-time history for a different fractional distance (or fractional residence time) between the injection and production wells. It is apparent that the reservoir volume closest to the injection well cools the fastest. Thermal breakthrough does not occur at the production well until approximately 12,000 hours into the operation of the reservoir.

The dashed vertical lines in Figure 3 at 2000, 6000, and 10,000 hours into reservoir operation correspond to times at which tracer tests involving a thermally-decaying tracer were simulated. The simulated breakthrough curves of the thermally-decaying tracer are shown in Figure 4 along with a conservative tracer that does not thermally decay. The Arrhenius constants used for the temperature dependence of the thermally-decay constant were $A = 5 \times 10^7$ s^{-1} and $E_a = 32,000$ cal/mol (comparable to parameters reported for fluorescein by Adams and Davis, 1991). The slight differences in the breakthrough curves of the conservative tracer at 2000 hr and 10,000 hr are due to the temperature dependence of matrix diffusion coefficients, which is accounted for in the model using:

$$\frac{D_{T_2}}{D_{T_1}} = \frac{T_2}{T_1} \frac{\mu_{T_1}}{\mu_{T_2}} \qquad (10)$$

where D_{T_x} = diffusion coefficient at temperature T_x, and μ_{T_x} = liquid viscosity at temperature T_x.
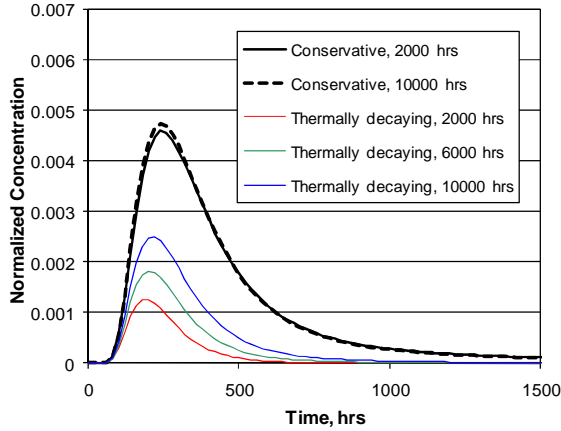
Figure 4: Breakthrough curves of a conservative (thermally stable and nonsorbing) tracer and of a thermally-decaying (nonsorbing) tracer corresponding to the reservoir temperature profiles of Figure 3 at 2000, 6000, and 10,000 hours. Injection was assumed to take place over 2 hours.

The key point in Figure 4 is that the difference in the breakthrough curves of the thermally-decaying tracer relative to the conservative tracer at the three different times (or even two of the three times) could be used to provide an indication of when thermal breakthrough will occur before it is actually observed at the production well (~12,000 hours). This early indication could be used to proactively plan reservoir operations to minimize decreases in power production efficiency caused by unexpected decreases in production fluid temperature. Inverse modeling could be used in conjunction with the best available information on reservoir geometry and reservoir thermal and mass transfer properties to predict thermal breakthrough based on the observed breakthrough curves.

It is logical to consider the optimal Arrhenius decay parameters for interrogating a reservoir in which temperatures and tracer residence times are relatively well known but cannot be controlled (note that residence times can sometimes be controlled to a limited extent by varying injection and production rates). The optimal parameters will result in tracer thermal decay that is sufficient to be distinguished from an undecayed response after consideration of analytical measurement error but not so great that the tracer becomes undetectable. Example sets of breakthrough curves for these two extremes are illustrated in Figure 5, although in the example provided for too much decay (right plot) significantly more decay might be tolerated if detection limits and background concentrations are favorable.
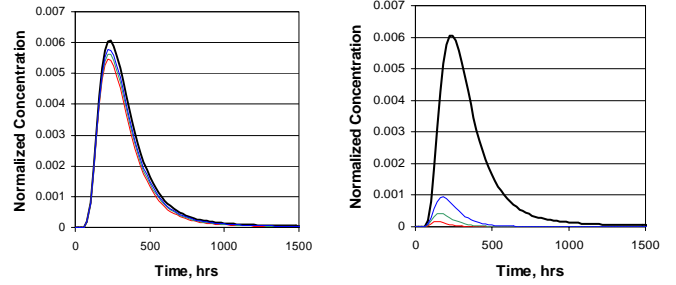

Figure 5: Breakthrough curves of thermally-decaying tracer relative to a conservative tracer (same conditions and times as Figure 4) with less than desirable decay (left) and more than desirable decay (right).

Figure 6 is a plot of $\log(A\tau)$ vs. E_a/RT (where τ is the mean tracer residence time in a geothermal system), which can be used to determine acceptable ranges of the Arrhenius parameters A and E_a as a function of temperature and residence time. The solid diagonal line corresponds to $g = 2/\tau$, which is considered an optimal decay rate constant that will result in significant decay over the time scale of a tracer test while still yielding relatively high tracer concentrations that can be readily quantified. The dashed lines on either side of the solid line correspond approximately to the situations shown in the two plots of Figure 5; the upper line corresponds to the right plot, and the lower line corresponds to the left plot of Figure 5.

Note that although the range of acceptable values of A and E_a in Figure 6 seems rather narrow, the log scale for the y axis and the fact that E_a/RT is the argument of an exponential function in equation (9)
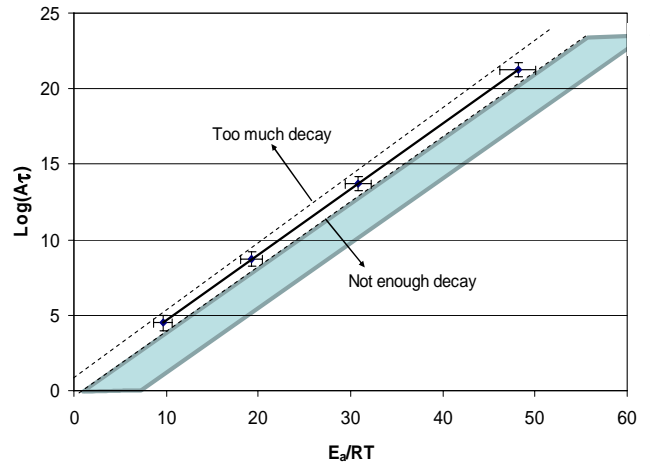

Figure 6: Plot of $\log(A\tau)$ vs. E_a/RT, showing acceptable ranges of the Arrhenius parameters A and E_a as a function of temperature and residence time.

allows for approximately a 2 order of magnitude range in A for any given E_a value and approximately a 15-20% range in E_a for any given A value. Also, the practical range of mean residence times for a tracer test is ~1 day to ~1 year, or about 2.5 orders of magnitude, which is a relatively small fraction of the full range of the y axis.

Importantly, if PFTs are encapsulated in shells that degrade quite slowly with temperature and time, they might allow a significant expansion of the acceptable region in Figure 6 in the direction of "too little decay". The extremely low detection limits of the PFTs would allow very small fractions of breached shells to be readily detected. In this case, rather than trying to measure a very small difference between the normalized concentrations of a conservative tracer and unbreached particles, the concentrations of the PFTs released by the breached particles could be used to determine the very small fraction of particles that breached, thus providing a very sensitive measure of thermal decay of the particle shells in the system.

Furthermore, the fraction of breached particles in any sample could be readily determined by first measuring the PFT concentrations in the sample without any treatment, and then treating the sample (chemically or otherwise) to intentionally breach all the remaining intact particles and (re)measuring the resulting PFT concentrations. The ratio of the PFT concentrations before and after the treatment should provide a good measure of the ratio of breached particles to total particles in the sample. The shaded region in Figure 6 is an approximation of the expanded region that could be exploited using this method (based on PFT detection/quantification limits). Of course, this assumes that the sampling and sample storage/handling problems that occurred in the laboratory experiments can be satisfactorily addressed, and it also assumes that the thermal decay properties (i.e., the Arrhenius parameters) of the shell materials are well characterized.

Single-well testing with encapsulated PFTs

Figure 7 shows a simulated set of breakthrough curves from a single-well injection-withdrawal test involving encapsulated PFTs and conventional conservative solute tracers. In this case, the shells of the PFTs are assumed to not degrade with temperature, and the responses of the encapsulated PFTs relative to the conservative solutes reflect differences in the diffusion coefficients of the different tracers in the matrix that makes up the walls of the fractures. The encapsulated PFTs have a higher peak concentration and more truncated tail than the solute tracers because they have much

smaller matrix diffusion coefficients than the solutes. The lumped mass transfer parameter controlling the
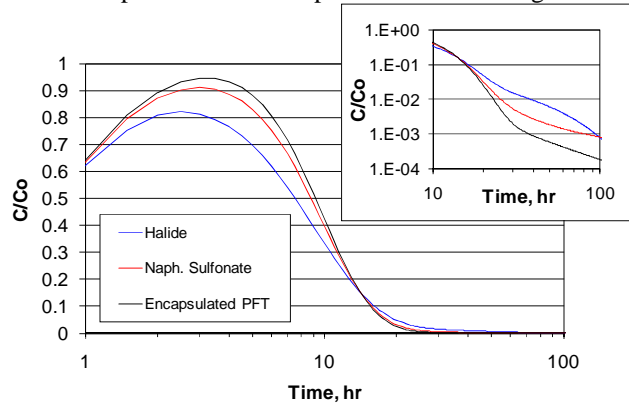

Figure 7: Simulated breakthrough curves of a halide, a naphthalene sufonate, and an encapsulated PFT tracer in a single-well tracer test. Pumping started at zero hours, with injection occurring at -10 hours and lasting 9.9 hours. Inset shows log normalized concentrations in the tails. The halide and naphthalene sulfonate have diffusion coefficients that differ by a factor of ~4.

differences in the responses of the tracers is $\frac{\phi}{b}\sqrt{D_m}$

(Reimus and Callahan, 2007) , so if ϕ and the ratio of D_m values for the different tracers is known, an estimate of b, the fracture half aperture, can be obtained. Note that b is equal to the fracture volume divided by the fracture surface area, so an estimate of b provides an estimate of the surface area to volume ratio in a flow system.

The advantage of using the encapsulated PFTs with this single-well testing method for interrogating fracture surface area is that the particle tracers have 2-3 orders of magnitude smaller diffusion coefficients than solute tracers, so they dramatically increase the sensitivity of the method compared to the use of solutes with different diffusion coefficients (which are limited to a factor of 3-4 difference in diffusion coefficient). This sensitivity could be especially helpful in systems with low matrix porosities where matrix diffusion is minimal (for example, granitic basement rocks).

If the encapsulated PFTs experience thermal degradation, the degradation can be readily accounted for using the approach described in the previous subsection. Also, additional information could be obtained regarding the heat transfer characteristics of the system if thermal degradation of the particle shells occurs. Although not explored in this paper, the heat transfer information obtained from thermally-decaying tracers in single-well tests should

be complimentary to the information obtained from temperature breakthrough curves (Pruess and Doughty, 2010).

The same concept (tracers with significant diffusion coefficient contrast) could also be used to interrogate surface area to volume ratios in cross-hole tests. However, the appeal of single-well testing methods relative to cross-hole methods is that the effectiveness of an EGS stimulation in generating fracture surface area could be evaluated without the need for a second well. This would allow decisions to be made regarding whether the considerable expense of drilling a second well to create a heat extraction loop is justified in a potential EGS system.

DISCUSSION AND CONCLUSIONS

The ability to detect PFTs at extremely low concentrations (part per quadrillion levels) makes them very appealing as potential aqueous-phase geothermal tracers. In a system where a 100 kg injection of a conventional geothermal tracer results in ppb concentrations in the production fluid, as little as 1-10 g of a PFT could be used to obtain an interpretable breakthrough curve.

Unfortunately, the experimental results reported here (or lack thereof) indicate that there are many challenges to be overcome if PFTs are ever to be practical as aqueous-phase geothermal tracers. Even if the sampling and sample handling/storage issues can be adequately addressed, the potential presence of steam or gas pockets in reservoirs and the degassing of solutions that can occur either during injection or production in an otherwise liquid system will likely limit the use of PFTs as aqueous-phase tracers to a very few special cases.

For these reasons, we are pursuing the development of encapsulated PFTs as submicron-sized particle tracers that either have shells that are stable with respect to thermal decay or that degrade at known rates as a function of temperature. We provided simulation examples of how particulate tracers with either of these characteristics could be used in cross-hole and single-well tracer tests to interrogate surface area and heat transfer characteristics of geothermal reservoirs. Of course, the methods involving thermally-decaying particle shells to release PFTs into solution and quantifying thermal decay by measuring free PFT concentrations relative to encapsulated PFT concentrations will require that the challenges mentioned above be overcome.

PFTs have already been incorporated into microcapsules made of 5 different materials. These capsules are currently under evaluation to determine their thermal stability at atmospheric pressure. After initial testing is finished we plan to test the thermal stability of the microcapsules in the same types of experiments as those described in the Experimental Methods section.

REFERENCES

Adams, M. C. and Davis, J. (1991), "Kinetics of Fluorescein Decay and Its Application as a Geothermal Tracer", *Geothermics*, **20**(17), 53-66.

Bloomfield, K. K. and Moore, J. N. (2003), "Modeling Hydrofluorocarbon Compounds as Geothermal Tracers," *Geothermics*, **32**, 203-218.

Draxler, R. R.; Dietz, R.; Lagomarsino, R. J.; Start, G., 1991, Across North America Tracer Experiment (ANATEX): Sampling and Analysis. *Atmos. Environ.*, **25A,** 2815-2836**.**

Pruess, K. and Doughty, C. (2010), "Thermal Single-Well Injection-Withdrawal Tracer Tests for Determining Fracture-Matrix Heat Transfer Area," *Proceedings, 35th Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, CA, Feb. 1-3 2010.

Reimus, P. W. (2002), "Software Management Report for Multran Version 1.0," *Yucca Mountain Project Report*, Los Alamos National Laboratory, Los Alamos, NM (contact corresponding author).

Reimus, P. W. and Callahan, T. J. (2007), "Matrix Diffusion Rates in Fractured Volcanic Rocks at the Nevada Test Site: Evidence for a Dominant Influence of Effective Fracture Apertures," *Water Resources Res.*, **43**, W07421, doi:10.1029/2006WR005746.

Reimus, P. W., Pohll, G., Mihevc, T. Chapman, J., Papelis, L., Lyles, B., Kosinski, S., Niswonger, R. and Sanders, P. (2003), "Testing and Parameterizing a Conceptual Model for Radionuclide Transport in a Fractured Granite using Multiple Tracers in a Forced-Gradient Test", *Water Resources Research*, 39(12), 1350, doi:10.1029/2002WR001597.

Senum, G. I., D'Ottavio, T. W., Loss, W. M., Goodrich, R. W., Cote, E. A., Spandau, D. J., and Dietz, R., N., 1997, HPFF Cable Leak Location Using Perfluorocarbon Tracers, *Electric Power Research Institute TR-109086*, 7905-01

Sugandhi, A., Hirtz, P. N., Mahagyo, P., Nordquist, G. A., Martiady, K., Roberts, J. W., Kunzman, R. J. and Adams, M. C. (2009), "Results of the First

Application of Perfluorocarbons and Alcohols in a Multi-Well Vapor and Two-Phase Tracer Test at the Darajat Geothermal Field, Indonesia, and Implications for Injection Management," *GRC Transactions*, **33**, 871-878.

Sullivan, E. J., Reimus, P. W., and Counce, D. A. (2003), "Transport of a Reactive Tracer in Saturated Alluvium Described using a Three-Component Cation-Exchange Model," *J. Contaminant Hydrology*, **62-63**, 675-694.