

TRACERS FOR CHARACTERIZING ENHANCED GEOTHERMAL SYSTEMS

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ABSTRACT

Information about the times of thermal breakthrough and subsequent rates of thermal drawdown in enhanced geothermal systems (EGS) is necessary for reservoir management, designing fracture stimulation and well drilling programs, and forecasting economic return. Thermal breakthrough in heterogeneous porous media can be estimated using conservative tracers and assumptions about heat transfer rates; however, tracers that undergo temperature-dependent changes can provide more detailed information about the thermal profile along the flow path through the reservoir. To be effectively applied, the thermal reaction rates of such temperature sensitive tracers must be well characterized for the range of conditions that exist in geothermal systems. Reactive tracers proposed in the literature include benzoic and carboxylic acids (Adams, Moore et al. 1992) and organic esters and amides (Robinson, Tester et al. 1984); however, the practical temperature range over which these tracers can be applied (100-275°C) is somewhat limited. Further, for organic esters and amides, little is known about their sorption to the reservoir matrix and how such reactions impact data interpretation. An alternative approach is to use of tracers where the reference condition is internal to the tracer itself. Two examples are: 1) mineral thermoluminescence, and 2) racemization in polymers of compounds such as amino acids. In these cases internal ratios of states are measured rather than extents of degradation and mass loss. Racemization of a polymeric amino acid is temperature sensitive and therefore can be used to infer temperature history depending on the rate of racemization and stability of the particular amino acid. Heat-induced quenching of thermoluminescence of pre-irradiated LiF can also be used. To protect the tracers from alterations (extraneous reactions, dissolution) in geothermal environments we are encapsulating the tracers in core-shell colloidal structures that will subsequently

be tested for their ability to be transported in geologic media and to protect the tracers from incidental reactions. In this report we review the criteria for practical reactive tracers, which serve as the basis for experimental testing and characterization and can be used to identify other potential candidate tracers. We will also discuss the information obtainable from individual tracers, and the possibilities for using multiple tracers to obtain improved information about the thermal history of a reservoir. Finally, we will provide an update on our progress for conducting proof-of-principle tests for reactive tracers in the Raft River geothermal system.

INTRODUCTION

Geothermal energy will be one component of the increasingly diversified global energy portfolio of the future. The magnitude of the contribution made by geothermal energy, like all energy sources, will depend on a combination of viable engineering and technological capabilities, market factors and social/political acceptance. Advances that reduce both cost and uncertainty will be critical to the design and operation of future geothermal energy sources. This paper summarizes initial progress at the Idaho National Laboratory toward the goal of determining whether synthetic colloidal tracers can be used in geothermal reservoir environments to record temperature along the flow path between points of injection and production.

“Traditional” systems rely on geothermal reservoir sources in relatively accessible, hydrologically conductive systems. Engineered geothermal systems (EGS, or “enhanced” geothermal systems) is a term applied to conditions where a larger and more uniformly distributed potential source of geothermal heat exists, but where fluid conductivity must be created, improved and maintained through fracturing or chemical alteration (Technology 2006). Model simulations of geothermal systems are used to predict the potential energy capacity of a reservoir and to

determine an optimal operation schedule, both of which are important for comparing the economic viability of a geothermal reservoir against alternative energy sources.

Developing and applying models for fluid flow and heat transport in conventional and engineered geothermal systems rely on field-scale characterization data. Such data can be obtained through the application of tracer tests. In this paper, we discuss some particle-based tracer approaches that are being developed at the Idaho National Laboratory.

BACKGROUND

Characterizations of the hydraulic properties of reservoirs use breakthrough data from injected conservative tracers, which are often soluble compounds (Rose, Johnson et al. 2001; Shook 2003; Shan and Pruess 2005). Conservative, artificial tracers can provide valuable information about reservoir residence times and flow paths that can be used to determine locations and operation of injection wells and heat transfer in the reservoir (Behrens, Ghergut et al. 2009). Geochemical modeling of the composition of produced fluids can provide evidence of temperature histories (Moller, Christov et al. 2006). Reactive tracers have been proposed and used where temperature-dependent reaction rates should provide a record of the temperature history along the flow paths (Robinson, Tester et al. 1984; Tester, Robinson et al. 1987; Nottebohm, Licha et al. 2009). This topic is discussed in a companion paper (Plummer, Palmer et al. 2009) in this workshop.

Colloid-based tracers

In some cases, particle-based tracers have been used for the characterization of subsurface flow (Harvey, George et al. 1989; Grindrod, Edwards et al. 1996; Vilks and Bachinski 1996; StrongGunderson and Palumbo 1997; Vilks, Frost et al. 1997; Niehren and Kinzelbach 1998; Becker, Reimus et al. 1999; Becker and Shapiro 2000; Knapp, Chiarappa et al. 2000; Vilks and Baik 2001; Becker 2003; Zvikelsky and Weisbrod 2006; Vilks, Miller et al. 2008). Most of these studies of colloid transport have involved low temperature systems and targeted issues related to contaminant or biological transport. Interpretation of colloid transport is difficult because of limitations in our understanding of filtration processes <refs> and because particle transport in physically heterogeneous and fractured systems deviates significantly from the transport of soluble species; breakthrough of colloids is often found to occur ahead of the breakthrough of soluble tracers.

For geothermal systems, colloids should have several useful properties compared to soluble tracers. Geothermal systems are generally characterized by flow paths with larger apertures than typical groundwater systems (fractures and voids), and flow rates can be high enough to reduce particle loss by classical filtration, straining and settling. Colloids have been used in low temperature systems to study the nature of fluid and solute transport in fractured systems (Toran and Palumbo 1992; McKay, Gillham et al. 1993; Vilks and Bachinski 1996; Chrysikopoulos and AbdelSalam 1997; Grindrod and Lee 1997; Vilks, Frost et al. 1997; Becker, Reimus et al. 1999; James and Chrysikopoulos 1999; Becker and Shapiro 2000; James and Chrysikopoulos 2000; Alonso, Missana et al. 2002; Missana, Gutierrez et al. 2002; Becker 2003; Reno, James et al. 2006; Zvikelsky and Weisbrod 2006; Vilks, Miller et al. 2008; Zvikelsky, Weisbrod et al. 2008). (We have not included the larger body of literature that addresses colloid-facilitated transport of contaminants.)

Colloidal tracer loss during transport can present interpretation challenges when the colloids are used to specifically to characterize flow in geologic media. Comparisons between the time and shape of breakthrough curves for colloids and conservative tracers provide useful interpretations.

In our current project we are investigating colloids that have temperature-recording properties. Such colloids could be applied to determine how the temperature profile of a geothermal system changes over time as heat is extracted. We are concentrating our efforts on colloidal tracers where the reference point for the temperature history is contained in the particle itself.

Temperature-time sensitive colloid tracers

For illustration, and as two models that will be tested in the course of the project, we will examine colloids that exploit the properties of thermoluminescence (see examples in (Mahesh, Weng et al. 1989; Mercier 2008)) and polymer racemization (see examples in (Bada, Maynard et al. 1970; Clarke and Murray-Wallace 2006; Kaufman 2006; Tsukegi, Motoyama et al. 2007)), which are both processes where the kinetics are temperature sensitive and where the reaction precursors and products can be contained within a particulate package. The advantage, then, is that tracer loss by dilution and filtration is acceptable as long as measurable quantities of the tracers can be recovered.

In the thermoluminescence model, a radiation activated mineral phase will be used where attenuation of the thermoluminescence glow curve is

a function of temperature and residence time. In the racemization model, the L form of a polymerized racemic compound (poly-L-lactic acid or polymerized amino acid) will be used. Changes in the D to L ratio will serve as the temperature-time indicator.

Colloid tracer encapsulation: an enabling approach

In many cases it may be advantageous or necessary to protect tracers (particulate or solutions) from unwanted reactions with components of a reservoir fluid or mineral surfaces. For example, dissolution of a thermoluminescent tracer, even if only partial, would obliterate the record of exposure to heat. Hydrolysis, oxidation or other unwanted reactions would compromise a racemic polymer tracer. Encapsulation of a tracer using heat and chemical resistant polymers offers several advantages. These include:

- Isolation from the chemical environment of a reservoir
- The possibility of modifying surface charge in order to optimize colloid stability and minimize attachment (filtration)
- The possibility of modifying the density of a particle-based tracer for improved transport (reduced settling of large or dense particles)

In addition, the ability to package multiple components in a capsule opens up additional possibilities for the design of other “smart” or novel tracers that can record temperature-time histories. For example, a core-shell structure could carry two solid components that fuse at selected temperatures. Further, the mixing of reactants could be used to quench a temperature-dependent reaction, which can then amplify the temperature history along the flow path of a geothermal reservoir (see (Plummer, Palmer et al. 2009) in this workshop).

Initial work on our project has involved testing methods for forming core-shell structures with materials that can survive under reservoir conditions and that record temperature-time history.

TASK OBJECTIVES

One of the initial tasks in our project was to test methods for encapsulation using organic polymers. There are three primary objectives in this task. The first is to test methods for coating small particles with organic polymers. The second is to determine whether the polymer coatings protect the colloid core from the outside environment. The third is to determine whether a polymer shell can be chosen that

survives exposure to relevant geothermal reservoir temperatures, and in the presence of representative solids and solutions.

For the development and evaluation of polymer coating methods and materials, surrogate minerals rather than the actual thermoluminescent minerals were used in order to facilitate evaluation of the polymer coatings. These surrogates have the advantage of providing simple visual indication if the coating fails to protect them from exposure to the suspending fluid (water). Sodium chloride (soluble, colored in the γ -irradiated form) and copper salts (blue in solution) were the surrogate minerals chosen for this task.

For use in the field we expect tracers will have to be relatively inexpensive since large quantities may be needed to compensate for loss and dilution factors. The next stage in tracer testing will involve readily available and relatively inexpensive candidate minerals or organic polymers. Using thermoluminescent minerals as temperature sensitive tracers might not require polymer encapsulation in some cases. However, there are several potential advantages. One is that some minerals that are soluble in geothermal extraction fluids could be used. This can make it easier to identify the actual tracer colloids against background colloids in the production waters through filtering and fractionation procedures. We have observed that even sodium chloride can be recovered from polymer-coated forms when the polymers are dissolved in dry organic solvents. A second advantage to polymer coatings is that the density of the core-shell particle can be made lower than, for example, the core mineral particle. As a result, larger particles can exist in stable suspensions without settling, and the larger sizes would be excluded from entry into small pore, lower permeability media. A third advantage is that the surface charge of the mineral can be masked. This can be important in cases where differences in electrostatic charge signs can result in filtration by electrostatic interactions. An additional issue we intend to explore is whether polymer coatings can be designed such that changes in tracer properties can be observed through the coating or if the coatings can be removed without disturbing the record of changes in the core tracer.

METHODS AND MATERIALS

The mineral phases used as the particle cores were sodium chloride (Aldrich), copper sulfate (Fisher) and copper acetate (Aldrich). The minerals were used without further purification prior to grinding.

Polymers used in test coatings were polystyrene (PS), polymethylmethacrylate (PMMA) and a polyimide (PI).

Sodium chloride, a thermoluminescent material, was γ -irradiated. The irradiation results in a brown color, which can be used as a visual indicator in addition to being used to evaluate our ability to record a thermoluminescent signature.

The particles were ground in a SPEX ball mill running at 1080 cycles per minute (18 Hz) for 2 twenty minute cycles using an agate ball and sample holder. The resulting powder was separated in an ATM ultrasonic sifter for two 15 minutes cycles. Two fractions were retained, the first being 38-83 micron size and the second being the fines that were < 38 microns.

Two polymer coating methods were used. One is the Wurster method (for example, see (Arimoto, Ichikawa et al. 2004)) shown in Figure 1.

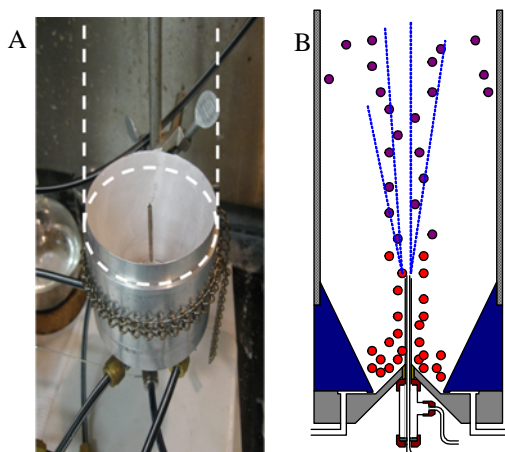


Figure 1: A) photograph of the base of the Wurster coater with the sleeve (dotted line) removed. B) a schematic of the cell showing how particles are entrained into a stream of polymer/solvent where the solvent is removed by evaporation and polymer layers are deposited on the core particles.

In this method a gas stream forces the particles upwards in the center where they are spray coated via an aspirated polymer solution (dissolved in organic solvent). The coated particles quickly dry and fall back down and the process is repeated several times, which determines the thickness of the coating.

The second coating method involves a solvent-safe blender where the particles, polymer and solvent are homogenized and aerosolized into a non-solvent where the polymer solvent is rapidly removed resulting in a dense polymer coating on the particles.

The success of this method is dependent upon the proper choices of the two solvents involved. First a polymer such as polystyrene or a polyimide is dissolved in a solvent. Then the tracer particles, which must be insoluble in the solvent, are added to form a suspension. Once this mixture is made, it is added drop wise to a second solvent that is being rapidly stirred in a blender. The second solvent is chosen to be miscible with the first solvent while at the same time does not dissolve the polymer. As the drops fall into the blender, the first solvent disperses into the second solvent and the polymer precipitates and encapsulates the tracer particles. This process has been used to coat two different copper salts and sodium chloride particles.

Samples prepared were:

- γ -irradiated NaCl in PS and PS/PMMA co-polymer
- CuSO_4 in PMMA
- $\text{Cu}(\text{COOCH}_3)$ in PMMA and PI

RESULTS

The primary objective for the initial experiments was to obtain evidence that the coated particles would not dissolve in water. In the case of NaCl, the colloids remained intact (see Figure 2). Subsequent removal of the polymer coating using a dry organic solvent released NaCl to the solvent, which settled to the bottom of the flask.

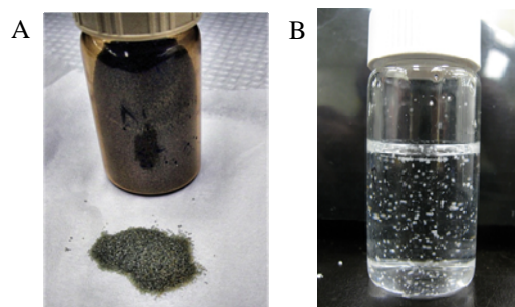


Figure 2: A) γ -irradiated NaCl, B) Polymer-coated NaCl suspended in water.

Water-soluble copper salt particles also appeared to be resistant to degradation in the presence of water. In some samples, a faint blue color could be seen, which indicated that at least some of the particles were not completely coated. (An equivalent mass of copper salt dissolved in water has a much more intense color that is easily distinguished from leachate in the presence of the coated particles.) However, after decanting the liquid and re-suspending the particles in water, a blue color was not visible to the eye, indicative that the percentage

of particles that were completely coated was very high (> 90%).

NEXT STEPS

In these initial studies we have demonstrated that the coating methods can be used to apply polymer coatings over mineral cores. This now opens the door to the subsequent synthesis and testing of candidate tracers that can record temperature-time histories. Subsequent research tasks include the following:

- Subjecting polymer coated particles to pressure/temperature/chemical conditions representative of geothermal reservoir conditions. The purpose is to determine whether the survival rate of the particles is sufficient to be used in the field.
- Modifying the polymer coating mass and composition to impart density and surface charge (or hydrophobicity) characteristics that are suited for transport in geothermal systems. Such tailoring of properties will also consider characteristics that result in preferential transport in fractures.
- Characterizing thermoluminescent properties of materials with and without polymer coatings.
- Testing sampling procedures for capture of the particle tracers as well as for distinguishing intact tracer particles from other suspended solids.
- Exploring other tracer models, particularly those that involve encapsulation of multiple reactants where reactions can be delayed until critical temperatures.

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