Advancing Reactive Tracer Methods for Monitoring Thermal Drawdown in Geothermal Enhanced Geothermal Reservoirs

Geothermal Resources Council Meeting

Mitchell A. Plummer Carl D. Palmer Earl D. Mattson George D. Redden Laurence C. Hull

October 2010

The INL is a U.S. Department of Energy National Laboratory operated by Battelle Energy Alliance



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint should not be cited or reproduced without permission of the author. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the United States Government or the sponsoring agency.

ADVANCING REACTIVE TRACER METHODS FOR MONITORING THERMAL DRAWDOWN IN GEOTHERMAL ENHANCED GEOTHERMAL RESERVOIRS

Mitchell. A. Plummer, Carl D. Palmer, Earl D. Mattson, George D. Redden, Laurence C. Hull

Idaho National Laboratory P.O. Box 1625, MS2208 Idaho Falls, ID, 83415, USA e-mail: Mitchel.Plummer@inl.gov

ABSTRACT

Reactive tracers have long been considered a possible means of measuring thermal drawdown in a geothermal system before significant cooling occurs at the extraction well. In this study, we examine the sensitivity of successive reactive tracer tests to reservoir cooling and demonstrate a means of analyzing tracer test results based on a simplified geometric description of a geothermal reservoir. Sensitivity tests suggest that the approach can provide valuable information about the thermal evolution of the reservoir. We propose several modifications to the basic flow-through method that could provide increased sensitivity, including pushpull tracer tests at the injection well and utilization of a tracer reaction that is quenched before background reservoir temperature is reached.

INTRODUCTION

Efficient operation of an engineered geothermal system (EGS) involving cold fluid reinjection requires accurate and timely information about thermal energy depletion of the reservoir in response to operation. In particular, accurate predictions of the time to thermal breakthrough and subsequent rate of thermal drawdown are necessary for reservoir management, design of fracture stimulation and well drilling programs, and forecasting of economic return. Periodic testing with reactive tracers has been proposed as one means of estimating thermal breakthrough before the temperature of the working fluid at the production well is affected (e.g., Robinson 1985), but testing of the approach has been limited. With repeated tests, the rate of migration of the thermal front can be determined, and the time to thermal breakthrough calculated. While the basic theory behind the concept of thermal tracers has been understood for some time, effective application of the method has yet to be demonstrated.

In this paper, we explore the sensitivity of reactivetracer breakthrough curves in EGS to reservoir and tracer properties, discuss alternative tracer approaches that could potentially enhance our ability to estimate thermal breakthrough, and describe preliminary efforts to develop and test means of constructing 'smart' reactive tracers. Finally, we describe an approach to analysis and interpretation of reactive tracer tests for measuring thermal drawdown in a reservoir.

THERMALLY REACTIVE TRACERS

To examine the sensitivity of the application of reactive tracers for measuring thermal drawdown, consider the thermal evolution of a single ideal fracture where flow is effectively one dimensional and the temperature along the flowpath, f(x), can be described by:

$$f(x) = erf\left(\frac{\lambda_r x}{\rho_f c_{p-f} b v \sqrt{\alpha_r t_{op} - x/v}}\right)$$
 Eq. 1

[Carslaw and Jaeger 1959, Section 15.3, Case III] where

 $\lambda_r = \text{rock thermal conductivity}$

x = flowpath distance traveled

b =fracture aperture

 ρ_f = carrier fluid density

 $c_{p f}$ = fluid specific heat

v = v velocity in the fracture

 α_r = rock thermal diffusivity

 t_{op} = operating time

The relative reaction rate along that flowpath, is often described by a first-order or pseudo first-order equation of the form

$$\frac{dC(t)}{dt} = -k(T)C(t)$$
 Eq. 2

where k(T) is the temperature-dependent rate coefficient given by the Arrhenius equation,

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right)$$
 Eq. 3

where T is the temperature in Kelvins, R is the gas constant, and E_a is the activation energy.

The goal of the prescribed tracer method is to measure the change in temperature along the flowpath before measurable cooling, (*ie.* thermal breakthrough) is observed at the production well. This period may be relatively long, even in short, or high velocity, flow paths. During this period, system operation feedback provides little or no information describing the thermal evolution of the reservoir. Methods of measuring cooling in the reservoir during this period, such as reactive tracer tests, could provide data critical to long-term system operation planning.

Taking 1% of the difference between the injection and initial reservoir temperature as an arbitrary indication of measurable cooling at the production well, from Eq. 1 we determine that the operating time of interest is that less than t_{crit} , where

$$t_{crit} = \frac{x}{v} + \frac{1}{\alpha_r} \left(\frac{\lambda_r x}{b \rho_f c_{p-f} v \cdot 1.821} \right)^2$$
 Eq. 4

Using t_{crit} as the reference time for the system, we define dimensionless time, t_D , $t_D = t / t_{crit}$. Figure 1 illustrates temperature profiles along a hypothetical fracture flowpath after dimensionless operating times of 0.001, 0.01, 0.1, and 1.

By conducting multiple thermal reactive tracer tests, the change in the reservoir temperature between two different operating times (Figure 1) can be determined and the working life of the reservoir can be estimated. (For a flow rate of 6 kg/s through a fracture with a surface area of 200,000 m^2 , t_{crit} is approximately 3 years, so these dimensionless times correspond to times of approximately 1, 11, 110, and 1,110 days). Theoretically, this is possible because the relative reaction rates vary with temperature (Figure 2A), and the amount of tracer conversion observed during transport between the wells should decrease as the reservoir cools. A second tracer test conducted at some Δt_D after an initial test at time t_{D init} should have higher breakthrough curve concentrations than for the first test.

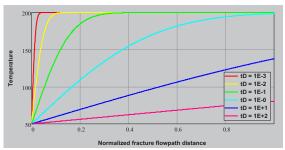


Figure 1. Temperature as a function of dimensionless distance in a hypothetical fracture in a geothermal system at a wide range of different flow times. Curves are given at $t_D = 0.001$, 0.01, 0.1, 1, 10, and 100.

To examine the sensitivity of the proposed method, we examined piston-flow transport of a reactive tracer undergoing first-order decay in a single fracture. The relative tracer concentration, $C_{\rm rel} = C/C_0$ with time, or equivalently, distance, can be obtained by substituting Eq. 3 into Eq. 2 and integrating to yield

$$C_{rol}(t) = \exp(-A\theta)$$
 Eq. 5

where θ , the thermal reaction time, is defined by

$$\theta(f) = \int_0^f \exp\left(-\frac{E_a}{RT}\right) \frac{L}{\nu} df$$
 Eq. (

and f is the fraction of the flow path traveled and L is the flowpath length (Tester et al., 1987). Examination of the relative concentration curves along the flowpath (Figure 2B) illustrates a problem with the proposed method. Only for very large differences in the operating time are the final thermal times significantly different, suggesting that the method is a relatively insensitive measure of thermal drawdown. As Behrens et al. (2009) point out, this appears to be the case for both large and small values of the activation energy, E_a . The primary difficulty is that the highest reaction rates occur in the downstream portion of the flowpath, where temperatures converge on the initial reservoir temperature. Unfortunately, this is true for all k(T)dependence relationships. sensitivity increases slightly with E_a , the net conversion with large E_a also decreases toward immeasurably small values.

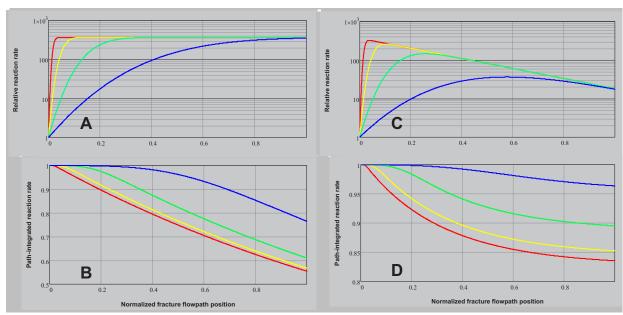


Figure 2. Reaction rate (A&C) and thermal reaction time (B&D) plots for a fracture flowpath for operating times and temperature profiles corresponding to those in Figure 1. Graphs A & B represent piston flow of a pulse of tracer transported through the fracture. Curves C & D approximate the effect of dispersion on a slug of tracer transported through the system, where the concentration decreases approximately exponentially with dimensionless position, f, according to the expression $C/C_0 = \exp(-3f)$.

While available tracers may provide some choice in E_a , the choices are limited, and each choice is explicitly tied to a corresponding pre-exponential factor, A. It is this pre-exponential factor that primary controls the absolute amount of conversion that will occur between the injection and production wells. In addition, for a class of tracers with different substituents, E_a and A are correlated. This effect (enthalpy-entropy compensation effect) is well known (e.g., Lasaga, 1998; Liu and Guo, 2001) and is illustrated here with the ester and amide hydrolysis data of Robinson and Tester (1990) (Figure 3).

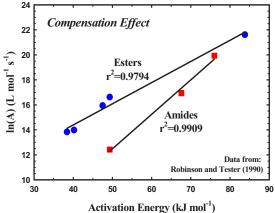


Figure 3. Entropy-enthalpy compensation effect for the second-order hydrolysis reactions of some ester and amide tracers.

The simple analysis described thus far overlooks a factor that could significantly increase the sensitivity of the method. The reaction term in the solute transport equation of interest is the reaction rate multiplied by the concentration, kC, not just k. The chemical concentration, C, is also affected by dispersion and sorption processes as well as chemical reaction. Concentration of a pulse of conservative tracer will typically decrease several orders of magnitude during flow through the system and fortuitously highest concentrations are near the injection well, the region of lowest reservoir temperature. As the tracer travels along the flow path, k(T) will increase and C will decrease. To illustrate the potential effect, we use a simple exponential term to describe the decrease with distance that a conservative tracer might undergo during transport, and recalculate the reaction rate (Figure 2C) and thermal time (Figure 2D) curves of Figure 2A & B. Separation between the thermal time curves is significantly increased, and net conversion is slightly reduced relative to the base case of Figure 2B. The success of illustrating that the proposed method becomes more sensitive when concentration of the tracer varies along a flow pathway suggests that a coupled heat flow and solute transport solution is needed to accurately assess the potential sensitivity of the reactive tracer approach to measuring thermal drawdown.

To illustrate how the tracer test might work in an actual system, we simulated heat flow and solute

transport using finite element methods, with the solute transport solution coupled to the output of the heat flow solution. The model represents water flow through a hypothetical fracture with a length of 1 km and flow velocity of 5E-3 m/s. The fracture aperture is 2 mm and the half-width between fractures is 10 m. Assuming that a 1% of the difference between the injection and initial reservoir temperature at the production well determines the reservoir life, t_{crit} for this system would be approximately 27 years.

Two tracer tests were simulated, one after a dimensionless operating time of 0.019 and a second at $t_D = 0.387$ (~0.5 and 10 years). Temperature profiles corresponding to these times are very different (Figure 4). Thermal drawdown extends to approximately 0.1 of the total flow distance (L) for the first profile and to approximately 0.6 for the second profile. For the simulations, conservative and reactive tracers were introduced into the injection well over an 8-hour period. Because solute transport is coupled to heat transport, the reaction rates are based on the simulated temperature history. Reactive tracer parameters are summarized in Table 1.

Numerical simulation results of conservative and reactive tracer breakthrough curves at the production well are plotted in Figure 5. The later tracer test shows significantly higher concentrations because the net conversion is lower for the slightly cooler system. For a system with a critical time of 27 years, the tracer test times in this case correspond to 0.3 years and 6 years of system operation, indicating the timescale over which the method may prove useful.

Table 1. Reactive tracer parameters.

| Tuble 1: Reactive tracer parameters: | |
|---------------------------------------|-----------------|
| Simulated tracer injection parameters | |
| Activation energy, E_a | 143300 [J/mole] |
| Pre-exponential factor, A | 5E9 [1/s] |
| Injection period | 8 hours |

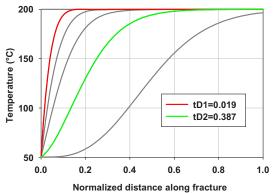


Figure 4. Temperature profiles at t_{D_init} and $t_{D_init} + \Delta t_D$. For comparison, the profiles for $t_D = 0.052$, 0.142, 1.05 are also shown (gray curves).

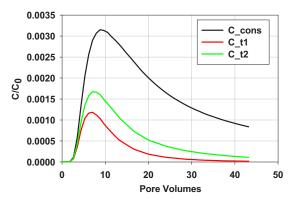


Figure 5. Conservative tracer test and base case reactive tracer test.

The relative sensitivity of the method is expected to increase with the magnitude of the E_a . To examine how an increase in E_a would affect results, we repeated the same tests after doubling E_a and increasing A by a factor of 5E16 to maintain approximately the same concentration range. The resultant breakthrough curves (Figure 6) suggest only minimally greater sensitivity to the difference in thermal profiles.

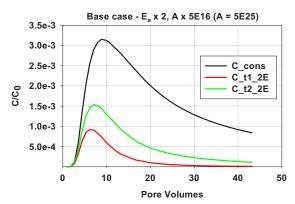


Figure 6. Breakthrough curves for flow-through tracer test with activation energy increased by 5E16 relative to the test results in Figure 5.

Because of the limited choice of kinetic parameters, and the relatively low sensitivity that the basic method gives, it appears that some means of enhancing the sensitivity of the method may be necessary in order to make thermal tracers a useful measure of thermal drawdown. In this study, we examine two modifications to the commonly described reactive tracer test approach:

1. Application of push-pull tests at the injection well, to limit the tracer movement to that zone over which significant temperature change has occurred.

2. Application of a quenching agent to limit the reactive tracer reaction to the interval over which reservoir temperature has changed.

Other alternatives (e.g., tracers with reactions other than simple first-order decay) not examined in this paper may also enhance the use of reactive tracers.

SINGLE-WELL, PUSH-PULL TESTS

Push-pull tracer tests conducted at the injection well have the advantage of avoiding contact with the fracture surface that remains at background reservoir temperature. While this may be impractical in some systems, breakthrough curves from a sequence of push-pull tests could be more sensitive to the thermal drawdown occurring between those tests. In addition, multiple tracers could be injected, at different times, to interrogate different zones around the well, which is important because the zone of thermal drawdown is not known *a priori*. Alternatively, different lengths

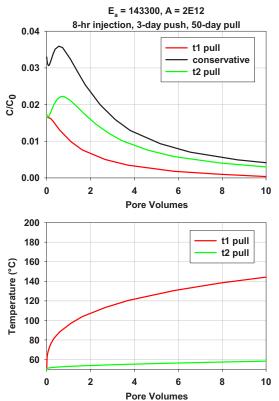


Figure 7. Breakthrough curves of solute concentration and temperature for the extraction phase of a push pull test.

of a rest stage between injection and extraction can be applied.

As an example of application of a pair of push-pull tests with a reactive tracer, we injected water at the same velocity used for the through-flow test

described in the previous example, but with flow direction reversed after approximately 2 pore volumes. The duration of the injection period was calculated to limit solute transport to the zone of strong thermal drawdown. While that distance would not be known in practice, this approach should provide an indication of the maximum sensitivity in this system.

The reversal in flow during the extraction phase of the push-pull test will cause the hot water to flow over the cooler rock, resulting in a lowering of the water temperature and an increase in the rock temperature. To accurately account for this change in thermal regime, coupled heat and solute transport equations are solved. Results, including the temperature at the well and the reactive tracer breakthrough curves (Figure 7) illustrate that there is significant separation between the first and second tests and that it should be feasible to determine the rate of migration of the thermal front.

REACTION QUENCHING

Another method of increasing the sensitivity of the reactive tracer method is suggested by the dominance of the late-time reaction rates. Quenching the reaction as the migrating tracer approaches the initial reservoir temperature should effectively reduce that influence, so that the resultant breakthrough curves are a more sensitive measure of the zone of thermal drawdown. To illustrate the potential of such a tracer, we altered the base case simulation by including a term that halts the reaction when the temperature reaches 10°C below the background temperature. For easier comparison with the previous results, we increased the value of A in these simulations to compensate for the dramatically reduced reaction time. In these scenarios, the difference in breakthrough curve concentrations (Figure 8) between the initial and final tests is significantly greater than for the base case, demonstrating that relatively limited control on the reaction kinetics could substantially improve the method sensitivity. Note also that breakthrough curve concentrations for the later tracer test are in this case lower than for the initial test (Figure 5), reflecting the longer reaction time induced by later quenching.

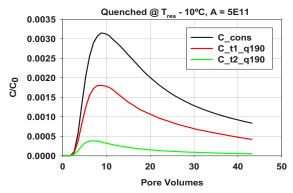


Figure 8. Breakthrough curves for base case conditions, but with reaction quenched at T_{res} - 10° C, and activation energy, A, increased to maintain same concentration range relative to conservative tracer.

The increased sensitivity demonstrated by the simulation of a reaction quenched at high temperature suggests that relatively limited control on the kinetics of reactive tracers may essentially provide a form of 'smart' tracer, that can provide more information about the reservoir than traditional compounds. Such quenching reactions may be feasible using encapsulation techniques, in which one or more compounds is encased in a protective shell, and inside which temperature-sensitive reactions or behavior is used to control other reactions. To to examine means of constructing such 'smart' tracers, we developed technologies for coating sub-millimeter radius particles with various polymers and conducted preliminary experiments to test these protective coatins on sodium chloride, copper sulfate and copper acetate. Results demonstrated that while work is needed to perfect the method, and develop useful reaction controls, the necessary technology for development of layered coatings on suitable particle sizes is available.

ANALYSIS APPROACH

As with conservative tracer tests, reactive tracers can provide information about the reservoir with only limited *a priori* knowledge of the reservoir. To provide an analysis method that can be easily implemented without extensive knowledge of the reservoir geometry, we are developing an approach that relies on a simplified model of the subsurface. The method is intended to incorporate and extend information from conservative tracer tests that provide information about the swept volume of the reservoir and residence time distribution. Because thermal evolution of the reservoir depends on fracture aperture, fracture length, fracture spacing and other geometric characteristics we require some geometric description, and choose a simple idealized set of disk-

shaped fractures as a starting point. The streamtube distribution of a single disk yields a breakthrough curve (Figure 9) that is asymmetric, as is commonly observed in tracer tests, and though somewhat unrealistic, provides a reasonable starting point for examining the effect of reservoir geometry on reactive tracers. Selection of a simplified reservoir geometry for analysis of reactive tracer behavior also provides an opportunity to use algorithms that are amenable to rapid solution via analytical, semianalytical or numerical methods that can be readily implemented in a stand-alone software package for distribution to the geothermal industry. Accordingly, our development efforts focus on methods that can be implemented in our chosen development environment, Mathsoft's Matlab, whose routines can be compiled as stand-alone programs.

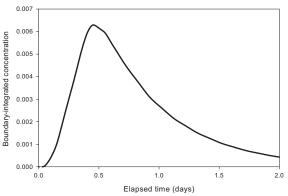


Figure 9. Breakthrough curve of a slug flowing through a single disk-shaped fracture, with flow according to Darcy's law. Simulated using 2-D finite element methods.

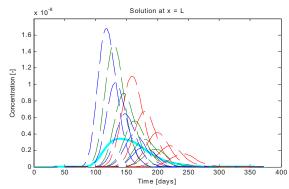


Figure 10. Conservative breakthrough curves for a conservative tracer in a reservoir of 5 sets of fractures. Different colors represent different paths within a single fracture. Cyan curve is flow-weighted average.

The analysis approach involves (1) fitting a simplified reservoir model geometry to a combination of conservative and reactive tracer data (2) using the assumed geometry to interpret changes

in reactive tracer concentrations (from tests conducted at different times) and (3) examining the sensitivity of inferences about thermal evolution to the assumptions about geometry. Conservative tracer tests are first used to constrain the volume and residence time distribution of the reservoir, using the method described by Shook and Forsmann (2005). Assuming the reservoir consists of several sets of disk-shaped fractures, each with constant aperture interfracture spacing, the flow-storage information, combined with reservoir operations data, is used to constrain the total fracture volume and ratio of fracture radius to aperture, which defines hydraulic conductivity, via the cubic law. Fracture systems that are consistent with those results produce a simulated breakthrough curve that matches the observed conservative solute breakthrough curve. Conservative tracer transport is modeled (Figure 10) with the 1-D advection dispersion equation, solved using the method of lines, which impicitly assumes that mixing is primarily a function of path distribution in the reservoir, rather than interaction of the solute with the rock matrix.

A range of fracture geometries that provide a reasonable fit to conservative tracer data are used to generate flowpath velocities and other parameters necessary for calculation of temperatures along each flowpath (Figure 11). Temperatures along the streamtubes through each fracture are calculated via numerical inversion of the Laplace transformed solution of Gringarten (1975). One-dimensional transport of a slug of reactive tracer, with temperature dependence of reaction rate described by the Arrhenius expression, is then calculated using the advection-dispersion equation (Figure 12) and the

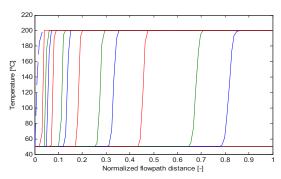


Figure 11. Temperature profiles for 5 sets of 20 fractures, for 3 paths through each fracture, where interfracture spacing ranges from 10 to 50 meters. Operating time is selected to demonstrate differences in temperature profiles between fractures. Different colors represent different paths within a single fracture. Dashed line represents temperature profile for infinite fracture spacing.

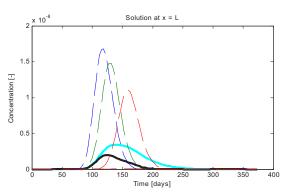


Figure 12. Breakthrough curves for a reactive tracer in a reservoir of 5 sets of 20 fractures each. Dashed lines represent different paths within a single fracture. Solid black curve is the flow-weighted average reactive transport breakthrough curve. Cyan curve is the conservative solute breakthrough curve.

flow-weighted average of the resulting breakthrough curves defines the reactive tracer breakthrough curve. The description of the fracture system is then altered, via an optimization routine, so that the modeled breakthrough curve fits all of the available observations. The ultimate goal is use both conservative and reactive tracer test data to define fracture geometries that fit the available data and then use the same modeling approach to predict the thermal evolution of the reservoir (Figure 13). Preliminary testing suggests that many different fracture geometries may combine to produce essentially the same tracer breakthrough curves in different ways, indicating that additional information, from other reservoir interrogation methods, will be necessary for reliable predictions of thermal evolution based on reactive tracer testing.

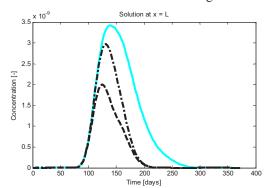


Figure 13. Comparison of breakthrough curves for conservative tracer (solid {cyan} curve), and reactive tracer at initial operating time and later operating time. Later time curve shows reduced loss of tracer via reaction because of lower temperatures in the system. Note that temperature at production remains at initial reservoir temperature.

CONCLUSIONS

The application of reactive tracers as a means of measuring thermal drawdown has long been proposed, but the sensitivity of the method has been questioned. Our preliminary analyses suggest that the basic flow-through tracer method may be more sensitive than a simple piston-flow analysis would indicate, because of dispersive processes that reduce the influence of downstream, higher temperature, conditions. In addition, the sensitivity of the flowthrough method appears to be significantly enhanced when the reaction kinetics are controlled. Simulations of tracers incorporating quenching behavior at nearbackground reservoir temperature, for example, demonstrate increased sensitivity relative to the commonly proposed method. When practical, pushpull tests at the injection well may also provide better estimates of the rate of thermal drawdown.

To test the application of reactive tracer testing to thermal drawdown monitoring of a geothermal system, we are developing an inverse modeling approach that focuses on identifying simplified reservoir geometries that are constrained by conservative and tracer tests and that can be used to predict thermal evolution of the reservoir. Results demonstrate how an assembly of simple fractures combine to produce the typical asymmetric breakthrough curve commonly observed in groundwater tracer tests, and illustrate the complexity of even this relatively simple approach to interpretation of reactive tracer test data.

REFERENCES

Behrens, H., I. Ghergut, M. Sauter, and T. Licha, 2009. Tracer properties and spiking results from geothermal reservoirs. Proceeding of the Thirty Fourth Workshop of Geothermal Reservoir Engineering, Stanford, University, Stanford, CA, February 9-11, SGP-TR-187.

Carlslaw, H.S., and J.C. Jaeger, 1959. Conduction of Heat in Solids. Oxford University Press, Oxford, U.K., 510 p.

Chrysikopoulos C. V. (1993) Artificial tracers for geothermal reservoir studies. *Environmental Geology*, v. 22, p. 60-70.

Gringarten, A.C., P.A. Witherspoon and Y. Ohnishi 1975. Theory of heat extraction from fractured hot dry rock. Journal of Geophysical Research, v. 80, p. 1120-1124.

Lasaga, A.C., 1998. Kinetic Theory in the Earth Sciences. Princeton University Press, 811 p.

Liu, L., and Q.-X. Guo, 2001. Isokinetic realationship, isoequilbrium relationship, and enthalpy-entropy compensation. Chem. Rev., v. 101, p 673-695.

Robinson, B.A. and J.W. Tester, 1990. Kinetics of alkaline hydrolyisi of esters and amines in neutrally-buffered solution. International Journal of Chemical Kinetics, v. 22, p. 431-448.

Rose, P.E., W.R. Benoit, and P.M. Kilbourn, 2001. The Application of the polyaromatic sulfonates as tracers in geothermal reservoirs. Geothermics, v. 30: p. 617-640.

Tester, J.W., B.A. Robinson, and J. Ferguson, 1987. The theory and selection of chemically reactive tracers for reservoir thermal capacity production. Proceeding of the Twelfth Workshop of Geothermal Reservoir Engineering, Stanford, University, Stanford, CA, January 20-22, SGP-TR-109.

ACKNOWLEDGEMENTS

Work supported by the U.S. Department of Energy, Office of Geothermal Technologies under DOE Idaho Operations Office Contract DE-AC07-05ID14517.