

## **SENSITIVITY OF A REACTIVE-TRACER BASED ESTIMATE OF THERMAL BREAKTHROUGH IN AN EGS TO PROPERTIES OF THE RESERVOIR AND TRACER**

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### **ABSTRACT**

Reactive tracers provide a potential method for measuring thermal drawdown in a geothermal system before significant cooling occurs at the production well. Because reaction rates generally have strong temperature dependence, the conversion of a reactive tracer carried through a reservoir is essentially an indicator of reservoir temperature between the injection well and the production well (Tester et al., 1987; Chrysikopoulos, 1993). With repeated tests, the rate of cooling may be estimated, which may provide critical planning data. While several recent studies have suggested that the sensitivity of this approach to reservoir cooling is low, those analyses were based largely on cooling behavior of isolated fractures. In this study, we examine the sensitivity of successive reactive tracer tests to reservoir cooling under a variety of conditions, and illustrate how that sensitivity relates to the kinetic parameters of a range of compounds suitable for this application. Notably, while the maximum change in the relative concentration between successive reactive tracer tests in a system cooling as an isolated fracture is approximately 35%, a 100% difference could be measured in a system where cooling proceeds as it would for closely spaced fractures, although the early time sensitivity is actually greater for the former system. To illustrate how this approach may be used in an actual system, we present results of our field test of two reactive tracers at U.S. Geothermal Inc.'s Raft River, Idaho site.

### **INTRODUCTION**

Geothermal reservoir management often requires injection of produced fluids to prevent them from entering shallow aquifers and surface waters, to help extract heat from the subsurface, and to maintain pressures within the reservoir (e.g., Rose et al., 2001). Knowledge of the time to thermal

breakthrough associated with these injected fluids is required for optimal management of the reservoir. While conservative, artificial tracers can provide valuable information about reservoir residence times and flow paths (Behrens et al., 2009), they provide little direct information about thermal breakthrough. It has been proposed that reactive tracers that degrade at rates that depend on temperature can be used to estimate reservoir temperatures between the injection well and the production well (Tester et al., 1987; Chrysikopoulos, 1993). 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. Recently, Behrens et al. (2009) indicated that reactive tracer breakthrough curves are not sensitive to changes in the thermal front and therefore the suggested method lacks the sensitivity necessary to provide a useful measure of thermal drawdown. In this paper, we explore the sensitivity of reactive-tracer breakthrough curves in EGS to reservoir and tracer properties and discuss alternative tracer approaches that could potentially enhance our ability to estimate thermal breakthrough.

### **THERMALLY REACTIVE TRACERS**

Reactive tracers can provide information about the thermal evolution of such a system because chemical reaction rates are temperature dependent. Reaction rates generally increase with temperature and the amount of conversion observed during transport between two wells should decrease as the reservoir cools. A second tracer test conducted some time after an initial test should thus have higher breakthrough curve concentrations than for the first test. Comparison of tracer tests conducted at different times can provide information about the corresponding change in reservoir, and thereby aid in predicting the working life of the reservoir.

To illustrate how reactive tracers could be used to monitor the evolution of temperature in the system described above, we consider the relative reaction rate along a flow path where the reaction rate can be described by a pseudo first-order equation of the form

$$\frac{dC_{abs}(t)}{dt} = -k(T)C_{abs}(t) \quad \text{Eq.1}$$

where  $C_{abs}$  is actual concentration and  $k(T)$  is the temperature-dependent rate coefficient given by the Arrhenius equation,

$$k(T) = A \exp\left(\frac{-E_a}{RT(\tau, f)}\right) \quad \text{Eq.2}$$

where  $T$  is the temperature in kelvins,  $R$  is the gas constant,  $E_a$  is the activation energy,  $\tau$  is the operating time of the reservoir, and  $f$  is the fraction of the flow path traveled.

To illustrate the fundamental sensitivity of reactive tracers to the thermal evolution of a reservoir, we first consider transport under the simplified case of piston-flow conditions, where concentration is affected only by reaction. For piston-flow transport of a reactive tracer undergoing first-order decay, the relative tracer concentration,  $C = C_{abs}/C_0$  with time, or equivalently, distance, can be obtained by substituting Eq. 2 into Eq. 1 and integrating to yield

$$C(t) = \exp(-A\theta) \quad \text{Eq.3}$$

where  $\theta$ , the thermal reaction time (Robinson and Tester, 1990), is defined by

$$\theta(\tau, f) = \int_0^f \exp\left(-\frac{E_a}{RT(\tau, f)}\right) \frac{L}{v} df \quad \text{Eq.4}$$

and  $L$  is the flowpath length (Tester et al., 1987).

The sensitivity of the relative concentration to mean reservoir temperature can be described by its derivative with respect to an effective temperature of the fracture path,  $T_{eff}$ , where the “effective temperature” is the temperature needed to match the reactive tracer concentration at the extraction well, assuming a constant temperature along the flow path:

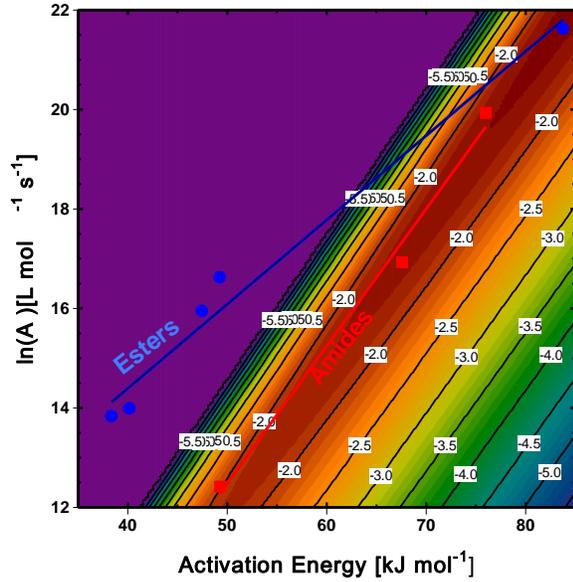
$$T_{eff}(\tau, E_a) = \frac{-E_a}{R \cdot \ln(\theta(\tau, 1))} \quad \text{Eq.5}$$

The sensitivity of the relative concentration to  $T_{eff}$  is a function of that parameter, the kinetic parameters  $A$  and  $E_a$ , and the residence time in the system,  $L/v$ :

$$\text{Eq.6} \\ \frac{dC}{dT_{eff}}(A, E_a, T_{eff}) = \frac{A \frac{L}{v} E_a \exp\left(-A \frac{L}{v} \exp\left(-\frac{E_a}{RT_{eff}(\tau, E_a)}\right) - \frac{E_a}{RT_{eff}(\tau, E_a)}\right)}{R \cdot T_{eff}(\tau, E_a)^2}$$

To illustrate how this sensitivity varies with the kinetic parameters and how it relates to kinetic parameters of compounds suggested for this application, we calculated the sensitivity for a tracer test that INL conducted at U.S. Geothermal Inc.’s geothermal reservoir in Raft River, Idaho for a range of  $A$  and  $E_a$  values. The reservoir temperature at Raft River is approximately 140°C and the travel time between wells is approximately 20 days. For a range of values of  $A$  and  $E_a$  encompassing esters and amides that Robinson and Tester suggested as tracers, the results (Figure 1) demonstrate that the maximum sensitivity is slightly greater than 1% per degree change in  $T_{eff}$  and that the maximum sensitivity is constrained to a narrow band running diagonally across the figure.

While the sensitivity plot identifies desirable values of  $A$  and  $E_a$  for a particular reservoir, the number of compounds suitable as reactive tracers is limited, and each choice of  $E_a$  is explicitly tied to a corresponding pre-exponential factor,  $A$ . In addition, for a class of tracers with different substituents,  $E_a$  and  $A$  are correlated because of the enthalpy-entropy compensation effect (e.g., Lasaga, 1998; Liu and Guo, 2001). The correlation of  $A$  with  $E_a$  for a particular class of compounds tends to be similar to the slope of the high sensitivity band illustrated in Figure 1. We illustrate this by showing regression lines for the ester and amide hydrolysis data of Robinson and Tester (1990) on the sensitivity plot for our hypothetical reservoir with pH and travel time similar to that at Raft River. Interestingly, the amide compounds, and associated regression line, are located precisely within the relatively narrow band of maximum sensitivity for the system. While this is largely a fortuitous circumstance for application of this approach at Raft River, the calculated sensitivity does not vary strongly with temperature, pH, and flow path residence time and those same compounds may be as well suited to many other systems. The slope of the high sensitivity band is primarily a function of the reservoir temperature, decreasing with increasing temperature. In contrast, changing the residence time or pH effectively shifts the high sensitivity band upward or downward relative to the entropy compensation lines, while maintaining the same slope.



**Figure 1. Log change in relative concentration per degree change in effective temperature of a flowpath, where the initial reservoir temperature is 140°C and the residence time is 20 days. Blue and red lines illustrate the entropy-enthalpy compensation effect for the second-order hydrolysis reactions of some ester (blue symbols) and amide (red symbols) tracers.**

The sensitivity given by equation 6 gives insight into the preferred values of  $A$  and  $E_a$  given a particular reservoir temperature and flow path residence time, demonstrating that a particular reservoir has good sensitivity only in a relatively narrow range that is constrained to a particular relationship between  $A$  and  $E_a$ . To translate this sensitivity to the actual change in the relative concentration that might be expected as flow path cools, we need an expression describing fracture cooling behavior, in order to estimate how the effective temperature of a flow path changes over time. To illustrate the temperature changes that are likely to occur, and the corresponding change in relative tracer concentration as cooling progresses, we consider cooling of two types of systems, (1) cooling of a single fracture without interference from surrounding fractures and (2) cooling in a system of parallel fractures where cooling fronts perpendicular to the fracture faces overlap and cause more rapid cooling than in the former case. Previous discussions of thermal tracer sensitivity have considered only the thermal evolution of a flowpath through a single isolated fracture, and we begin with that case, where the relative temperature as a function of operating time,  $t_{op}$ , and distance,  $x$ , is given by

$$f(x) = erf\left(\frac{\lambda_r x}{\rho_f c_{p-f} b v \sqrt{\alpha_r t_{op} - x/v}}\right) \quad \text{Eq.7}$$

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

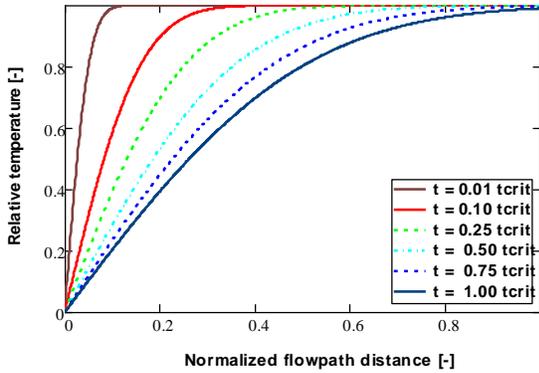
$\lambda_r$  = rock thermal conductivity  
 $x$  = flowpath distance traveled  
 $b$  = fracture aperture  
 $\rho_f$  = carrier fluid density  
 $c_{p-f}$  = fluid specific heat  
 $v$  = velocity in the fracture  
 $\alpha_r$  = rock thermal diffusivity  
 $t_{op}$  = operating time

Following initiation of pumping, thermal drawdown in the fracture first occurs at the injection side of the fracture and is not felt at the production well until a significant portion of the fracture has cooled (Figure 1). During this period, there is little or no discernible temperature change at the production well, so system operation feedback provides little or no information about the thermal evolution of the reservoir. Methods for 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, this implies, using Eq. 1, that the operating time of interest for system interrogation via reactive tracers is that less than  $t_{crit}$ , where

$$t_{crit} = \frac{x}{v} + \frac{1}{\alpha_r} \left( \frac{\lambda_r x}{b \rho_f c_{p-f} v \cdot 1.821} \right)^2 \quad \text{Eq.8}$$

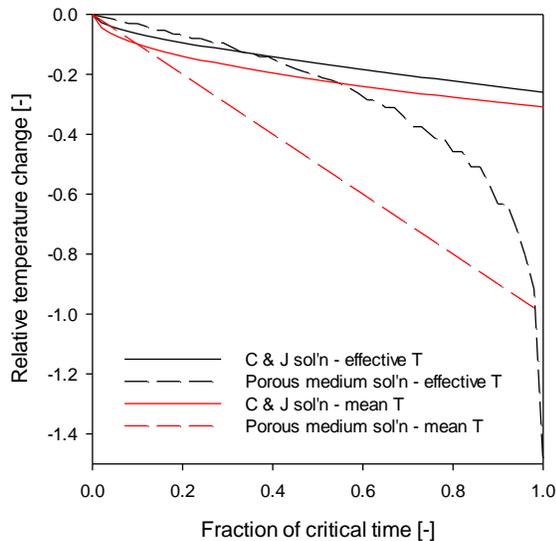
Using  $t_{crit}$  as the reference time for the system, we define dimensionless time,  $t_D = t / t_{crit}$ . The temperature profiles shown in Figure 2 represent dimensionless operating times ranging from 0.01 to 1. Temperature is plotted as relative temperature, i.e.,

$$T_{rel} = \frac{T - T_{res}}{T_{res} - T_{inj}} \quad \text{Eq.9}$$



**Figure 2. Evolution of temperature in a single fracture in a hypothetical geothermal system. Curves are given at  $t_D = 0.01$  to 1. The time at which thermal breakthrough occurs in the production well is defined as  $t_{crit}$  ( $t_D = 1$ ).**

Examination of temperature profiles at different times indicates that cooling to the injection temperature is restricted to the zone immediately adjacent to the well, and that cooling is rapid at first but decreases as  $t_{crit}$  is approached. The shape of the cooling curve – convex, and pinned to the injection temperature only very near the injection well – suggests that the effective flow path temperature does not change dramatically until after  $t_{crit}$  is reached. A plot of effective relative temperature,  $T_{eff}$ , versus dimensionless time, (Figure 3) illustrates this effect. The effective temperature changes most quickly when  $t_D$  is less than 0.1, and the total change in temperature when  $t_{crit}$  is reached is only 26% of the difference between the reservoir temperature and

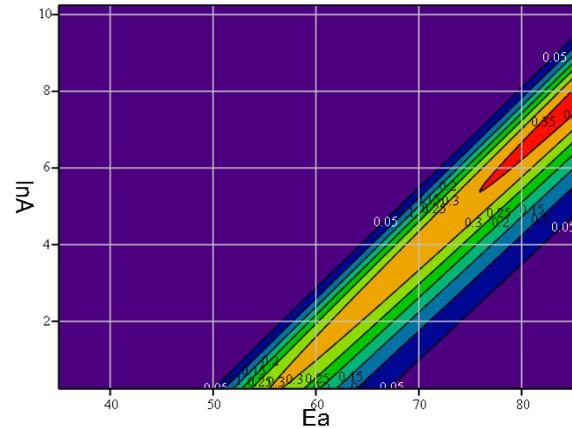


**Figure 3. Temperature change, relative to critical time, for an isolated fracture (solid line) and a porous medium (dashed line). Red curves show mean flowpath temperature; black curves show effective flowpath temperature, as defined in Eq.5.**

injection temperature. Figure 3 also illustrates that the effective temperature is significantly different from the mean reservoir temperature, because it is dependent on the value of  $E_a$ .

Because the effective temperature depends on  $E_a$ , concentration changes between tracer tests conducted at different times are greatest at the edges of the maximum sensitivity band where  $E_a$  is largest. For example, for a difference in those temperatures of  $100^\circ\text{C}$ , the change in relative concentration between reactive tracer tests conducted at  $t_D = 0$  and  $t_D = 1$  is as shown in Figure 4. The maximum change for a given value of  $A$  is approximately 30%-35%, and occurs in the  $A - E_a$  band of greatest sensitivity illustrated in Figure 1. Assuming an initial reactive tracer test is conducted at  $t_D = 0$ , the increase in tracer concentration in successive tests, at  $t_D > 0$ , varies with the evolving effective temperature and the maximum change. The change in concentration is therefore also a function of  $A$  and  $E_a$ . The general behavior, however, is well illustrated via isopleths of the change in relative concentration as a function of dimensionless time and activation energy,  $E_a$  (Figure 5). For the cooling of an isolated fracture, the change proceeds as does the effective temperature, more rapidly at first, before  $t_D = 0.1$ , and then at an essentially constant rate.

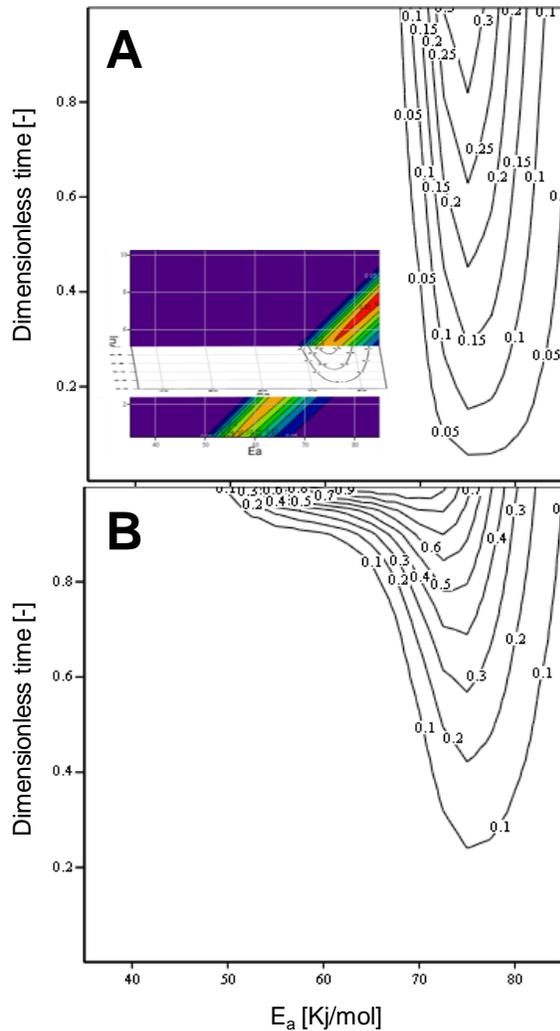
While this effectively provides greater early time sensitivity, the total difference from the relative



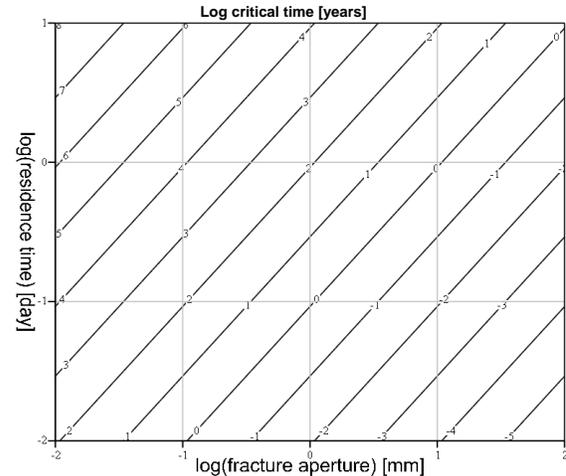
**Figure 4. Change in relative concentration between  $t_D=0$  and  $t_D=1$ , when cooling proceeds as in an isolated fracture.**

concentration at  $t_D = 0$  is also only a fraction of the maximum value at  $t_D = 1$ , so that those concentration changes might be hard to measure given the uncertainty associated with laboratory analysis and the reproducibility of the tracer test at different times.

As mentioned previously, discussions of the sensitivity of reactive tracers to the thermal evolution of a reservoir have been limited to cooling of isolated fractures, for which cooling occurs only extremely slowly. Figure 6 illustrates how  $t_{crit}$ , in years, varies with fracture aperture and flow velocity. For all fractures with aperture less than one mm and residence time greater than one day, critical times are at least 100 years. Because those are the expected conditions for natural geothermal systems, and premature cooling through some flow paths is known to occur, we conclude that cooling in many systems behaves not as that of isolated fractures but as collections of fractures that are spaced closely

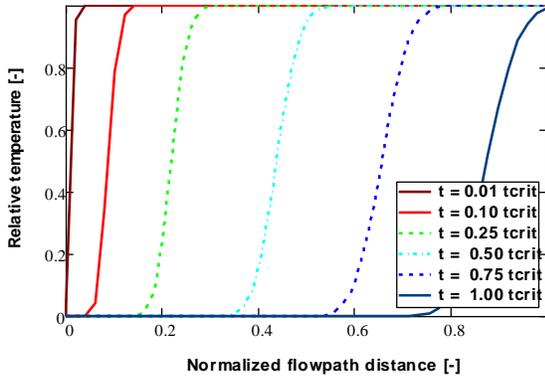


**Figure 5.** Change in tracer concentration, from initial condition at time  $t_D=0$  to time  $t_D=1$ , relative to critical time, for temperature change in an (A) isolated fracture and for a (B) highly fractured system with behavior similar to that of a porous medium. Calculations are shown for a plane representing  $\ln(A)=5$ , as illustrated in the upper figure.

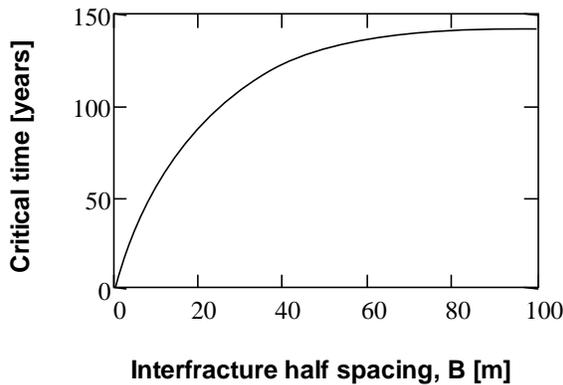


**Figure 6.** Critical time,  $t_{crit}$  in years, for fracture of aperture and residence time defined by, respectively, the ordinate and abscissa, for thermal properties typical of hydrothermal systems.

enough that cooling fronts propagating through the rock overlap and cause more rapid cooling than would occur for isolated fractures. To examine cooling under these conditions, we consider the case of infinite sets of parallel fractures of constant spacing. The solution for the evolution of temperature profiles under those conditions was described by Gringarten (1975). Applying that solution and calculating temperature profiles for a hypothetical fracture with thermal properties identical to those considered for the isolated fracture case (Figure 7), we see that cooling progresses quite differently for sets of closely spaced fractures than for isolated fractures. As the fracture spacing decreases, cooling progresses increasingly as a sharp front and the propagation rate of the cooling front becomes increasingly constant. In the extreme case, where the spacing is such that the time for transfer of heat from the center of the matrix to the fluid is equivalent to the time for fluid to flow past the surface the working fluid may be assumed to be in equilibrium with the rock and the cooling front moves through the fracture essentially as a step function. Under those conditions, the mean temperature of the flowpath changes at a constant rate and the fracture is effectively cooled to the temperature of the injection fluid at  $t_{crit}=1$ . Sets of fractures of intermediate spacing fall between these two extremes. The time to thermal breakthrough, for practical purposes  $t_{crit}$ , is proportional to the fracture spacing (Figure 8), with endpoints effectively defined by the isolated fracture cooling scenario and the cooling of a porous medium. While the cooling for the former case may be hundreds of years, the cooling front typically propagates through a porous medium at about half the velocity of the fluid itself.



**Figure 7. Evolution of temperature in a single fracture in a hypothetical geothermal system. Curves are given at  $t_D = 0.01$  to 1. The time at which thermal breakthrough occurs in the production well is defined as  $t_{crit}$  ( $t_D = 1$ ).**



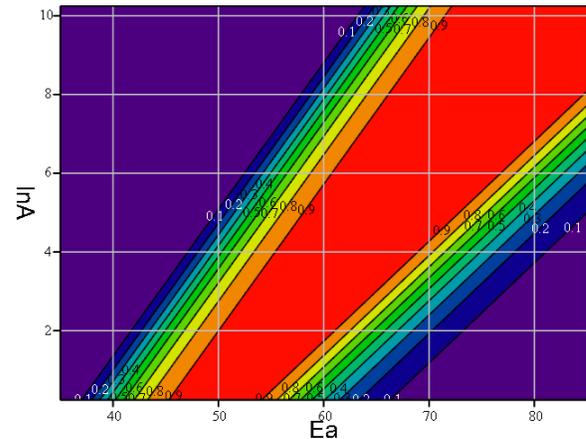
**Figure 8. Critical time as a function of fracture spacing, for a fracture aperture of 1 mm, and fluid velocity of  $5E-3$  m  $sec^{-1}$ .**

Because the mean temperature for a flowpath in a fracture that is part of a set of closely spaced fractures changes much more than that of an isolated fracture, we expect that the signal-to-noise ratio should be greater when reactive tracers are used to monitor that thermal evolution. The effective temperature, however, is much more sensitive to even small decreases in time at highest temperatures, so the effective temperature does decline to a lower value than that provided by cooling of an isolated fracture until  $t_D=0.4$  (Figure 3). Thereafter, however, the effective temperature declines at an increasing rate and at  $t_D=0.6$ , it declines to a value lower than would occur for an isolated fracture at thermal breakthrough ( $t_D=1$ ).

With the isolated fracture representing the end member with lowest signal-to-noise, application to a porous medium should represent the end member with highest signal-to-noise ratio. Examination of effective temperature for this type of cooling (Figure

3) indicates that very large changes in the effective temperature occur during cooling of the flowpath. Under this scenario, the relative concentration difference between tracer tests conducted at  $t_{crit}=0$  and  $t_{crit}=1$  (Figure 9) is 100% for a relatively wide range of combinations of  $A$  and  $E_a$ . Again, these changes occur most rapidly on the high  $E_a$  side of the high sensitivity band visible in Figure 1, because of the additional dependence of effective temperature on that parameter.

We conclude that the basic sensitivity of the reactive tracer approach to monitoring thermal evolution of the reservoir is sufficient in some cases for application to systems where cooling behavior is best represented by that of isolated fractures, but is much better for systems where cooling behavior is better represented by that of sets of parallel fractures, particularly where the cooling front has extended to approximately half way along the flow path.



**Figure 9. Change in relative concentration between  $t_D=0$  and  $t_D=1$ , when cooling proceeds as in a porous medium.**

## 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. Previous discussions of the potential sensitivity of the method have, however, focused on measuring temperature changes induced by cooling of an isolated fracture. We demonstrate that the sensitivity of the method is much greater for systems in which cooling is better represented one or more sets of parallel fractures, because of the greater cooling that occurs along the path before thermal drawdown occurs at the production well. Real fracture systems are likely to have behavior somewhere between the end members represented by an isolated fracture and a porous medium. The equations presented herein provide a general means

of evaluating the kinetic parameters suitable for application of reactive tracers and are illustrated using characteristics of the Raft River geothermal reservoir.

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