# VAPOR, LIQUID, AND TWO-PHASE TRACERS FOR GEOTHERMAL SYSTEMS

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## **ABSTRACT**

Several new tracers have been developed over the last decade and a half for the purpose of tracking steam, liquid, and two-phase flow derived from injected fluid. In addition to a tracer's traditional role of identifying injection-production flow paths, its specific properties can be used to elucidate and quantify certain reservoir properties and processes. In this paper I review and discuss recent developments in tracer research, which range from new gas tracers to methods for calculating the effective temperature, surface area, or boiling parameters from tracer test data.

#### 1. INTRODUCTION

Tracers have traditionally been used to detect and quantify the timing and mass fraction of water movement from one location to another, such as from an injection to a production well. The primary emphasis in tracer research has been to find compounds that will act as conservative tracers, that is, compounds that will not be removed from the fluid by chemical reaction or delayed by retention on the solid phases of the reservoir (Davis et al., 1985). However, it has been found that fluorescent dyes decay (Adams and Davis, 1991) or adsorb (P. E. Rose, personal communication) to some extent, aromatic acids have a finite decay rate (Adams et al., 1992), and halogenated alkanes and  $SF_6$  are rapidly partitioned to the steam phase (Adams et al., 1991a; Glover and Kim, 1993).

Tracers that display "imperfect" properties can be used to produce information on reservoir properties. For example, decaying tracers have been used to deduce the effective temperature of the injection—production flow path while still allowing the calculation of a conservative return profile (Tester et al., 1986; Adams et al., 1989). The volatility of naturally— occurring gases have been used by geochemists for years to produce information on reservoir saturation, boiling parameters, and injection returns (Beall, 1993; D'Amore et al., 1993; Adams, 1992, and many others). These techniques can also be applied to data from tracer tests in which tracers with known properties are used. A higher degree of confidence can be ascribed to the results of calculations based on introduced tracers, rather than naturally occurring compounds, because these compounds have low natural backgrounds and the injection parameters are well—constrained.

## 2. RECENT TRACER DEVELOPMENTS

A number of tracers have been developed for use in geothermal systems in the past decade and a half, as listed in Table 1. The most recent of these developments are discussed below.

# 2.1 Halogenated Alkanes

Halogenated alkanes were developed for use in vapor—phase systems such as The Geysers and Larerello (Adams et al., 1991a). These compounds are generally nontoxic, and extrapolation of tabulated thermodynamic data indicates that some are relatively nonreactive in a geothermal environment. The solubilities and stabilities of these compounds, some of which form homologous series, vary according to the substituent ratios of fluorine, chlorine, bromine, and hydrogen, where fluorine is the most stable and nontoxic, and chlorine, bromine,

Table 1. Summary of geothermal tracers.

Tracer	Advantages	Drawbacks	References
Halides	-Stable -Inert	-High natural background	Home (1982) Adams (1985)
Radioisotopes	-Detectable at low concentrations	-Toxicity (radioactive halides) -Natural backgmund (tritium)	Gulati et al. (1978) McCabe et al. (1983) Tester et al. (1986)
Activable	-Detectable at low concentrations	-Low and poorly defined stability	Chrysikopoulos and Kruger (1986)
Fluorescent Dyes	-Well-defined kinetics -Detectable at low concentrations -Simple field analysis	-Decay rapidly at high temperatures -greater than 260°C for fluorescein -greater than 230°C for rhodamine WT	Smart and Laidlaw (1977) Gudmundsson et al. Mash (1985) Adams et al. (1989) Adams and Davis (1991) Rose and Adams (1994)
Aromatic Acids	-Large variety -Some stable at high temperatures	-Require liquid chromatograph for analysis	Adams et al. (1989) Adams et al. (1992)
Halogenated Compounds	-Volatile -Some stable at high temperatures	-Require specially- equipped gas chromatograph for analysis	Adams et al. (1991a; 1991b) Glover and Kim (1993) Beall et al. (1994)

and hydrogen provide the highest water solubility. Chlorine and especially bromine also impart the worst ozone depletion potential to these compounds, and should be avoided. For example, dichlorodifluoromethane (R-12) has ten times the ozone depletion potential of chlorotrifluoromethane (R-13). All of these compounds are quite volatile and will fractionate readily into the steam phase.

The first tracer test using halogenated alkanes to follow the movement of injection-derived steam was performed at The Geysers in a joint venture of the U. S. Department of Energy (DOE) and three of the operators at The Geysers (Adams et al., 1991b). This tracer test involved two halogenated alkanes, R-12 (324 kg) and R-13 (100 kg), one injection well (C-11), and 49 production wells. The tracer R-12 was detected in 13 of the 16 wells sampled one day after injection (day 1). By the end of the test at day 51, R-12 had been detected in 38 of the 49 wells sampled. Peak concentrations ranged from 3.2 nanograms per kilogram (ppt) to 31.1 milligrams per kilogram (ppm) for R-12, and from 29 ppt to 1.7 ppm for R-13. Transit times were very rapid for some wells. Tracer was detected in fluid from wells as far away as 0.8 km from the injection well on day 1. By day 5, tracer was detected 1.6 km from the injection well. Ratios of the two tracers indicated that R-12 underwent rapid decay during the test. However, the test was still considered a success because of the excellent detectability of R-12, and because its concentrations could be corrected using an empirically-derived rate law, as described in Adams et al. (1991b).

Several tracer tests using R-13 have been performed at The Geysers since the joint DOE-industry test in 1991, two of which are described in Beall et al. (1994). These tests were conducted in portions of the

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reservoir that ranged from highly-water depleted, with low reservoir pressure and liquid saturation, to significantly less depleted, with high reservoir pressure and liquid saturation. Tracer returns from the highly water-depleted portions of the reservoir displayed sharp peaks, rapid transit times, and high recoveries, while those from less depleted portions exhibited broad peaks, slower transit times, and extremely low recoveries.

The most recent test at The Geysers (spring, 1994) was another cooperative venture of DOE and industry (Voge et al., 1994). In this test three tracers were used, R-13,  $SF_6$ , and tritiated water (tritium). The purpose of the test was to evaluate the performance of  $SF_6$  with respect to R-13, and to compare the behavior of these two volatile tracers to that of tritium, whose volatility is nearly identical to that of the water injected at The Geysers. At this time (summer, 1993) the test is still being conducted.

## 2.2 Sulfur Hexafluoride

Sulfur hexafluoride (SF<sub>6</sub>) was first tested as a tracer of injection fluid by Glover and Kim (1993) at the Wairakei geothermal system in New Zealand. SF6 is easily detectable in geothermal fluids at concentrations down to one ppt. Its solubility is very low, similar to that of nitrogen and the less–soluble of the halogenated alkanes (Adams et al., 1991a). The excellent detection limit of SF<sub>6</sub> allows it *to* be used as a liquid–phase tracer despite its high volatility, as long at the liquid does not come into contact with a steam phase. When a volatile tracer comes in contact with a steam phase, it will quickly fractionate into the steam and become a steam tracer.

Glover and Kim (1993) performed their tracer injection experiments by propelling approximately one gram of SF<sub>6</sub> into the reservoir with either water or nitrogen. The experiments were performed in two wells that penetrated different portions of the reservoir, one in the liquid reservoir and one in the steam cap. Peak tracer concentrations in wells that produced from the steam cap ranged from 25 to 275 ppt, while those in wells that produced from the liquid-dominated reservoir ranged from 0.022 to 3.3 ppt. Straight-line velocities for peak arrivals were 3 to 6 m/hr for the steam-cap wells, while those in the liquid-dominated reservoir ranged from 9 to 21 m/hr. The high liquid velocities contrast with those of Beall et al. (1994), in which the tracer velocity is inversely proportional to the liquid saturation of the reservoir. An explanation of this discrepancy between the two studies is provided by the tracer experiments of McCabe et al. (1983). In this study extremely high liquid velocities were also found at Wairakei, and were attributed to gravity flow of injectate down permeable fault zones. The data of McCabe et al. (1983) imply that the majority of injection-production flow velocities at Wairakei are an order of magnitude slower, in accord with the results of Beall et al. (1994).

Glover and Kim (1993) also compared the performance of  $SF_6$  to that of other tracers in tests conducted between the same well pairs. They found that  $SF_6$  performed well as a liquid-phase tracer when compared to similar tests using rhodamine WT and iodide. In the steam phase  $SF_6$  was tested against xenon, and performed similarly well.

Both Glover and Kim (1993) and Beall et al. (1994) found that much less tracer was recovered in the liquid—phase tests than in the vapor—phase tests. Glover and Kim (1993) showed that this was not due to tracer loss in the liquid phase. Thus, dilution seems to be intrinsically higher in the liquid phase, perhaps due *to* its higher density, or a stronger component of flow towards the production well in the steam phase.

SF<sub>6</sub> will be evaluated further as a tracer of injection-derived steam at The Geysers, using data from the most recent DOE- industry test.

## 2.3 Fluorescent Dyes

Fluorescent dyes are preferred by most geothermal operators of liquid-dominated systems because of their excellent detection limits and the ease of on-site analysis using a filter fluorometer. However, dyes are generally complex molecules and decay to some extent at

geothermal temperatures. Their decay rate is dependent on temperature and their concentrations in the production fluid must be corrected for decay in order to obtain an accurate recovery profile. The rate laws and constants necessary for such a correction have been quantified for two dyes, fluorescein (Adams and Davis, 1991) and rhodamine WT (Rose and Adams, 1994).

It is often desirable to use more than one tracer in an injection test. Multiple tracers can be injected into separate wells to completely characterize the field, or they can be simultaneously injected into one well to allow for the correction of thermal decay (Adams et al., 1989). However, the emission peaks of the dyes must be well-separated if they are to be analyzed with the simplest and most inexpensive instrument, a filter fluorometer. Fluorescein and rhodamine WT can be analyzed simultaneously, because they emit in the green and red region of visible light, respectively. A dye that emits in the blue region could be used because it would not significantly interfere with either fluorescein or rhodamine WT. One possibility for a geothermal blue dye is amino G. Amino G is one of the simplest optical brighteners. Our initial work indicates that amino G may be suitable for low- to moderate-temperature systems. However, amino G has not been tested in the field under geothermal conditions. A blue dye that we have field-tested is tinopol CBS-X. Unfortunately, the return curves from this test, in which Tinopol and fluorescein were simultaneously injected, suggest that Tinopol adsorbed onto the reservoir rock. This does not imply, however, that amino G will adsorb because Tinopol is a large and complicated molecule while amino G is half the size of either fluorescein or rhodamine WT.

Decay rates can be affected by fluid chemistry as well as temperature. Fluorescein appears to be relatively insensitive to fluid chemistry other than low pH (Adams and Davis, 1991). Rhodamine WT and amino G, however, decay at rates that are influenced by the concentration of oxy-anions. Comparison of the decay rates of these dyes in distilled water and phosphate buffer solutions demonstrates that complexation by the biphosphate ion alters the decay rates. effect is not simple, in that the decay rate of rhodamine WT is increased while that of amino G is decreased. Field data from a tracer test at Steamboat Springs (Rose and Adams, 1994) indicate that the bicarbonate ion also affects the decay rate. Fortunately, our experimental and field data imply that the effect is catalytic, and that the effect of the bicarbonate ion in geothermal fluids will be independent of concentration at the levels found in most geothermal fields. Thus, a pseudo-first order rate law can be used to compensate for thermal decay. Constants for such a rate law are listed in Table 2 for rhodamine WT and amino G.

# 2.4 Two-Phase Tracers

A significant weakness of vapor-phase tracers is that they do not always follow the same path as the injected water that does not immediately boil as it enters the reservoir. For example, there are indications from the results of the latest DOE/industry test at The Geysers (Voge et al., 1994) that the wells in which the vapor-phase tracers appeared have a different geographic distribution than those of the tritium tracer, even though the two types of tracers were simultaneously injected. In contrast, there is considerable evidence from other tracer tests at The Geysers that the path of the vapor-phase tracers and the bulk of the injection-derived steam coincide (Adams et al., 1991b; Beall et al., 1994). A tracer that is more soluble than the current vapor-phase tracers would remain with the liquid through a larger boiling fraction, which would alleviate this uncertainty. In some cases, a distribution coefficient similar to that of water may be desirable in order to more closely follow the behavior of the injected fluid. In other instances, a distribution that is skewed towards the steam phase may be preferred, allowing for rapid transfer of the tracer to the steam phase and reducing the test duration. A volatile tracer will also fractionate to the atmosphere prior to re-injection, and will not be recycled during the test.

Alcohols are a class of compounds that we have investigated as potential two-phase tracers. They have significant solubility in both the liquid and steam phases and appear to be relatively stable at geothermal temperatures. Alcohols, especially ethanol, have low toxici-

Table 2. Rate equations as a function of temperature for fluorescein (Adams and Davis, 1991), rhodamine WT (Rose and Adams, 1994), and amino G (Adams, unpublished data). The rates are in units of day<sup>-1</sup>.

ty. The Threshold Limit Value for ethanol, which is an OSHA standard for continuous exposure, is 1000 ppm in the vapor phase (ACGIH, 1979). Under most circumstances the human body can eliminate ethyl alcohol at the same rate that it is absorbed (Lester and Greenberg, 1951).

To date we have tested alcohol-water solutions in our pressurized autoclaves at temperatures of up to 320°C for periods ranging up to one month. The results, shown on an Arrhenius plot in Figure 1, display an inverse relationship between the thermal stability of straight-chain alcohols and the number of carbons in the molecule. Data for fluorescein and rhodamine WT are also shown for comparison in Figure 1. The one branched alcohol tested, isopropanol, decayed rapidly at temperatures as low as 240°C. Isopropanol was also detected as a decay product of n- propanol. The rapid reaction of isopropanol and its shallow temperature dependence imply that the decay of secondary alcohols will reach equilibrium within the time span of a tracer test, and should not be used as tracers. Decay of the straight- chain alcohols, in contrast, are kinetically controlled and can be used as tracers, especially in moderate-temperature systems such as The Geysers.

A series of experiments for n-propanol were carried out in which the liquid to steam ratio in the reaction vial was varied from pure steam to nearly complete liquid. The results indicate that no significant decay of n-propanol took place in the steam phase.

The alcohols have not been used in a tracer test yet because they are not sufficiently detectable by themselves. However, work is currently underway to develop an extremely sensitive method that will tag the alcohols with fluorescent molecules for subsequent analysis on a liquid chromatograph.

## 3.0 POTENTIAL NEW USES OF TRACERS

# 3.1 Definition of Injectate Boiling Parameters

The use of tracers that are more volatile than water opens up the possibility of defining the conditions of injectate boiling. Vapor–phase tracer tests conducted at The Geysers (Adams et al., 1991b; Beall et al., 1994) displayed rapid velocities and complex pathways. However, the degree to which the recovery of the vapor–phase tracers represents the recovery of the majority of the injected fluid has been questionable because of the high volatility of the tracers. This question was partially addressed by using data from the most recent test at The Geysers to define the injection boiling fraction represented by each sample. The test consisted of three simultaneously injected tracers, two vapor–phase tracers, R–13 and SF<sub>6</sub>, and tritium (Voge et al., 1994). This combination allows for dilution along the flow path to be calculated from the change in the tritium concentration:

$$C_{\tau} = D \cdot C_{\tau}^{i}$$

Where  $C_T$  and  $C_T^I$  are the concentrations of tritium in the production and injection stream, respectively. The dilution factor, D, can then be

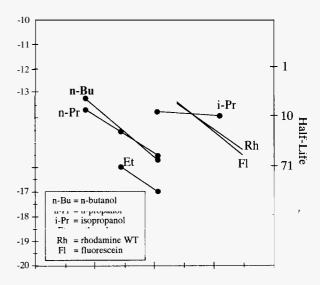


Figure 1. Arrhenius plot of alcohol decay data. Half—lives and temperatures are shown on the alternate axes. Rhodamine WT and Fluorescein rates, computed from the equations listed in Table 2, are shown for comparison.

applied to the concentrations of the R–13 (C,) and sulfur hexafluoride ( $C_8$ ) tracers:

$$C_R = D \cdot C_R^I$$
 and  $C_S = D \cdot C_S^I$  (2)

The vapor-phase tracer concentrations in the production steam, corrected for dilution, are assumed to reflect their concentrations in the steam phase as it left the vicinity of the injection well. For example, it is assumed that no chromatographic separation due to retention in adsorbed reservoir water took place. Thus, the liquid and steam tracer concentrations can be related to the liquid phase by their respective distribution coefficients, B<sub>i</sub>, where:

$$B_i = \frac{C_{i,\nu}}{C_{i,\nu}} \tag{3}$$

Here, i designates the tracer species, v and 1 indicate the vapor (steam) and liquid phases, respectively, and C is the tracer concentration in molal units.

The distribution coefficients of R–13 and SF<sub>6</sub> have not been measured at temperatures above 100°C. For the purposes of this study the solubility data were extrapolated to higher temperatures by transforming the Henry's Law constants (Kh) to volatility ratios (B), which represent the ratio of the molal concentration in the gas to that in the liquid. It has been shown empirically that log(B) is an approximately linear function of temperature (Drummond, 1981). The compressibility factors required for the transformation of Kh to B were calculated from the critical constants compiled in Adams et al. (1991a) using the three–parameter corresponding states correlation of Lee and Kesler (1975). The solubility functions obtained in this manner are:

$$Log B_R = 10.7566 - 0.01507 *T(K)$$
 (4)

$$LogB_s = 11.6093 - 0.01591 \cdot T(K)$$
 (5)

Three models of boiling can be used to fit vapor-phase tracer data: single-stage, multi-stage, and continuous boiling. Single-stage and continuous boiling can be considered as boiling mechanism end-members, where single-stage boiling is a static, equilibrium relationship between the steam and the liquid, and continuous boiling occurs where the steam is immediately removed from the liquid as it

<sup>\*</sup> This is a correction of Rose and Adams (1994), in which a zero was inadvertently omitted.

forms, and only instantaneous equilibrium is achieved. Multiple-stage boiling is an intermediate case, where the steam is modeled as being removed in discrete batches of specified size. Single-stage is computationally the simplest relationship, and is defined by:

$$C_{i}^{o} = y \cdot C_{ip} \cdot (1 - y) \cdot C_{il}$$
 (6)

where  $C_i^\circ$  is the original concentration of the tracers, and y is the fraction of original liquid boiled. Combining this relationship with eqn. 3 and solving for y provides one estimate of the steam fraction for each tracer:

$$y = \frac{\left(C_{i}^{o} - \frac{C_{i,\nu}}{B_{i}}\right)}{\left(C_{i,\nu} - \frac{C_{i,\nu}}{B_{i}}\right)}$$
(7)

Unfortunately, the single-stage model could not provide the range of concentrations and tracer ratios found in the data from the tracer test performed at The Geysers.

The other extreme, continuous boiling, is derived from distillation studies (Rayleigh, 1902) and has been applied to both isotopic (Gat, 1980) and gas (Drummond, 1981) boiling relationships. The basic form of the equation is:

$$\frac{C_{ij}}{C_i^{\sigma}} = x^{B_i - 1} \tag{8}$$

where x equals the fraction of liquid remaining, or 1–y. Solving for y:

$$y = 1 - 10 \left[ \frac{\log \left( \frac{C_{ir}}{C_i \cdot B_i} \right)}{B_i - 1} \right]$$
 (9)

Before using eqn. 9, the temperature of boiling must be estimated in order to calculate  $B_i$ . The temperature of boiling can be determined by calculating y for each tracer as a function of temperature and plotting the resultant lines against temperature. The lines for the two different tracers will intersect at the boiling temperature and steam fraction that produced that particular package of steam.

The results of the continuous boiling model were compared to the data from the test at The Geysers. The model easily produced the range of concentrations found in the data set, but failed to match the observed tracer ratios.

The intermediate case, multi-stage boiling, has been defined by Henley et al. (1984) as:

$$\frac{C_{i,l}}{C_i^{\sigma}} = [1 + y(B_i - 1)]^{-n}$$
 (10)

The variable n in eqn. 10 represents the number of boiling stages with steam fraction y. In the case of multi-stage boiling, y is a measure of the efficiency with which steam is removed from equilibrium with the remaining liquid, while the total steam fraction is approximately the product of y and n, or in a more exact form:

$$y_{total} = \sum_{m=0}^{n-1} (n-m) \cdot y^{m-1}$$
 (11)

The efficiency of steam removal is probably a function of fracture size, fracture spacing, and steam velocity. Alarge y might imply larger or more numerous fractures, while a small y might indicate high steam velocities through small fractures.

For multi-stage boiling, the temperature of boiling must also be estimated first. This can be accomplished by the relationship:

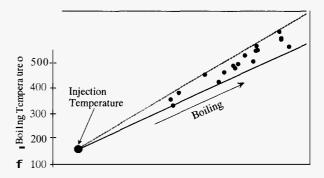
$$T(K) = \frac{\log\left(\frac{C_{i,\nu}}{C_{i}^{o}}\right) - a_{i}}{-b_{i}}$$
(12)

where a<sub>i</sub> and b<sub>i</sub> are constants from the solubility function:

$$\log B_i = a_i - b_i \cdot T(K) \tag{13}$$

The constants for R-13 and SF<sub>6</sub> are given above in eqns. 4 and 5.

Temperatures derived from eqn. 12 will not necessarily produce the correct temperature because the injection concentration, C<sup>I</sup>, will be valid for only the first boiled steam, after which the composition of the liquid will change according the solubility of each gas tracer. This process has been simulated for multistage boiling at 150°C, and the results are shown in Figure 2. It can be seen in this figure that the lowest temperature recorded will be the boiling temperature. However, because vapor—phase tracers can travel rapidly through the reservoir, especially in low pressure portions such as the southeast Geysers, the lowest temperatures may not be recorded. This is illustrated in Figure 2 with data from the DV–11 test at The Geysers (Voge et al., 1994), in which samples were only taken daily.



--- y = 0.03% — y = 1.7% • Field Test Data

Figure 2. **An** illustration of the effect of multi-stage boiling on the temperatures inferred from the tracer concentrations in the production steam, the initial concentration, and the temperature dependence of the distribution coefficients, as shown by eqn. 13. The data are taken from the tracer test discussed in Voge et al. (1994). The solid lines represent the theoretical shifts predicted by eqn. 10.

Once a boiling temperature is known or estimated, the steam fraction y can be deduced from the reduced concentrations of the two tracers,  $C_i$  and  $C_i$ :

$$k_{i} = (1 \cdot y(B_{i} - 1))^{\frac{\log k}{\log(1 \cdot y(B_{i} - 1))}}$$
 (14)

where  $k_i = \frac{C_{i,j}}{C_i^{\hat{o}} \cdot B_i}$ 

The appropriate value of y can be found by an iterative solution of eqn. 14 or by graphing this equation as a function of the steam fraction. Once the steam fraction is known, the number of stages can be calculated using eqn. 10. The data from the Geysers test were reduced in such a manner, and the results are shown in Figure 3. The combinations of n and y shown for the sample points indicate that the vapor—phase tracers were derived from the first 10%of injectate boiling

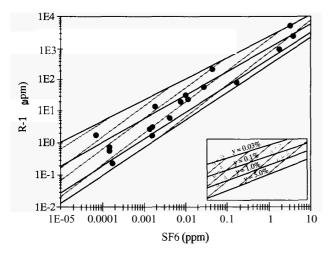


Figure 3. Multi-stage boiling parameters calculated from the tracer data of a recent injection test performed at The Geysers (Voge et al., 1994). The concentrations shown have been corrected for dilution using tritium tracer concentrations. The steam fractions (y) for each stage and the number of stages (n) are shown in the insert.

### 3.2 Definition of Effective Temperature

It can be shown that one temperature can be used to describe the change in concentration of a thermally decaying tracer during its travel through a temperature gradient, even though the tracer actually decays at a variety of different temperatures (Robinson, 1985). This parameter, the effective temperature, will generally be similar to the average temperature of the flow path. However, it is weighted towards higher temperatures because of the Arrhenius temperature dependence. Where two tracer with different decay rates are injected simultaneously into the same well, the effective temperature can be derived by examining the change in the ratio of the tracer concentrations with time in the production fluid. If the kinetic decay rates calculated from the laboratory are appropriate to field conditions, the ratio will change according to the relationship:

$$\frac{C_1}{C_2} = \frac{C_1}{C_1} e^{(k_2 + 1)t}$$
 (15)

where C, and  $C_2$  are the concentrations of the two tracers in the production fluid,  $C_1^{\circ}$  and  $C_2^{\circ}$  represent the initial concentration of the tracers, k, and k, are the tracer decay rates, and t equals the time in seconds between injection and sampling of the tracers.

This technique was applied in tracer tests conducted at the Dixie Valley (Adams et al., 1989) and Steamboat Hills (Rose and Adams, 1994) geothermal systems. The tracers used at Dixie Valley were benzoic acid and fluorescein. In this test, the maximum reservoir temperatures were approximately 240°C and fluorescein was the decaying tracer. At Steamboat Hills fluorescein and rhodamine WT were used. The maximum reservoir temperature was approximately 160°C, and rhodamine WT was the decaying tracer.

## 3.3 Adsorption

The ratio of phases within a reservoir can be quantified by using tracers that partition into the various phases. The varying solubilities imply that compounds that are more soluble in the condensed phase spend more time in that phase, i.e., in adsorbed water or rock. As the conservative tracer front passes, equilibrium returns the adsorbed compound to the vapor or liquid fluid. This is a chromatographic shift, which results in the separation of tracer peaks according to their properties.

For example, a test that is commonly performed in the oil wells is to inject ethyl acetate into a well and force it out into the reversely water (Sheely and Baldwin, 1982). Once the ethyl acetate is at the

desired distance into the reservoir, injection is stopped to allow it to react to form ethanol and acetic acid. The ethanol partitions into the oil and water phases, and when the water is backflowed the residual oil saturation can be calculated from the ethanol concentration. The purpose of injecting ethyl acetate rather than ethanol is to allow partitioning only on the return path, which simplifies the calculations. This technique has also been applied to two-well tests (Allison et al., 1991). Similar tests have been performed on gas—rich reservoirs using volatile tracers (Tang and Harker, 1991).

In vapor-dominated geothermal systems, tracers of varying solubility, such as the alcohols and the vapor-phase tracers, could be used to measure the relative amount of adsorbed or matrix water along the injection-production path of a vapor-phase or two-phase system. The difference in solubilities would result in a chromatographic shift of the two tracer peaks. The amount of shift could be related to the amount of liquid water encountered along the pathway, and provide a measure of the change with time of water saturation from injection.

In liquid—phase systems, adsorption could be used to measure the relative amounts of solid surface area encountered along different injection—production paths. Greater surface areas would result in more tracer retained by adsorption, altering the peak shape and timing. This would reveal the difference in surface areas between different injection—production pathways, and provide a measure of their heat—transfer capability. This occurred in a tracer test at the Beowawe geothermal system, where adsorption of the blue dye Tinopol CBS—X (P. Rose, pers. comm.) was accompanied by broad peaks of the more conservative tracer, fluorescein. The broad peaks indicated multiple—fracture pathways, which would provide more surface area than those with single fractures.

#### 4.0 SUMMARY

Tracers have been or are being developed to tag injection—derived liquid, steam, or two-phase fluids. The properties of these tracers may be used to define the boiling parameters of fluid injected into vapor—phase systems, to calculate the effective temperature of an injection—production flow path, or to characterize the relative surface area of different areas of the reservoir.

## **5.0** ACKNOWLEDGEMENTS

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