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TRACING GEOTHERMAL FLUIDS: TWO-PHASE TRACER DEVELOPMENT

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Key Words - Tracers, Vapor-Phase Tracers, Two-phase tracers, Geysers, Fluorinated alcohols, Hydrofluorocarbons

Abstract

The development of geothermal tracers is a vital component of geothermal research. Industry uses these compounds to maximize power production from geothermal fields. All of the tracers currently in use have been developed at EGI. These tracers are designed to tag either steam or liquid. Research under the current contract is focused on developing two-phase tracers, which will be used to trace both steam and liquid. Candidate compounds have been chosen and appear to be thermally stable. The detection limit and acidity of these compounds still needs to be determined.

Project Background and Status

Geothermal Tracers

Tremendous volumes of water are cycled through any power plant that produces electrical power from geothermal water. This water must be injected back into the reservoir to maintain power production and avoid contamination of local groundwater. Injection can dramatically increase the number of years that power can be produced from a geothermal field. The direction and rate of the injectate must be controlled so that it provides fluid recharge but does not cool the fluid that is being produced from the wells. Tracers are the only method of tracking the speed and pathways of the injected water. Before 1983, when the DOE-sponsorship of injection research began, few tracers were available to the industry (Adams, 1985). Since 1983, research performed at EGI has defined the stability and use of the tracers fluorescein (Adams et al., 1989; Adams and Davis, 1991), rhodamine WT (Rose and Adams, 1994), and many aromatic acids (Adams et al., 1992). Dr. Peter Rose has extended this research to the development of the very stable naphthalene sulfonates under a separate DOE contract to EGI (e.g., Rose et al., 2001).

Vapor-Phase Tracers

Research under this contract has branched to the development of tracers that are capable of following steam and/or liquid water. In 1989 the operators at The Geysers asked DOE for research that would help them stem reservoir pressure decline and maintain production from this important resource.

Tracers were specifically called out. Several CFC gas tracers were quickly developed by us (Adams et al., 1991b) and deployed at The Geysers. (Adams et al., 1991a). From 1991 to 1997, several tests were performed with one of these gas tracers, R-13 (Beall et al., 1994). When production of the chlorofluorocarbon R-13 was cut back because of international agreements to alleviate ozone depletion, two hydrofluorocarbons, R-134a and R-23, were chosen to replace it (Beall et al., 1998; Adams, 1999). Since their introduction, both R-134a and R-23 have been used in multiple tracer tests to quantify the benefits of injecting water from Clear Lake and Lake County effluent into the reservoir at The Geysers (Goyal, 1999).

Vapor-phase tracers are much more soluble in the steam than the liquid phase. This is a necessary attribute that allows the tracers to track the steam through the reservoir. This increased volatility makes vapor-phase tracer tests more difficult to design and interpret than liquid-phase tests (Adams et al., 2001). The primary effect of the high volatility is that steam is the only phase that comes out of the production wells, but liquid water is only phase injected back into the reservoir. Therefore, vapor-phase tracers, which are sparingly soluble as a consequence of their high volatility, must be injected at low concentrations. When the injection water reaches boiling temperature in the reservoir, the tracers immediately transfer into the steam phase. Very little is left in the residual water to track it to its ultimate destination. A secondary effect of the high volatility is that different tracers enter the steam phase at different rates. The rate for each compound depends on its solubility, which vary considerably from compound to compound (Fig. 1). Consequently, the decay rate of vapor-phase tracers cannot be used to define pre-decay concentrations or any temperature parameters of the flow path, because there is no index compound to compare them to. This situation creates a solubility-dependent ratio in production steam of any two volatile tracers that were simultaneously injected. This has been detected in two tests conducted at The Geysers, in which tritiated water was injected simultaneously with a vapor-phase tracer (Adams, 1999).

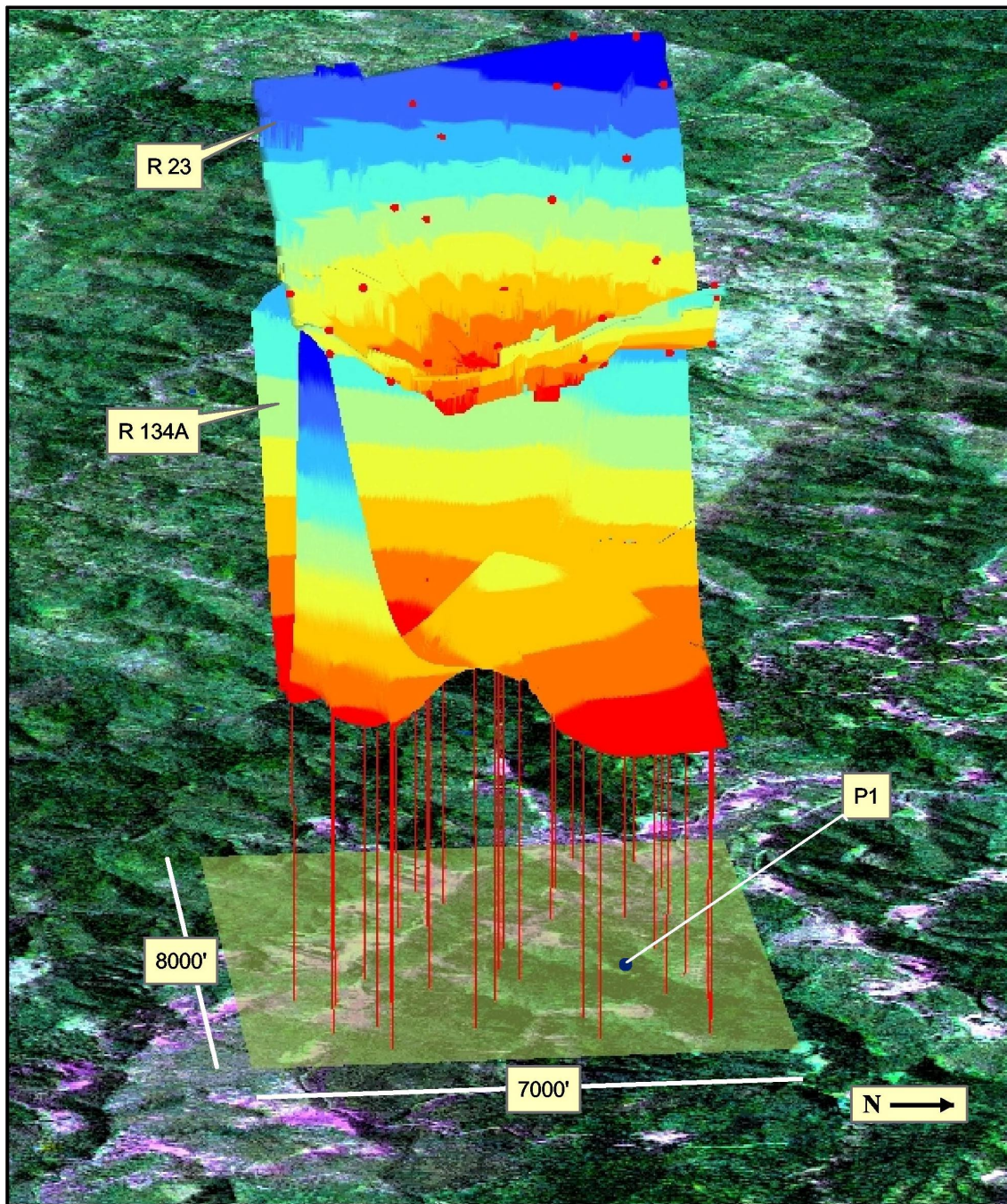


Figure 7. Results of one day of the P-1 tracer test at The Geysers in which two different tracers, R-134a and R-23, were used.. The colored surfaces represent the concentrations of the tracers in a logarithmic scale. Blue is the highest concentration, red the lowest. The surfaces are overlain on a satellite photograph of The Geysers. The locations of wells involved in the test are shown by the vertical lines and the dots on the upper surface.

Because of their volatility, vapor-phase tracers do not always follow the same path as the majority of the injected water. For example, Adams et al. (1999) has shown that in one tracer tests the vapor-phase tracers had a different geographic distribution than the tritium tracer, even though the two tracers were simultaneously injected. Calculations of injectate recovery using the two different tracers differ when this situation occurs. This is an important consideration, one that will become increasingly relevant as the amount of injection increases due to the Lake and Sonoma County pipelines. It should be noted, however, that the path of the vapor-phase tracers and the bulk of the injection-derived steam coincide in many cases (Adams et al., 1991a; Beall et al., 1994; Adams, 1999).

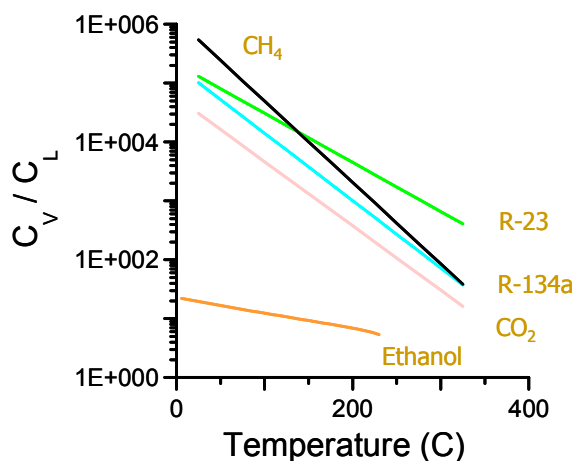


Figure 8. Solubility of some vapor-phase tracers in steam. C_v = concentration in steam, C_L = concentration in liquid. Ethanol, a two-phase tracer, has a much lower solubility in steam and thus will stay with the water much longer during a tracer test.

A tracer with significant solubility in water but which volatilizes at a rate near that of water can be termed a two-phase tracer (water and steam) (e.g., ethanol in Fig. 2). Our initial investigations indicate that alcohols have the most potential for use as 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 toxicity. 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).

Alcohols were also chosen because of their low acid dissociation constant. This implies that the compound will not ionize until the pH of the water is quite high. This is important because water can get quite basic when it boils, due to the loss of carbon dioxide. This is a strong limitation on the type of compound that will be suitable as a two-phase tracer. For example, organic acids can be quite stable but they are ionized at the pH typical of a geothermal reservoir.

To date we have tested several alcohol-water solutions in our pressurized autoclaves at temperatures of up to 320°C for periods ranging up to one month (Adams, 1995). The results display an inverse relationship between the thermal stability of straight-chain alcohols and the number of carbons in the molecule. 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.

However, the alcohols by themselves are very difficult to use in the field because they have no properties that make them strongly detectable. We believe that the addition of fluorine to the alcohols would provide a much lower detection limit. For instance, some of the detection techniques developed for use with the hydrofluorocarbons that we developed for use at The Geysers might be used to analyze fluorine-containing molecules at extremely low levels (Adams, 1999). Therefore, we are currently examining the potential of fluorinated alcohols as two-phase tracers.

Project Objectives

The overall objective of this research is to develop tracers that will help increase and maintain the power production of geothermal systems through injection management. Specifically, our objectives are to:

- 1) Identify a class of compounds with the desired properties of a two-phase tracer.
- 2) Select several members of this class and test them in the laboratory.
- 3) Perform a field test at The Geysers.
- 4) Transfer the technology to industry.

Approach

The first task was to identify the necessary or desired properties of a two-phase tracer. These include stability, toxicity, detection limit, solubility, volatility, acidity, and cost. The criteria were:

- 1) Stability – The compounds should be stable in a simple water-tracer system for 50 days at 240°C. If they decay, they should follow a first-order rate law and decay no more than 20%.
- 2) Toxicity – Compounds with specific toxicity will not be considered. Compounds labeled as irritants will be considered.
- 3) Good detection limit – Detection limits should be in the parts per trillion range. The search for two-phase tracers will focus on fluorinated compounds because the gas chromatography detectors adapted for fluorine detection have been successfully optimized for use with fluorinated vapor-phase tracers.
- 4) Solubility – Compounds with infinite or limited solubility will be considered. This implies that the elements should include hydrogen, oxygen, , and carbon to raise the polarity of the tracer. Fluorine will be included for detectability.
- 5) Volatility – Compounds should be neutral at reservoir boiling pH's
- 6) Inertness – Any ions that can be naturally produced by the compounds should be negative to avoid interaction with the reservoir rock.
- 7) Acidity – The compounds should not be so acidic that it interferes with volatility.
- 8) Cost -- Ultimately cost will be an issue. It will not be considered in the initial stages of the investigation.

A class of compounds with attributes that are closest to the desired properties will be chosen, and a few tested for thermal stability. These will be run in pressurized autoclaves at 280°C for four days as a screening test. We will continue testing the most stable compounds to determine the kinetic parameters in simple water-tracer systems.

Research Results

The results of the literature survey are shown in Figure 3. At the present time we are restricting our selections to soluble compounds due to a lack of high-temperature EOS for fluorinated compounds at

high temperatures. Thus, the most suitable compounds are the soluble alcohols.

Three fluorinated alcohols were chosen for laboratory testing. These are the most soluble of this class of compounds. Specifically, 1,1,1-trifluoro-2-propanol, 1,1,1-trifluoro-2-propanol, 4,4,4-trifluoro-1-butanol were selected. The structures of these compounds are shown in Figure 4.

The results so far are encouraging. The preliminary data on the stability of all of the compounds indicates that they are sufficient for tracing in moderate-temperature systems (Fig. 5). However, the detection limit and acidity of these compounds still needs to be determined.

Future Plans

We hope to finish the qualifying autoclave tests during FY2002. During this time the detection limits will be determined. If the detection limits can be pushed low enough for use in tracing, the acidity will be determined experimentally during FY2003.

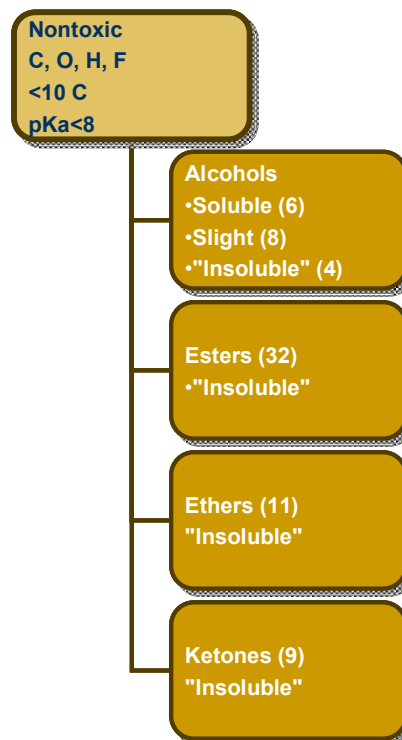


Figure 9. Results of the search for potential two-phase tracers. The criteria for the search are given in the top box, and the results for the various compound classes are given in the lower boxes.

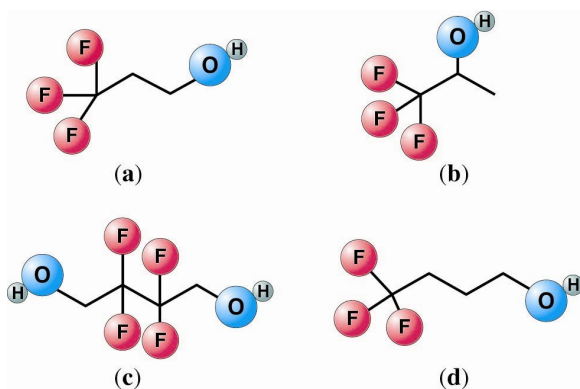


Figure 10. Structure of the fluoroalcohols chosen for the screening tests. (a) 3,3,3-trifluoro-1-propanol; (b) 1,1,1-trifluoro-2-propanol; (c) 4,4,4-tetrafluoro-1,2-butandiol; and (d) 4,4,4-trifluoro-1-butanol. The tests on the dialcohol (c) have not yet begun because of analytical difficulties.

Table 1. Results of the laboratory experiments.

1,1,1-trifluoro-2-propanol		
Temperature	Time	% Remaining
280°C	4 days	99.91%
320°C	7 days	97.15%
320°C	10 days	76.05%
330°C	7 days	91.45%
330°C	10 days	91.26%
330°C	14 days	59.56%
3,3,3-trifluoro-1-propanol		
280°C	4 days	8.13%*
320°C	4 days	42.16%
320°C	7 days	28.85%
4,4,4-trifluoro-1-butanol		
280°C	4 days	81.44%
300°C	4 days	82.84%
300°C	7 days	75.16%
320°C	7 days	72.20%

*Excessive decay from oxygen contamination

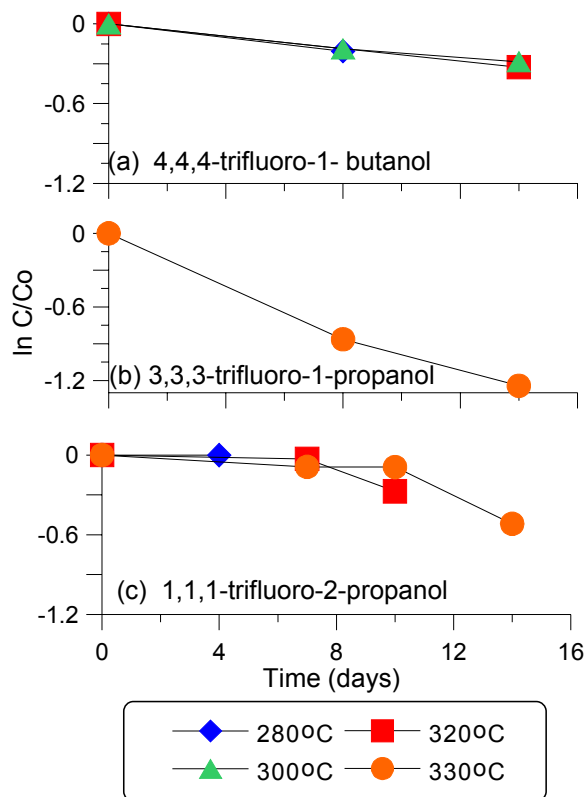


Figure 11. Thermal stability of fluorinated alcohols. C/C_0 is the fraction left after heating at the specified temperature and time.

Collaborations, Papers Published and Technology Transfer

This project has been strongly collaborative with industry. As stated by Paul Hirtz of Thermochem, Inc. in June, 1998:

“To date at least 30 liquid and vapor-phase tracer tests have been performed using tracers developed by EGI. Of these tests, 10 were funded entirely by private industry. This demonstrates the value and overall acceptance of the tracer technologies for solving important geothermal development and utilization problems. I am not aware of any other DOE-funded geothermal program that has resulted in such widespread use by industry.”

“The reservoir tracers are now used routinely to monitor important water injection projects, such as the wastewater injection programs at The Geysers. The results are used to optimize injection strategy for maximum conversion of wastewater to steam. The liquid tracers have been used to monitor brine injection breakthrough in fields such as Dixie Valley and Coso, and both liquid and vapor tracers have been recently used in high-temperature

systems in Hawaii and Indonesia. The results of these tests weigh heavily in multi-million dollar decisions by developers regarding injection placement and the drilling of new injection wells."

The tracer tests mentioned by Hirtz were performed in conjunction with Calpine Geothermal, Northern California Power Authority, Unocal Geothermal, California Energy Corporation, and Caithness Corporation.

All of the major papers on tracer development have been published by EGI. During the last three years eight were published under the current contract (Adams et al., 1999; Adams and Kilbourn, 2000; Adams et al., 2000; Moore et al., 2000; Adams, 2001; Adams et al., 2001; Beall et al., 2001; Nash and Adams, 2001). A special issue of the journal *Geothermics* devoted to the topic of tracers was published this year as a task under the current contract.

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