PROCEEDINGS, Twenty-Ninth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 26-28, 2004
SGP-TR-175

# ALCOHOLS AS TWO-PHASE TRACERS

Michael C. Adams[1], Yasuo Yamada[2], and Masahiko Yagi[2], Christian Kasteler[1], Phaedra Kilbourn[1], and Nick Dahdah[1]

[1]Earth & Geoscience Institute, 423 Wakara Way, SLC UT USA
[2]JAPEX Research Center, 1-2-1 Hamada, Mihama, Chiba, 261 Japan
e-mail: madams@egi.utah.edu

## ABSTRACT

The alcohols methanol, ethanol, n-propanol, and n-butanol are potential two-phase geothermal tracers. Their thermal stability ranges from very stable at high temperatures (>300°C; methanol) to somewhat stable at moderate temperatures (~250°C; n-butanol). Their distribution between liquid and steam also varies systematically, with methanol solubility being very close to that of water (VR=6 at 150°C) and n-butanol being more soluble in steam by a factor of seven. Preliminary, qualitative analysis indicates that the decay of the alcohols produces shorter-chain alcohols, giving rise to intriguing possibilities as reactive tracers. In this paper we present the results of several largely-unpublished short studies on the stability of the alcohols that were performed over the last decade.

## INTRODUCTION

Geothermal tracers have been developed that are soluble in the liquid phase (ROSE et al., 2001) or the vapor phase (ADAMS et al., 2001). These compounds have liquid-vapor distribution coefficients of zero and >2000, respectively. 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. For example, geothermal systems in desert regions such as the Coso geothermal field may transport water from injection to production wells through both liquid and vapor-dominated zones (Adams, in press). Another example would be The Geysers, where injected water can flow for considerable distances before completely boiling (ADAMS, 2001).

An ideal two-phase tracer should have low toxicity. It should be released from boiling injectate at a rate similar to that of water. It should, of course, be stable and not adsorb significantly on rock or pipe. Use on an industrial scale dictates that it also be cheap and easily available. Alcohols were selected as potential two-phase tracers several years ago. They have been since been used in at least one tracer test in Mexico (E. Tello, personal communication) and are routinely used to determine total discharge enthalpy in New Zealand (LOVELOCK, 2001). Alcohols have significant solubility in both the liquid and steam phases and appear to be relatively stable at geothermal temperatures (ADAMS, 1993; ADAMS, 1995; ADAMS et al., 2000). The hydroxyl group, which defines an alcohol, dissociates less than organic acid groups do under geothermal conditions, allowing the compounds to fractionate to the steam phase from a boiling geothermal liquid. Organic acids, in contrast, ionize under these conditions and are therefore less volatile. Steam-liquid distribution ratios of the lowest molecular-weight alcohols range from five to 100 in binary water-alcohol solutions. This contrasts strongly with 3,000 and 75,000 for the vapor-phase tracers R-134a and $SF_6$, respectively. However, alcohols are currently not as detectable as either liquid- or vapor-phase tracers. Detection limits were approximately 100 parts per billion at the time the alcohols were first being considered as tracers. Consequently, the focus of two-phase tracer research for the last few years has been on fluorinated compounds, which are generally more detectable. These compounds have proved to be unreliable as tracers and the focus is back on the non-fluorinated alcohols. The detection limit of these compounds has recently been lowered to 1 ppb using solid phase microextraction technology. Details of this method are available upon request.

This paper presents the results of cooperative studies on the thermal stability of alcohols conducted by EGI and Japex personnel between 1993 and 1999 (ADAMS et al., 2000; YAGI et al., 1997).

## PROPERTIES OF THE ALCOHOLS

Alcohols are essentially natural gases such as methane (one carbon), ethane (two carbons), propane (three carbons), and butane (four carbons) with a hydroxyl attached. The hydroxyl imparts a polar nature to the molecule and thus makes it soluble in water. The smaller alcohols such as methane, ethane, and propane are completely soluble in water, while butane and the heavier alcohols get less soluble in water as the molecular weight increases. The solubility of butane in water at room temperature is

7.1% by weight. Although alcohols contain an OH group, they have a pKa of greater than 14 at room temperature and should be neutral molecules under boiling conditions. The neutral charge allows them to fractionate easily to the steam phase.

The toxicity of alcohols varies. One measure is the TWA, which is the time-weighted average airborne concentration over an 8 hour working day, for a 5 day working week over an entire working life. These are 200, 1000, 200, and 150 ppm for methanol, ethanol, propanol, and butanol, respectively (ACGIH, 1979). Additional care should be taken with methanol because it can cause blindness at less-than-toxic concentrations.

These alcohols are relatively easy and inexpensive to purchase. Ethanol must either be denatured to prevent imbibition or a permit must be obtained for its purchase.

## Liquid-Steam Distribution of Alcohols

The solubility of two-phase tracers such as the alcohols cannot be described by a simple temperature-dependent Henry's Law coefficient. This is because the same properties that produce solubility also modify the properties of the water as the concentration of the tracer increases. A more appropriate equation in this temperature range is the Wilson equation. This type of solubility predictor requires data sets in which concentration as well as temperature is varied. These data are used to produce optimized constants for the Wilson equation. Optimized parameters for methanol, ethanol, n-propanol, and n-butanol (the "n-" indicates no branching of the molecule) were taken from (GREEN, 1997), and were used to calculate the distribution coefficients ($C_V/C_L$) at various temperatures. Two caveats to these calculations are 1) they are for alcohol-water binary systems, and 2) activity coefficient equations such as these are not dependable near or above the critical temperature of the solute, which for the alcohols are in the mid-200$^o$C range. They are, however, sufficiently accurate to demonstrate that methanol will follow water very closely during boiling, with the other alcohols distributing more to the steam phase as the molecular weight increases (Fig. 1).

The discussion of solubility introduces another benefit of using the alcohols as tracers; they can be sampled as a liquid by quenching the steam in a cooling coil as it exits through the sample tubing. Figure 2 illustrates this point for n-propanol. At 10$^o$C less than 20% of the tracer is in an equal volume of vapor at equilibrium with the liquid. If the sampling temperature is recorded the total amount of tracer can be back-calculated.

## Thermal Stability of the Alcohols

### *Experimental Method*

The thermal stabilities of the alcohols were tested in batch reactors at temperatures of up to 320$^o$C at the corresponding vapor pressure of water. Aliquots of the solutions were sealed in quartz ampules in order to avoid catalysis by the metal walls of the autoclave. Quartz was used because it is present in most geothermal reservoirs and would give a realistic rate of decomposition even though it may also affect the rate of reaction. The surfaces of the vials were treated with a 5% solution of HF prior to use to provide a similar surface for each experiment. The 30 ml ampules were filled with approximately 25 ml of solution and then sealed with an oxygen-methane flame. The vials were purged with argon for twenty minutes with the vial submerged in ice, and the neck of the ampule was aspirated to prevent oxygen contamination by the oxygen-methane flame. No buffer was used in the experiments in order to avoid possible interactions between the buffer and the alcohols, but the solutions were adjusted to a pH of 6.6 with NaOH or HCl and to 4.0 using $H_2SO_4$ prior to heating. Three samples and one control were prepared for each experiment. The samples were heated in a water-filled self-heating batch reactor.

Some experiments were designed to detect any adverse effects of rock on the stability or concentration of the tracers. In these experiments, rock chips were immersed in both liquid and steam during the experimental run. It was decided to fix the amount of rock at 20 and 40 grams. This was equivalent to filling half of the vial and the entire vial, respectively, and would vary the surface area proportionately. Since the purpose of the experiments was to examine vapor-phase tracers, the water was kept to a minimum. The amount of water was empirically determined by adding water to the rock chips, sealing and heating the sample, and then examining the free water left after the sample cooled down to room temperature. The results of this process indicated that nine milliliters of water was sufficient to expose the rock to both steam and water during the heating run and to provide enough water to sample for analysis after the run. The question of what rock to use was determined by the desire to find rock with absolutely no organic contaminants. The granite used was provided by Japex personnel, who ground it to a size of 1 to 2.4 mm. The salinity of the water was varied from 0 to 20 g/l and the pH's from 4 to 7. Thus, the variables in the experiments were pH, salinity, and rock volume. No differences were found between the rock and no-rock experiments, implying that the presence of the rock produced no additional decay under these conditions.

The data presented in this paper are the result of several different studies in four different facilities

over the last decade. These studies were funded independently by the United States Department of Energy and the New Energy and Industrial Technology Development Organization. The experiments were performed using the similar equipment, but the techniques evolved somewhat over the years. This evolution in techniques has produced some scatter in the data. Another source of data scatter was probably sporadic bacterial contamination. In retrospect, an antibacterial agent should have been added to the solutions after heating but before analysis.

***Results***

The data that are presented in Table 1 were selected from a larger pool of experimental results. Final concentrations in the experiments that are not included were, in general, substantially lower than those in similar experiments. It was concluded that this was the result of sporadic microbial action on the samples. Many of these experiments were performed within a specific time frame, so repeats were not always possible. The lack of repeats renders these results qualitative.

First-order kinetic rates were calculated from the data in Table 1, and are displayed on an Arrhenius plot in Figure 3. This type of plot is based on the relationship:

$$\ln k = -E_a\left(\frac{1}{T}\right) + \ln A_O$$

where k is the rate constant, Ea is the activation energy, R is the Universal Gas Constant, T is the temperature in degrees Kelvin, and $A_0$ is the collision frequency factor. The minimum, maximum, and average of each temperature and pH condition are plotted. Salinity is not broken out because no significant difference was found between experiments that used 20 g/l NaCl solvents and those that used distilled water. The qualitative nature of the data is obvious from the scatter of the points. However, the data are sufficient to make some generalizations and predictions.

Figure 3 shows that the order of stability is methanol (no decay, hence not on diagram) > ethanol > propanol > (propanol in acid solution) > butanol. This order is consistent with the observation that these compounds form a homologous series. A homologous series is a group of compounds with similar functional groups and a steadily varying but non-reactive carbon backbone. The activation energies calculated from the rates can be used to make rough predictions of the decay rates at other temperatures. These are shown for 200°, 250°, and 300°C in figure 4. In this figure the data scatter was incorporated as minimum and maximum rates, shown by the shaded area in the plots. It can be seen that any of the tracers could probably be used at 250°C, depending on the length of the test. The use of any but methanol could be problematic at temperatures above 300°C. However, methanol appears to be one of the decay products of ethanol, and propanol is among those produced from n-butanol. The byproduct identification was qualitative, so the absolute abundances of the byproducts are not known. If the lower-weight alcohols are significant products of the upper-weight alcohol, then they may be useful as reactive tracers.

## CONCLUSIONS

The alcohols methanol, ethanol, n-propanol, and n-butanol may be useful as geothermal tracers. Methanol is stable for long periods of time at temperatures over 300°C. Ethanol, n-propanol, and n-butanol are successively less stable, to the extent that butanol could only be used as a purely non-reactive tracer at temperatures less than 250°C. However, n-propanol has been reported as a decay product of butanol, as has methanol from ethanol decay, which opens the possibility of using them as reactive tracers. These alcohols are true two-phase tracers. Their liquid-vapor distribution coefficients at infinite dilution range from 6 to 42 at 150°C, which is far lower than the vapor-phase tracers, with distribution coefficients in the thousands.

## ACKNOWLEDGEMENTS

Financial support for this research was provided by the New Energy and Industrial Technology Development Organization, High-Temperature Tracer Research Project, and by U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, under DOE Idaho Operations Office Financial Assistance Award DE-FG07-00ID13893 and DE-ACO7-95ID13274.

## REFERENCES


ACGIH. (1979) *TLV's - Threshold limit values for chemical substances and physical agents in the workroom environment.* American Conference of Governmental Industrial Hygenists.

Adams M. C. (1993) Geothermal tracer development. *U.S. Department of Energy Geothermal Reservoir Technology Research Program, Abstracts of Selected Research Projects*, 62-67.

Adams M. C. (1995) Vapor, liquid, and two-phase tracers for geothermal systems. *World Geothermal Congress*, 1875-1880.

Adams M. C. (2001) A comparison of two multiple-tracer tests conducted at The Geysers. *Twenty-Sixth Workshop on Geothermal Reservoir Engineering*.

Adams M. C., Beall J. J., Enedy S. L., Hirtz P. N., Kilbourn P., Koenig B. A., Kunzman R., and Smith J. L. B. (2001) Hydrofluorocarbons as geothermal vapor-phase tracers. *Geothermics* 30, 747-775.

Adams M. C., Yamada Y., Yagi M., Kondo T., and Wada T. (2000) Stability of methanol, propanol, and SF6 as high-temperature tracers. *World Geothermal Congress*, 3015-3019.

Green D. W. (1997) Perry's Chemical Engineer's Handbook. McGraw-Hill.

Lovelock B. G. (2001) Steam flow measurement using alcohol tracers. *Geothermics* 30, 641-654.

Rose P. E., Benoit W. R., and Kilbourn P. (2001) The application of the Polyaromatic sulfonates as tracers in geothermal reservoirs. *Geothermics* 30(6), 617-640.

Yagi M., Yamada Y., Yasuda Y., Uchida T., Adams M., Akazawa T., and Wada T. (1997) Experimental study for thermal stability of tracers with a view to applying them to high-temperature geothermal fields. *Japanese Geothermal Society Annual Meeting '97*.