STABILITY OF METHANOL, PROPANOL, AND SF$_6$ AS HIGH-TEMPERATURE TRACERS

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ABSTRACT

Tracers are needed for the development of high-temperature geothermal resources. Several candidate tracers have been tested for that purpose in hydrothermal autoclaves at the Energy & Geoscience Institute in Salt Lake City, Utah. One gas tracer, SF$_6$, and two of the two-phase tracers, the straight-chain alcohols, were tested. They were tested at temperatures ranging from 220 to greater than 300ºC, pH's of 3 to 7, and times of up to two weeks. The data indicate that SF6 is stable at a temperature up to about 300ºC in a simple SF$_6$-water system. Methanol is the most stable of the alcohols, with no decay being detected from a two-week run at 320ºC and a pH of 4. Propanol, in contrast, showed a 10% decay in a similar test. SF$_6$ displays a strong vulnerability to the presence of rock that should be tested further before being used in a geothermal reservoir.

1. INTRODUCTION

Vapor-phase tracers are needed for the development of high-temperature resources associated with volcanic systems, particularly around the Pacific rim. The current set of tracers that are being used in vapor-dominated resources such as The Geysers, R-134a and R-23, decay increasingly with temperature above about 280ºC (Adams, 1997; Beall et al., 1998). Tracers that will partition nearly equally between the steam and liquid phases are also needed, because high-temperature systems nearly always develop subsurface steam zones to some extent. Organic tracers have been developed that will survive temperatures in excess of 300ºC (Adams et al., 1992; Rose et al., 1999), but these compounds are ionic under typical geothermal boiling conditions, and will not fractionate extensively to the steam phase.

In this study we discuss the results of tests conducted to determine the suitability of sulfur hexafluoride, methanol, and propanol as vapor-phase and two-phase geothermal tracers.

2. SELECTION OF TRACERS

Sulfur hexafluoride (SF$_6$) was chosen as the vapor-phase tracer to be tested for this study. It was chosen because of its complete fluorination, which may make it the more thermally stable than the geothermal gas tracers currently in use. R-134a and R-23, both hydrofluorocarbons, are used extensively at The Geysers but decay rapidly at the temperatures found in high-temperature resources (Beall et al., 1998). SF$_6$ can be detected in the parts per trillion range quite easily. In fact, almost all gaseous tracers containing several fluorine atoms can be detected at very low levels using gas chromatographs equipped with halogen-specific detectors. The solubility of SF$_6$ is very low, similar to that of nitrogen and the less-soluble of the halogenated alkanes (Adams et al., 1991; Mroczek, 1997). The excellent detection limit of SF$_6$ allows it to also be used as a liquid-phase tracer despite its high volatility (Bixley et al., 1995; Glover and Kim, 1993; Upstill-Goddard and Wilkins, 1995). Vapor-phase tracers can be used as liquid-phase tracers as long at the liquid does not come into contact with a steam phase. When a highly volatile tracer contacts a steam phase, it will generally fractionate completely into the steam (Adams et al., 1999).

Alcohols were selected as potential two-phase tracers. Alcohols have been identified as a class of compounds that have significant solubility in both the liquid and steam phases and appear to be relatively stable at geothermal temperatures (Adams, 1993; Adams, 1995). 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. Approximate calculations for ethanol indicate that a steam to liquid concentration ratio of five to fifteen may be reached at geothermal injection temperatures, as opposed to three thousand for R-134a and seventy-five thousand for SF$_6$. Our initial tests showed that some of the alcohols had sufficient stability to be used as geothermal tracers (Adams, 1995). Alcohols are not as detectable as SF$_6$. Current detection limits are approximately 100 parts per billion for butanol, which is the most detectable of those being considered for use in geothermal systems (Thermochem, Inc., unpublished data).

Alcohols and SF$_6$ have very low toxicity. The Threshold Limit Value for ethanol and SF$_6$, which is a continuous exposure standard used by the United States Occupational Safety and Health Agency, is 1000 ppm in the vapor phase (ACGIH, 1999). Under most circumstances the human body can eliminate ethanol at the same rate that it is absorbed (Lester and Greenberg, 1951).

In this study the stability data of SF6 and methanol and propanol were extended to temperatures beyond 300ºC, pH's down to 3, chlorinities from zero to 20,000 ppm, and the presence of rock. Data on ethanol and butanol were obtained in a parallel series of tests conducted in the Japex laboratories, and will be reported on in future papers.

3. EXPERIMENTAL METHODS

The thermal stabilities of the alcohols were tested in batch reactors at temperatures of up to 320ºC 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.

SF_6 was obtained as a 56.5 ppmw mixture with nitrogen. The gas was encapsulated in fused quartz ampules before testing it at high temperatures. To avoid atmospheric contamination of the gas the upper portion of the ampule neck was fitted with a thin-wall small diameter tube (4 mm O.D.). Four of the ampules were attached to plastic tubes running off of a gas line. The ampule was purged with anhydrous Ar and then the ampules to be used for the hydrous experiments were filled with 5 mls of water adjusted to pH 4 or 7. Air was removed from the water by purging it with Ar for 20 minutes by inserting a smaller diameter tube (3 mm O.D.) into the water at the bottom of the ampule and bubbling argon through it. The flow rate of the gas was adjusted by observing the water and keeping the bubbling vigorous but not explosive. The air was purged because oxygen is not present as its reactive diatomic form in geothermal waters. The ampules were then purged and filled with the 56.5 ppmw mixture of SF_6 in nitrogen through the same tube for ten minutes. The tube was then withdrawn to a position above the fused junction of the ampule neck and the small-bore quartz tube while an oxy-acetylene flame was used to seal the neck. A fixed flame was used so that the ampule could be turned and pulled by one operator. Four ampules were prepared for each experimental run. Three were heated to test the thermal stability and one was cooled until the heating run was over and then used as an experimental control sample. The ampules were weighed and the weights recorded and compared to the post-run weights to check for a loss or gain of mass, which would indicate a leaking or dissolving vial.

A few of the experimental runs were performed with rocks as a variable. The amount of rock was fixed at 20 and 40 grams. This was equivalent to filling half of the vial and all of the vial, respectively, with a proportional change in surface area. 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 samples containing rock, water, and tracer were prepared by inserting the rock chips (20 or 40 g) into the silica ampule. The rock was a granite obtained from a commercial supplier, ground to a size of between 1 and 2.4 mm. Distilled water was added until the rock was covered. A tube was inserted into the ampule and a flow of argon established. The ampule was then heated on a mantle until the water boiled off. The purpose of this was to remove adsorbed oxygen. The pH-

adjusted tracer solution (or water in the case of SF_6) was then purged with argon, and 9 ml was added to the ampule. The gas flow was changed to SF_6 at this point for the gas tracer experiments. The argon flow was continued while the ampule was sealed using an oxy-methane flame.

Once the ampules were sealed they were inserted into a pressurized autoclave, which was a self-heated one-liter container. The pressurized autoclave had a 316 stainless steel liner, which was filled with 400 mls of distilled water. Analysis was performed on an HP 5890 gas chromatograph equipped with an FID detector for the alcohols, and an electron capture detector for the SF_6. Nitrogen was used as the carrier gas.

4. RESULTS

The tests were run from temperatures of 250 up to 330°C, at pH's from 3.3 to 7, and with or without the presence of rocks. The data that resulted from these tests are summarized in Table 1 and Figure 1. These data show that methanol is more stable than propanol, and did not decay in any of the tests. Propanol did show some decay, especially at the higher temperatures and lower pH's. The decay of SF_6 was not affected by pH, and did not occur until temperatures in excess of 300°C were reached, except in the presence of rock. Although only one SF_6-rock-water experiment is shown in Table 1, several others were performed with an altered dacite obtained by grinding drill core taken from the Fushime geothermal field. Almost all of the SF_6 rapidly decayed in these experiments. However, GC/MS analysis of the gas phase that resulted from heating the dacite revealed many organic compounds that may have resulted from lignite contamination of the core during drilling. In addition, the dacite rock sample includes hydrothermal alteration minerals. Although these experiments with rock were confounded by the presence of the extra gases and the possibility of adsorption onto alteration minerals, and therefore cannot be listed, the vulnerability to rock in the steam phase may explain why SF_6 gave anomalous results in several tests conducted at The Geysers (Voge et al., 1994).

Methanol and SF_6 appear to have sufficient thermal stability to function as steam tracers in high-temperature geothermal systems. We recommend, however, that more research be done to lower the detection limit of methanol unless it is acceptable to use large quantities. In that case, ethanol should be used because it is the least toxic. In addition, more tests need to be performed on the interactions of SF_6 and propanol with rock. Our tests that involved rock as a variable were preliminary, and difficulties were encountered in getting rock that was not contaminated by drilling material. This resulted in fewer experiments than planned.

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Table 1. Results of the thermal stability experiments. C° is the initial concentration, C is the final concentration after heating. The chlorinity was adjusted by adding NaCl. C/C° greater than 0.95 should be considered as not decaying. Ethanol data is included for comparison.

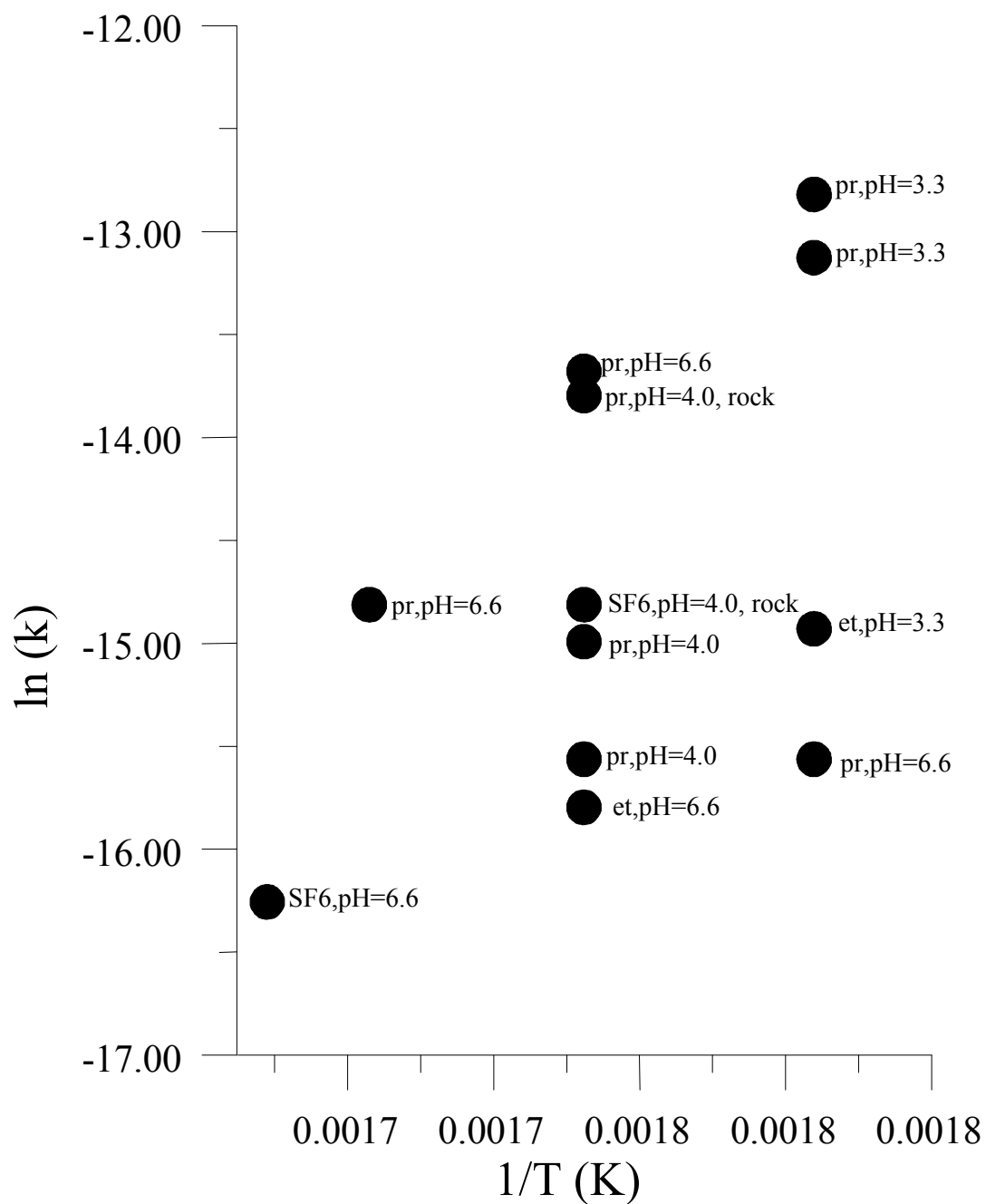| Species	Year	Temp. (C)	Time (days)	PH	C/C°	Comments
Ethanol	1993	280	7	3.3	0.82	
Ethanol	1993	300	7	6.6	0.92	
Methanol	1997	250	7	4	0.99	
Methanol	1997	250	14	4	0.97	
Methanol	1997	250	14	6.6	0.90	
Methanol	1993	280	7	6.6	1.00	
Methanol	1997	280	14	6.6	1.01	
Methanol	1997	300	7	4	1.00	
Methanol	1997	300	7	6.6	0.97	
Methanol	1998	300	7	4	1.04	20 g rock, 0 g/l Cl
Methanol	1998	300	7	4	97.6	40 g rock, 20 g/l Cl
Methanol	1998	300	7	4	1.01	20 g rock, 20 g/l Cl
Methanol	1998	300	7	7	0.96	40 g rock, 20 g/l Cl
Methanol	1998	300	7	7	0.95	20 g rock, 20 g/l Cl
Methanol	1997	300	14	4	1.01	
Methanol	1997	300	14	6.6	1.00	
Methanol	1997	320	7	6.6	1.00	
Methanol	1997	320	14	6.6	0.99	
n-Propanol	1997	250	7	4	0.99	
n-Propanol	1997	250	14	4	0.96	
n-Propanol	1993	280	7	3.3	0.30	
n-Propanol	1993	280	7	6.6	0.97	
n-Propanol	1993	280	14	6.6	0.81	
n-Propanol	1993	280	15	3.3	0.03	
n-Propanol	1997	300	7	4	0.83	
n-Propanol	1998	300	7	4	0.54	40 g rock, 20 g/l Cl
n-Propanol	1997	300	14	4	0.81	
n-Propanol	1997	320	14	6.6	0.64	
SF$_6$	1996	250	7	6.6	1.00	Anhydrous
SF$_6$	1996	250	7	4	1.00	
SF$_6$	1996	250	7	7	1.00	
SF$_6$	1995	280	14	6.6	.97	
SF$_6$	1996	300	7	6.6	1.00	Anhydrous
SF$_6$	1996	300	7	4	1.00	
SF$_6$	1996	300	7	7	1.00	
SF$_6$	1998	300	7	4	0.8	40 g rock, 20 g/l Cl
SF$_6$	1996	300	14	4	1.00	
SF$_6$	1995	330	14	6.6	.90	

Figure 1. Ahrrenius plot of the data from this study. Samples with less than 5% change are not considered to have decayed, and are not plotted here. Abbreviations: pr = n-propanol, me = methanol, k = the rate constant in seconds^{-1}, K is the temperature in Kelvins.