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## DERIVATIZED HYDROCARBONS AS GEOTHERMAL TRACERS

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Tucson, Arizona 85705ABSTRACT

Thirty-nine potential geothermal tracers have been tested for thermal stability at temperatures up to 250°C. The tracers were aromatic hydrocarbons with moieties of trifluoromethyls, sulfonates, methyls, fluorides, or carboxyls. Significant decay of these tracers, except for the perfluorinated compounds, was noted only between 200°C and 250°C. At 200°C, 32 of the 39 tracers survived for one week; at 250°C, 15 survived. The perfluorinated tracers decayed completely at all temperatures tested. These results show that certain derivatized hydrocarbons are potentially suitable as geothermal tracers. Future research will include testing these tracers in the presence of solid, liquid and gas phases that are common in geothermal reservoirs.

INTRODUCTION

In most geothermal fields, the spent brines must be injected back into the formation. The purposes of injection are to maintain reservoir pressure and avoid subsidence and environmental pollution. However, injection can lower the temperature of the produced fluids in a field by mixing with the hotter formation fluids. In order to mitigate this problem, the subsurface paths of injected fluids must be known. Tracers can be used to label and track fluid movement and monitor chemical changes of the injected fluid (Wright et al., 1984). Despite their potential importance to the geothermal operator, very few tracers are presently available and of those that are available, little is known about their stabilities or behavior at the elevated temperatures that typify resources capable of electric power generation. During the past two years, the University of Utah Research Institute has been involved in the development and testing of chemical tracers for geothermal use. The purpose of this paper is to describe the chemical characteristics of these tracers and summarize the results of ongoing laboratory investigations.

TRACER DEVELOPMENT

The ideal tracer should be detectable in small quantities, non-reactive with reservoir rocks and fluids, inexpensive, environmentally

safe, and absent from natural geothermal fluids and groundwaters. The tracers currently in use in high-temperature environments fall into three major categories: 1) radioactive isotopes; 2) salts of iodide, bromide, and chloride; and 3) organic dyes. Each of these classes of tracers has significant limitations.

Radioactive isotope tracers should be limited to those not used as natural process tracers, such as <sup>3</sup>H and <sup>36</sup>Cl. In addition, the half-life of the tracer must be of a suitable duration so that errors from decay corrections are kept small. An additional drawback to the use of radioactive tracers is their toxicity. For example, the tracer used during injection tests at the Wairakei and Broadlands geothermal fields, <sup>131</sup>I, is one of the more toxic radionuclides (McCabe et al., 1983).

The salts, although relatively stable and inexpensive, are limited by the high-halide background in many geothermal systems, requiring large quantities of salt for adequate tracer detection. In addition, because most of the salts are compounds of Na, K, Li and Mg, they interfere with cation geothermometry of the fluids (Adams, 1985).

The most significant restriction in the use of organic dyes is their lack of diversity. Only one species, fluorescein, has been used with complete success in injection tests (Adams, 1985; Adams et al., 1986; Tester et al., 1986). Rhodamine WT has been used with limited success at Klamath Falls, Oregon, and Svartsengi, Iceland (Gudmundsson et al., 1984).

The lack of diversity among the commonly used tracers restricts the number of wells that can be individually monitored in a producing field at one time. Thus, in geothermal fields where several injection wells are in use, it is not yet possible to independently trace the movement of fluids injected into each of them.

The derivatized hydrocarbons are a new class of tracers now being tested that appear to meet all of the requirements, including diversity. Four substitutional groups of hydrocarbons are currently being studied. These are the ring fluorinated, trifluoromethylated, sulfonated, and methyl- or carboxylated groups. The substrates for the substitutions are benzene, benzoic acid,

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and phenylacetic acid.

The salts of substituted benzoic acids were originally selected as groundwater tracers (Bentley, 1982) because they possess many of the characteristics of ideal tracers (Davis et al., 1980; 1985). These compounds are negative ions at the pHs of natural groundwaters and are therefore non-sorbing. They are low in toxicity, especially at the trace concentrations used. They are detectable at concentrations in the ppb to ppt range and are available as a large suite of similar species. The addition of fluorine to the benzene ring lends greater resistance to microbial degradation, with stability increasing in direct relationship to the degree of substitution (Bentley, 1983). Selected fluorinated benzoic acids, particularly pentafluorobenzoic acid, p-fluorobenzoic acid, and m-trifluorobenzoic acid have been used extensively in numerous groundwater studies over the past few years (for example, see Hydro Geo Chem, 1985a,b.).

One of the objectives of our tracer program is to extend the use of tracers to vapor-dominated systems. Therefore, we have included potentially stable tracers with a variety of volatilities in our experiments. If the distribution coefficients between the steam and liquid are known, then the subsurface processes can be elucidated. To this end, we have also been testing the sulfonic, acetic, and methylated derivatives.

#### EXPERIMENTAL PROCEDURES

Five experimental reaction vessels were put into operation during 1985. These vessels are housed at the University of Utah's Department of Metallurgy. One is capable of sustaining temperatures up to 350°C. The use of multiple reaction vessels makes it possible to perform experiments of relatively long duration on several different tracers or under different conditions simultaneously.

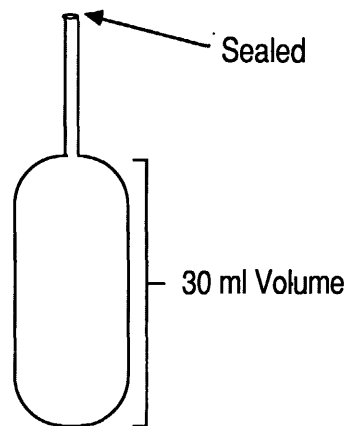


FIGURE 1

Annealed quartz vial used to contain the tracers in a closed system during hydrothermal experiments.

At the beginning of each experiment, aliquots of the solutions containing the tracer are encap-

sulated in sealed quartz tubes (Fig. 1). The ampules are filled with approximately 30 ml of solution and sealed in a oxygen-methane flame. At least two ml of the ampule are occupied by a gas phase during each experimental run. The gas phases used for these experiments are either pure nitrogen or an atmospheric mixture of oxygen and nitrogen that is approximately 20% oxygen by volume. The solutions in the experimental runs with nitrogen as the gas phase are purged with nitrogen gas in the ampule for up to 2 hours. During sealing, the neck of the ampule (see Fig. 1) is aspirated to prevent oxygen contamination from the oxygen-methane flame. Oxygen concentrations were measured for several solutions, and these averaged 6.9 ppm  $O_2$  in the atmosphere-equilibrated solutions and .27 to .05 ppm in the nitrogen-equilibrated solutions, depending on the purge time.

#### ANALYTIC METHODS

Analysis of hydrocarbon concentrations down to 20 ppb can be achieved by direct injection of up to 0.2 ml of sample into a high-pressure liquid chromatograph (HPLC). When necessary, on-column enrichment techniques can be utilized to lower detection limits (Stetzenbach et al., 1982). For HPLC analysis of the benzoic acids, the eluent buffer is prepared by adding sufficient phosphoric acid to reduce the pH to 1.9 with acetonitrile added in the 17-45% range. For analysis of benzene sulfonic acids, an iron-pairing reagent is added (tetrabutyl ammonium phosphate) and the pH adjusted to 6.0. In both cases, the column used is polymer based because it is more resistant to degradation than silica-based resins. Detection is by UV absorption at 200-205 nm.

Some of the analytic results were affected by the similarity between the retention times of the surviving compounds and those of the degradation products of the perfluorinated compounds. These effects resulted in overestimation of some of the final concentrations. These experiments will be repeated without the presence of rapidly decaying compounds in the future.

#### EXPERIMENTAL RESULTS

The experimental runs were designed to produce a rapid evaluation of the thermal stabilities of many derivatized hydrocarbons. In the initial set of experiments, the stabilities of five of the commonly used groundwater tracers were tested at 125, 150, 200, and 250°C. The second set was expanded to 39 related hydrocarbon species that had been considered for groundwater tracing but had been rejected on the basis of biodegradation. Biodegradation is not a problem in geothermal systems above about 100°C. In the second set of experiments, the runs were carried out at 200°C and 250°C. Run times were one week in all of the experiments reported here.

A typical plot of temperature vs. percent recovery is shown in Figure 2. The compounds tested in this set of experiments are from the ring-fluorinated, trifluoromethylated, perfluori-

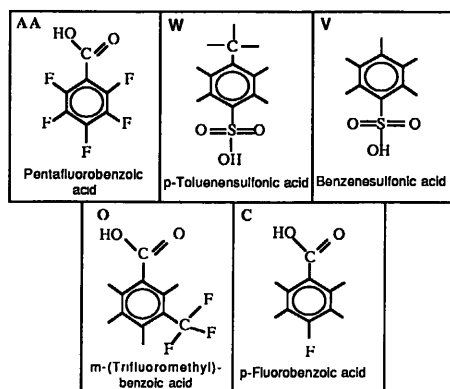
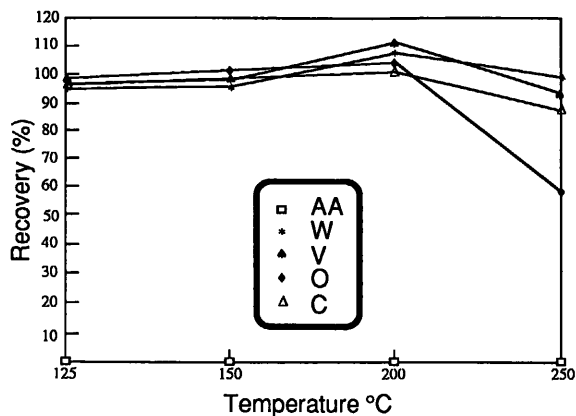


FIGURE 2

Temperature vs. recovery plot for five commonly used groundwater tracers. Recovery is defined as the final concentration divided by the initial concentration. Percent recoveries over 100 are due to analytic interference of the rapidly degrading perfluorinate species. Molecular structures of the tracers (designated on the graph by letter codes) are shown below the graph. Note the complete degradation of perfluorobenzoic acid at all temperatures tested and the decrease in stability of some species over 200°C.

nated, and sulfonated groups. As shown in this figure, the tracers do not degrade below 200°C, with the exception of pentafluorobenzoic acid. At 250°C, the sulfonates reacted least, while the trifluoromethyl- and p-fluorobenzoic acids reacted most. The runs that had high oxygen concentrations are not shown in Figure 2. Under high oxygen concentrations all of the compounds demonstrated a vulnerability to molecular oxygen at temperatures in excess of 150°C. Similar sensitivities to oxygen have been found for the organic dye tracers (Adams et al., 1986). Because high oxygen levels are not found in geothermal fluids and care is generally taken to exclude oxygen from injected brines, these results should merely serve as a cautionary note on tracer preparation and will not be discussed further.

Our tracer program was initially designed to test the thermal stabilities of fluorinated aromatic hydrocarbons. Fluorinated aliphatic compounds are known to be stable with respect to biodegradation and temperature (Sheppard and Sharts, 1969). These compounds, however, are insoluble in liquid water and therefore are unsuitable as tracers in liquid-dominated geothermal reservoirs. Fluorinated aromatic compounds have a higher solubility in liquid water, are non-biodegradable, and were untested with respect to temperature when we began our program. The low stability of fluorinated aromatic compounds above 200°C, discussed below, prompted the addition of sulfonated and methylated benzoic acids as potential tracers.

The two fluorinated groups tested were substitutions of ring-fluorinated or trifluoromethylated moieties on benzoic or phenylacetic acids. A histogram of species vs. percent recovery for the autoclave tests run with distilled water and nitrogen at 200°C and 250°C for one week is shown in Figure 3. The figure shows that many more

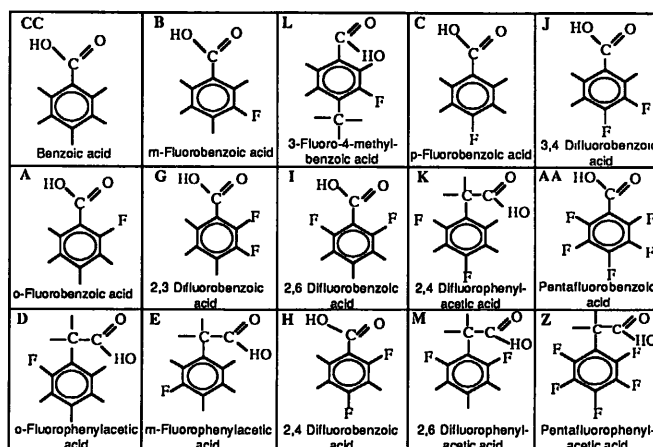
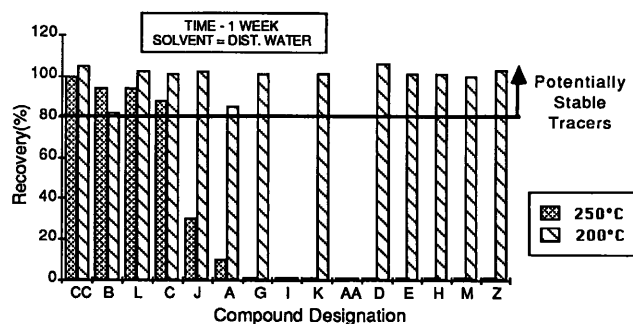


FIGURE 3

Recovery histogram of the ring-fluorinated benzoic and phenylacetic acids. Explanations and definitions are given in Figure 2.

compounds were stable at 200°C than were stable at 250°C. The relative amounts of decay of the various fluorination positions on the benzoic ring

indicate that the dominant mechanism of decay is substitution of a negative ion, probably a hydroxyl, for fluoride. These data fit a mechanism commonly referred to as bimolecular aromatic substitution (Kobrina, 1974). If this mechanism is operative, then bromide- and chloride-substituted benzoic acids will react slower, and be more stable with respect to temperature, than fluoride substitutions. Since bromo- and chloro-substituted benzoic acids are no more toxic than fluoro-substitutions, our future tests will include the former compounds as potential high-temperature tracers.

A bimolecular aromatic substitution mechanism also implies that the effects of fluoro-substitution are additive, i.e., the more fluorides on the ring the more rapid the decay. The effect of this substitution is demonstrated in Figure 2 by the low recovery of perfluorobenzoic acid at temperatures as low as 125°C. The most stable fluorinated hydrocarbons are m- and p-fluorobenzoic acids and 3-fluoro-4-methyl benzoic acid. These compounds survived the 250°C temperatures at greater than 80% of their initial concentrations.

The data for trifluoromethyl substituted compounds, shown in Figure 4, do not show a

sequence of decay that indicates bimolecular aromatic substitution. These compounds have an increase in stability with a decrease in distance between the trifluoromethyl moiety and the carboxyl group. This indicates that steric hindrance, or crowding, is the main factor preventing a rapid rate of reaction (Filler, 1970). The trifluoromethylated benzoic acids, although widely used as groundwater tracers, are not suitable as tracers over 250°C. At temperatures below 250°C, however, they may be acceptable.

Aromatic sulfonic acids are heavier and more acidic than benzoic acids. These properties increase their liquid and decrease their steam solubility to a greater degree than the other tracers we have tested. Thus, sulfonates are the best tracers for following the movement of liquid in a two-phase system. At 200°C and 250°C these compounds showed little or no decay, with the exception of pentafluorobenzenesulfonic acid (Fig. 5). Like all other perfluoro compounds examined in this study, pentafluorobenzenesulfonic acid decayed completely. Where temperatures are below 100°C, the aromatic sulfonic acids are potentially subject to biodegradation, so that special handling procedures such as the addition of formaldehyde may be necessary.

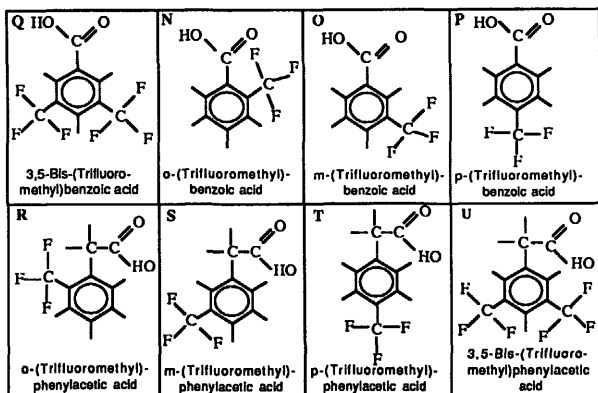
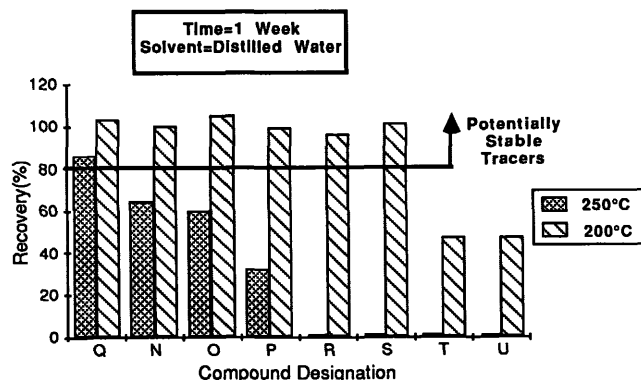


FIGURE 4

Recovery histogram of the trifluoromethylated benzoic and phenylacetic acids. Explanations and definitions are given in Figure 2.

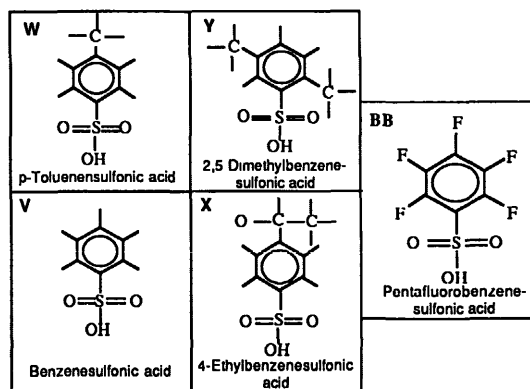
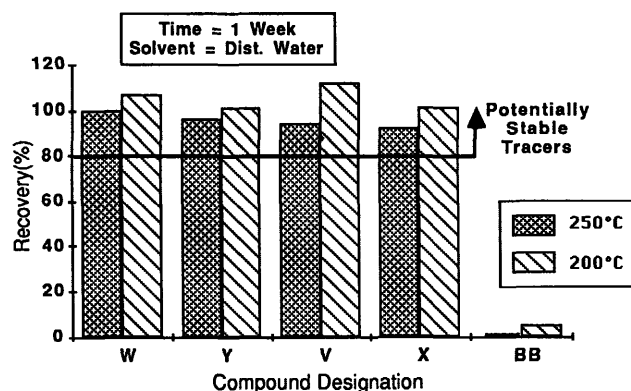


FIGURE 5

Recovery histogram of the sulfonated alkyl benzenes. Explanations and definitions are given in Figure 2.

Methyl-substituted benzoic acids were tested because of their non-toxic nature and expected stability. At 250°C, seven of the eleven compounds tested survived at greater than 80% of their initial concentration (Fig. 6). The most stable compounds were those with the methyl or second carboxyl groups separated from the primary carboxyl group by at least one ring carbon. These compounds may prove to be good high-temperature tracers.

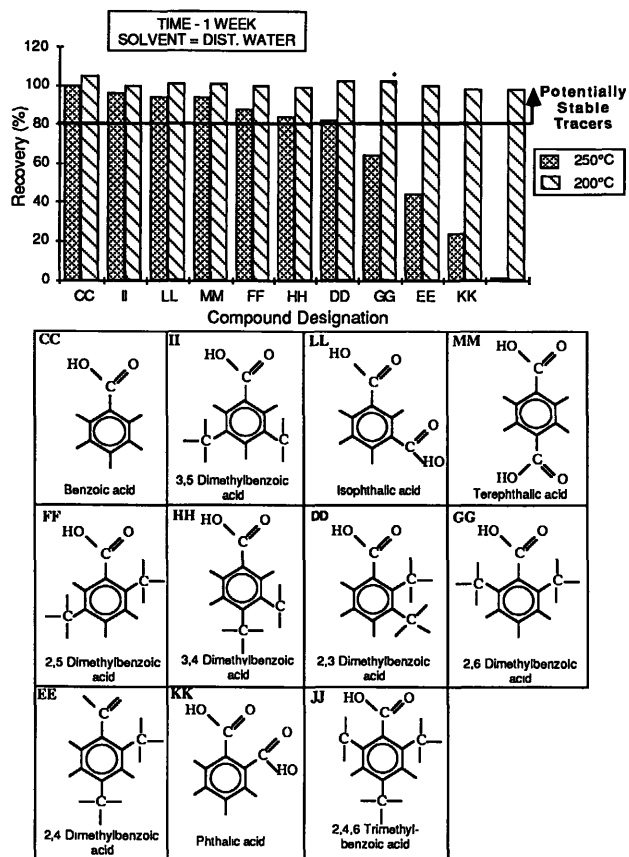


FIGURE 6

Recovery histogram of the methylated and carboxylated benzoic acids. Explanations and definitions are given in Figure 2.

Background concentrations for aromatic sulfonic and methyl-substituted benzoic acids are unknown in geothermal systems. While it is expected that the background levels will be zero, the assumption will have to be tested on a case by case basis. If any background level is detected, it will probably be due to contamination at the wellsite rather than natural sources.

#### SUMMARY AND CONCLUSIONS

The thermal stabilities of thirty-nine derivatized hydrocarbon tracers have been determined at temperatures ranging from 125° to 250°C. The compounds were tested in distilled water for one week at molecular oxygen concen-

trations consistent with geothermal conditions. At 200°C, 32 of the 39 tracers survived at over 80% of their initial concentration; at 250°C, 15 survived. The most stable groups at the higher temperatures were the sulfonates, methylates and carboxylates. Mono- and di-fluorinates were considerably less stable, and perfluorinates decayed completely at all temperatures. Thus, a number of diverse hydrocarbon compounds are potentially suitable as geothermal tracers.

Our future studies will include: 1) testing chloro- and bromo-benzoic acids as high temperature (> 250°C) tracers; 2) testing the most stable tracers at 200°C for extended periods of time; 3) heating the tracers in the presence of solid phases, reactive gases (H<sub>2</sub>S and CO<sub>2</sub>), and saline brines, and 4) developing and testing freons and perfluorinated alkanes as gas phase tracers.

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