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TRACER DEVELOPMENTS: RESULTS OF EXPERIMENTAL STUDIES

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INTRODUCTION

Tracers can be used to monitor the movement of groundwaters and geothermal fluids and they can be used as a reference to quantify changes in fluid chemistry as a result of injection. Despite their potential importance to the geothermal operator, very few tracers are presently available and of those that are, little is known about their stability 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 tracer research and testing, largely through the DOE Injection Research Program. The purpose of this paper is to summarize the results of these laboratory and field investigations.

TRACER DEVELOPMENT

The ideal tracer should be detectable in small quantities, inexpensive, environmentally safe, and be 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 must be limited to those not used as natural process tracers, such as ^{3}H and ^{36}Cl. In addition, the half-life of the tracer must be chosen such that errors from decay corrections are not large. Another problem with radioactive tracers is their toxicity. For example, the tracer used during injection tests at the Wairakei and Broadlands geothermal fields, ^{131}I, is one of the more toxic radionuclides (McCabe et al., 1983). The salts, while relatively stable and inexpensive, are limited by the high halide background in many geothermal systems, requiring large quantities of salt for adequate tracer detection. An additional drawback to the use of salts is that the cation of the salts will interfere with cation geothermometry of the injected fluid (Adams, 1985).

Relatively little is known about the commonly used organic dyes, fluorescein and rhodamine WT. Adsorption at geothermal temperatures has not been demonstrated for these compounds. Although fluorescein is light sensitive, it has been used successfully during injection tests at East Mesa, California (Adams, 1985). Rhodamine WT has been used with limited success at Klamath Falls, Oregon, and Svartsengi, Iceland (Gudmundsson et al., 1984).

One drawback of all the commonly used tracers is their lack of diversity, which restricts the number of wells that can be individually monitored in a producing field at one time. Thus, in geothermal fields where many injection wells are in use, it is not yet possible to independently trace the movement of fluids injected into each of them. A new class of tracers is now being tested that will meet the requirement of diversity. These are the fluorinated, methylated, and sulfonated hydrocarbons.

The tracers being tested can be divided into six substitutional groups. These are ring fluorinated, methyl perfluorinated, sulfonated, ring perfluorinated, methylated, and carboxylated. The substrates for the substitutions are benzene, benzoic acid, 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; Davis et al., 1985). These compounds are negative ions at the pHs observed in natural groundwaters and are therefore non-sorbing. They are low in toxicity, especially at the tracer concentrations used, chemically stable, exotic to the environment, detectable at trace concentrations 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

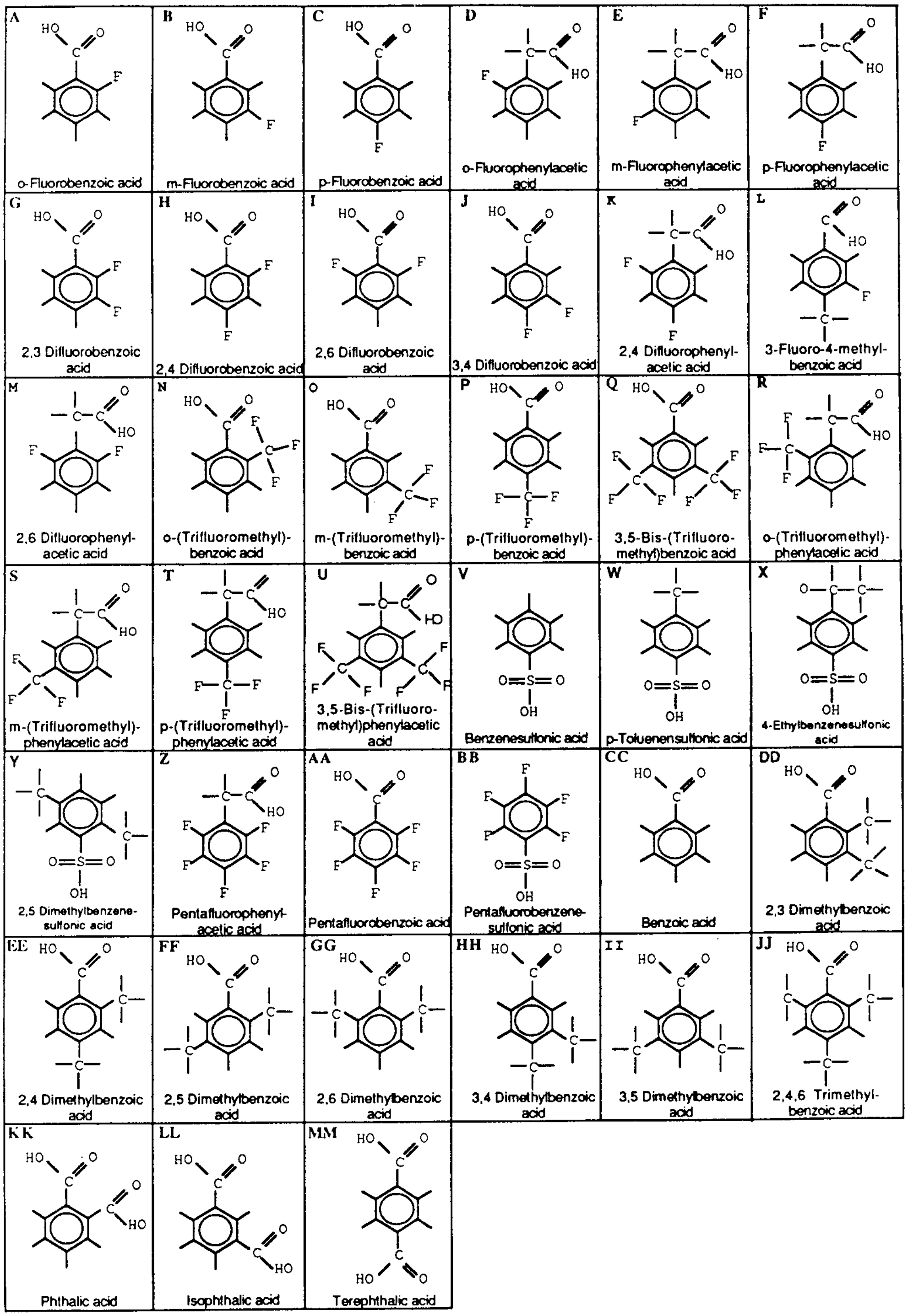

Figure 1. Chemical names and structures of hydrocarbons being tested.

is to extend the use of tracers to vapor-dominated systems. Therefore, we have attempted to include potentially stable tracers with a variety of volatilities. This will enable steam as well as liquid to be tagged; and if the distribution coefficients are known, subsurface processes can be elucidated. To this end we have also been testing the less volatile sulfonic- and acetic-derivatives. Methylated derivatives were also tested because of their probable thermal stability. The compounds tested are shown in Figure 1.

EXPERIMENTAL PROCEDURES

Five experimental reaction vessels have been put into operation since 1985. These vessels are housed at the University of Utah's Department of Metallurgy. One of these is capable of sustaining temperatures of 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.

At the beginning of each experiment, aliquots of the solutions containing the tracer are encapsulated in sealed quartz tubes (Fig. 2). The ampules are filled with approximately 30 ml of solution and sealed in an 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 pure nitrogen or an atmospheric mixture of oxygen and nitrogen that is approximately 20% oxygen by volume. The solutions of the experimental runs that used a nitrogen gas phase were purged with nitrogen gas in the ampule for up to 2 hours. The neck of the ampule (see Fig. 2) was aspirated to prevent oxygen contamination from the oxymethane flame during sealing.

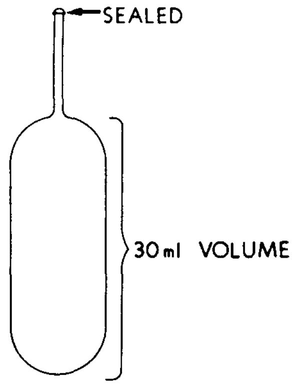

Figure 2. Illustration of quartz tube used for hydrothermal experiments.

Three oxygen concentrations were used in the test solutions in order to bracket the variable oxidation potentials that may result from surface treatment prior to injection. These oxygen concentrations were created by: 1) allowing the solution to equilibrate with atmospheric oxygen at room temperature and leaving atmospheric oxygen in the head space, 2) equilibration of the solution with atmospheric oxygen and filling the head space with nitrogen, and 3) nitrogen-purging of the solution and filling the head space with nitrogen. Oxygen concentrations were measured and oxygen to fluorescein molar ratios calculated for several of these solutions. Oxygen conditions in (1) and (2) averaged 6.9 ppm O_2 and in (3) ranged from .27 to .05 ppm, depending on purge time. Molar ratios of oxygen to fluorescein were 351, 18, and .69 to .13, for oxygen conditions 1, 2 and 3, respectively.

ANALYTIC METHODS

Analysis of hydrocarbons down to the 20 ppb level can be achieved by direct injection of up to 0.2 ml of solution into a high pressure liquid chromatograph (HPLC). If desired, on-column enrichment techniques can be utilized to significantly 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 ion-pairing reagent is added (tetrabutyl ammonium phosphate) and the pH adjusted to 6.0. In both cases, the column used is polymer based which is more resistant to degradation than silica-based resins. Detection is by UV absorption at 200-205 nm.

Fluorescein and rhodamine WT were analyzed using a colorimeter and a fluorometer for high and low concentrations, respectively.

EXPERIMENTAL RESULTS

The initial experimental runs were designed to produce a rapid evaluation of the thermal stability of many derivitized hydrocarbons. These runs were carried out at 250°C with high and low oxygen concentrations. In addition, because of its past usage as a tracer and ease of analysis, fluorescein was tested under a variety of other conditions.

The factors chosen to test fluorescein stability were temperature, pH, salinity, and oxygen concentration. Our results indicate that oxygen is the major destabilizing factor. At high oxygen concentrations, high pH and salinity have a stabilizing effect, while high temperatures have a very slight destabilizing effect.

The effect of varying the oxygen concentration is shown in Figure 3. These data demonstrate that fluorescein is very stable in oxygen concentrations typical of geothermal reservoirs. Any scatter in the nitrogen curve is probably due to the variable oxygen concentrations left from the purging process. In a geothermal reservoir the oxygen would be even lower than that in the nitrogen purged fluid, and fluorescein should be very stable. In contrast, higher oxygen concentrations result in rapid degradation of fluorescein (Fig. 3).

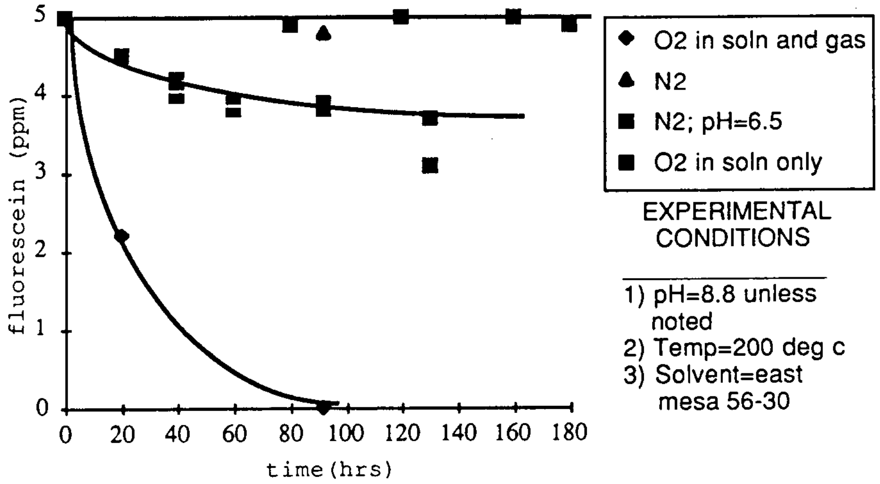

Figure 3. Fluorescein decay vs. time. The initial concentration of fluorescein was 5 ppm.

The effect of varying the solution pH is shown in Figure 4. These data are for experimental runs at an oxygen concentration of approximately 7 ppm. It can be seen that lower pH values strongly promote degradation of fluorescein. This is most likely due to a fluorescein species change in the pH range of 6 to 8.

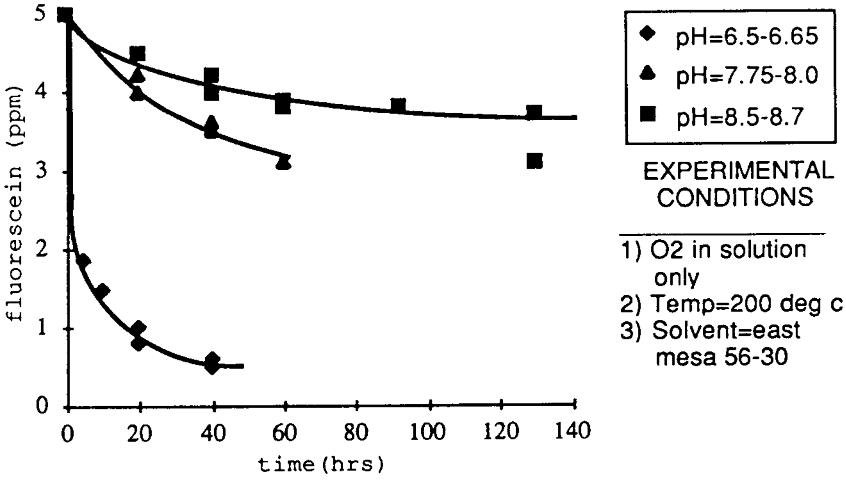

Figure 4. Fluorescein decay vs. time. The initial concentration of fluorescein was 5 ppm.

The in-situ stability of fluorescein has been demonstrated at the East Mesa geothermal field by Adams (1985). During one of the injection tests at that field, a 2500 gallon slug of fluorescein and thiocyanate (SCN) was injected and left in the 174°C reservoir for six months, before the fluid was drawn back from the well and analyzed. This data is presented in Figures 5a and b. Here it can be seen that the fluorescein to SCN ratio was frequently higher than the injection ratio, implying that SCN and not fluorescein was lost to the formation. Furthermore, the fluorescein/SCN ratio is consistently subequal to the injected ratio at the tail end of the fluid withdrawn, where the pH and oxygen concentration were identical to the reservoir conditions. Thus fluorescein

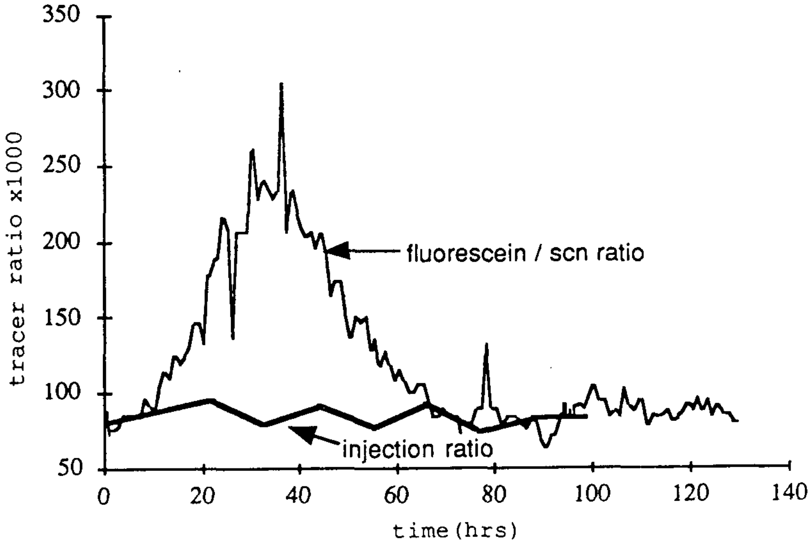

Figure 5a. Ratio of two tracers, SCN and fluorescein, after remaining in the 174°C reservoir for 6 months. The zero time on the x-axis represents the beginning of fluid withdrawal.

appears to be thermally stable, in accordance with the experimental results.

One set of tests was performed on rhodamine WT at 200°C in oxygen and in nitrogen. The results show that rhodamine WT is similar to fluorescein in its sensitivity to the presence of oxygen. In addition, however, it was found that rhodamine WT adsorbs onto colloidal silica as well as filter paper at room temperature. We hope to quantify these effects in the future.

Two sets of experiments were conducted on the hydrocarbons. One set used a monofluorinated, a perfluorinated, and a trifluoromethyl substituted benzoic acid as well as two forms of sulfonic acid. These were tested at temperatures of up to 150°C for 172 hours and in oxygen and nitrogen atmospheres. The results are shown in Figure 6. All compounds were stable with the exception of the perfluorinated benzoic acid. This is the opposite of what would be expected from groundwater studies where the perfluorinates are the most stable tracers.

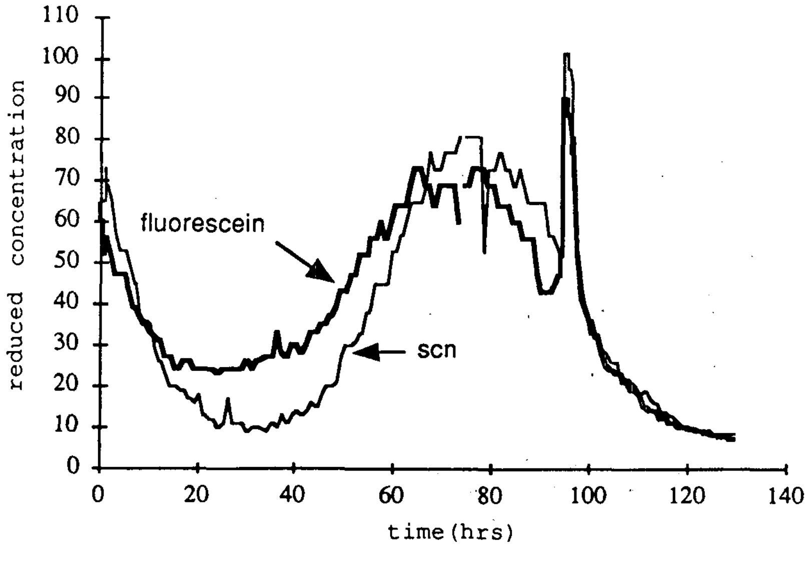

Figure 5b. Reduced concentration normalized to injected concentration of tracers vs. time. Time axis is as in Figure 5a.

The second set of experiments was run for 168 hours at 250°C in oxygen and in nitrogen atmospheres. At the present time 26 of the tracers have been tested and analyzed. Of the 26, only 7 were reasonably stable. Those were compounds B, L, Q, DD, FF, HH, and II, shown in Figure 2. The unifying factor of the stable species appears to be related to a low degree of fluorination and the location and inclusion of a methyl group on the benzene ring, primarily at the carbon that is meta to the carboxyl group. Results on the remaining hydrocarbons are expected during January of 1986.

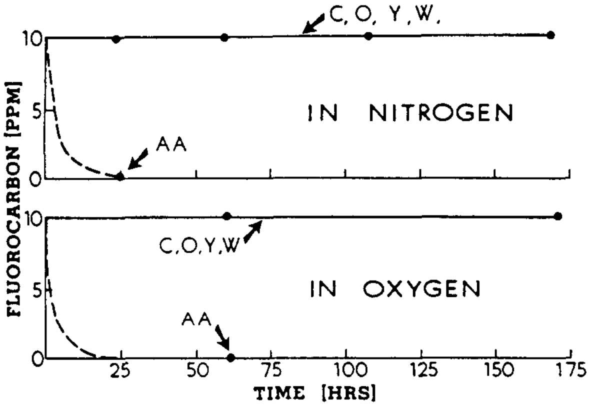

Figure 6. The stability with time of five commonly used groundwater tracers. Compound names and structures are listed in Figure 1.

CONCLUSIONS

Twenty-six derivitized hydrocarbons as well as fluorescein and rhodamine have been tested for thermal stability in pressurized autoclaves. Of these 28 compounds, 7 derivitized hydrocarbons and fluorescein have proven to be stable at high temperatures. The compounds have a variety of liquid-steam distribution coefficients, and will thus be applicable to vapor- as well as liquid-dominated geothermal systems. Testing of additional tracers is in progress.

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