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THE USE OF POLYAROMATIC SULFONATES AS TRACERS IN HIGH TEMPERATURE GEOTHERMAL RESERVOIRS

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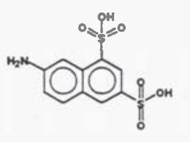
SUMMARY - A recently identified family of candidate fluorescent tracers, the polyaromatic donates, was shown to be resistant to thermal decay under simulated geothermal reservoir conditions at 300°C. Laboratory techniques have been identified for the simultaneous analysis of several compounds from this family by reverse-phase high-performance liquid chromatography (HPLC) in combination with ion pairing and fluorescence detection. One of the polyaromatic sulfonates, pyrene tetrasulfonate, was used in a tracer test at Dixie Valley, Nevada, USA, which produces fluids at 250°C. It showed breakthrough in several production wells with a detection limit of approximately 200 parts per trillion.

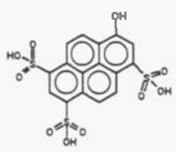
1. INTRODUCTION

The xanthene dye fluorescein has been used extensively in hydrothermal tracing applications due to its low detection limit, low cost, resistance to adsorption, and good thermal stability in reservoirs as hot at 250°C. However, with the exception of rhodamine WT, which has been used successfully in low-temperature hydrothermal applications only (Gudmundsson et al., 1983; Rose and Adams, 1994), the successful use of additional fluorescent dyes as tracers has not been reported.

Of the eight ground water tracers studied by Smart and Laidlaw (1977), two compounds, amino G and pyranine, whose structures are shown below, were shown by our laboratory to possess good thermal stability upon exposure to simulated geothermal reservoir conditions at 250°C (unpublished results).



Amino G



Pyranine

Their good thermal stability was not surprising, since polyaromatic hydrocarbons (e.g. naphthalene, anthracene, and pyrene) are known to be very refractory, due, in large measure, to pi-bonding within the condensed aromatic rings. In addition, these compounds are detectable at concentrations in the low parts per trillion by conventional fluorescence spectroscopy techniques.

In studying aromatic acids for use as hydrothermal tracers, Adams et al. (1992) found that four aromatic sulfonic acids showed no measurable decay upon exposure to simulated hydrothermal conditions for two weeks at 300°C. The structure of the simplest of these tracers, benzene sulfonic acid, is shown below:

benzene sulfonic acid

This study indicated that the aryl-sulfonyl bond is remarkably strong. The aromatic sulfonates are not as detectable, however, as the polyaromatic sulfonates. This is because the aromatic acids are detected by adsorption spectroscopy, whereas the polyaromatic sulfonates are detected by fluorescence spectroscopy.

In view of the excellent detectability of the substituted polyaromatic sulfonates in conjunction with the excellent thexmal stability of the aryl-sulfonyl bond, we initiated a study of the polyaromatic sulfonates with the objective of identifying a class of compounds for use as tracers in hydrothermal environments having fluids hotter than 300°C. In this paper, we present the preliminary results of laboratory studies designed to test the polyaromatic sulfonates under simulated hydrothermal conditions. We also show the results of a recent field test at Dixie Valley, Nevada, USA, where one of the studied compounds, pyrene tetrasulfonate, was successfully used in a tracer test (Rose et al., 1998). Although the fluid temperatures at Dixie Valley do not exceed 250°C, tracer residence times approaching one year are sufficient to provide a good initial test of these tracers.

2. METHODS

2.1 Laboratory Experiments

The candidate compounds were tested in the laboratory under controlled conditions of temperature, pressure and solution chemistry in order to simulate a hydrothermal environment (Rose and McPherson, 1997). These compounds included 1-naphthalene sulfonic acid, 1,5-naphthalene disulfonic acid, 2,6-naphthalene disulfonicacid, 1,3,6-naphthalene trisulfonic acid, 7-[(7-sulfo-2- naphthyl)methyl]- naphthalene-2-sulfonic acid (Crisotan R5), and 1,3,6,8-pyrene tetrasulfonic acid. All compounds were obtained and tested as salts of their respective acids.

In atypical experiment, a candidate compound was dissolved in a buffered aqueous solution at a concentration of 25 ppm by weight and adjusted to a room-temperature pH of 6.5. The buffer consisted of 5 mM KH_2PO_4 and 3 mM Na_2HPO_4. Eighteen-ml aliquots of the buffered tracer solution were transferred to 30-ml quartz ampules and purged with argon to remove elemental oxygen. The ampules were carefully sealed using an oxymethane flame, while being purged with argon. The sealed vials were transferred to water-filled, one-liter autoclaves (Autoclave Engineers, Philadelphia, PA), which were heated to the target temperature. The pressure inside the autoclave was the pressure of steam under saturated conditions at the target temperature.

The candidate tracers were scanned and analyzed using a Perkin Elmer LS30 spectrofluorometer. Excitation maxima ranged between about 220 and 280 nm, whereas emission maxima were between about 330 and 390 nm. For analyzing multiple compounds and compounds in a sample matrix that included reservoir contaminants, we used a High Performance Liquid Chromatograph (HPLC) with a fluorescence detector (Waters Corporation, Milford, MA). An HPLC equipped with variable wavelength detection allowed for the efficient separation of analytes both spectrally and chromatographically.

In order to take advantage of the high resolution of reverse-phase chromatography, we used a C18 column (e.g., Waters NovaPak 150 mm x 4.6 mm) and ion-pairing agents. The mobile phase consisted of a pH 7.5, phosphate-buffered, 5 mM solution of tetrabutyl ammonium phosphate (TBAP) in varying proportions of methanol and water.

2.2 Field Experiments

On September 3, 1997, 1818 kg of a 10 wt% aqueous solution of pyrene tetrasulfonate was injected into well 45-5 at Dixie Valley, USA, over a period of about 20 minutes. Ten production wells were sampled twice weekly throughout the subsequent year, with PTSA being detected in seven of the ten.

Tracer tests involving the three additional polyaromatic sulfonates 1,5-naphthalene disulfonic acid, 1,3,6-naphthalene trisulfonic acid, and 7-[(7-sulfo-2- naphthyl)methyl]-naphthalene-2-sulfonic acid (Crisotan R5) were recently initiated at Dixie Valley. The initial production of Crisotan R5 has been observed.

3. RESULTS

Results of the laboratory experiments are summarized in Table 1, which lists the candidate compounds and shows the chemical structures of the compounds in their acid forms. It is evident from the structural formulas that two of the compounds, 1,5-naphthalene disulfonic acid and 2,6-naphthalene disulfonic acid, are isomers. The suggested paired-ion HPLC technique is incapable of distinguishing between isomers. This means that 1,5-naphthalene disulfonate and 2,6-naphthalene disulfonate could not be distinguished in production fluids, and that these two tracers could not be used to independently track produced fluids from two injection wells. All of the remaining compounds listed in Table 1, however, possess distinct molecular weights and are easily baseline resolved. Therefore, using five of the six compounds listed, it would be possible to distinguish the fluid-flow patterns of five injection wells simultaneously.

Column 3 of Table 1 summarizes the results of the thermal stability screening studies, listing the percent decay of each compound upon exposure to hydrothermal conditions for one week at 300°C. Our experimental error was 5%. Therefore, any results reporting values less than 5% indicate that there was no discernable thermal decomposition.

Shown in column 4 of Table 1 are the excitation and emission maxima for fluorescence for each compound studied. All compounds fluoresce in the ultraviolet region of the spectrum. In addition, most compounds have similar excitation and emission maxima. This indicates that chromatographic separation is required if these tracers are to be used simultaneously. In addition, reservoir interferences occur in the far uv and a chromatographic separation is required in order to distinguish tracers fiom those natural reservoir contaminants. Nevertheless, with the exception of the two isomers, all of the compounds are capable of being analyzed simultaneously by the paired-ion chromatographic technique suggested above.

Figure 1 plots the return curves of PTSA for the field test at Dixie Valley. The first arrival was about 90 days into the test, with the strongest return to well 73-7. The next strongest returns were to wells 73B-7 and 63-7, followed by 82A-7. These returns confirmed the results of a tracer test conducted at Dixie Valley during the previous year in which a well very close to well 45-5 was tagged (Rose et al., 1997). This was the first documented use of PTSA in either a groundwater or hydrothermal environment.

4. SUMMARY AND CONCLUSIONS

A family of refractory fluorescent compounds, the polyaromatic sulfonates, has shown promise for use as tracers in high temperature hydrothermal systems. Laboratory experiments have demonstrated that these compounds are resistant to thermal decay upon exposure to hydrothermal conditions for one week at 300°C.

A laboratory procedure involving HPLC and ion pairing chromatography was developed that allows for the analysis of several polyaromatic sulfonates simultaneously. This, in turn, allows for multiple-well tracer testing in reservoirs containing many injectors.

A tracer test using PTSA was successfully completed at Dixie Valley, Nevada. In a subsequent tracer test at Dixie Valley, the first arrival of Crisotan R5 was recently observed.

5. ACKNOWLEDGMENTS

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6. REFERENCES

Adams, M.C., Moore, J.N., Fabry, L.G., and Ahn, J.H. (1992). Thermal stabilities of aromatic acids as geothermal tracers. *Geothennics,* 21(3), 323-339.

Gudmundsson, J.S., Johnson, S.E., Home, R.N., Jackson, P.B., Culver, G.G. (1983). Doublet tracer testing in Klamath Fall, Oregon. Proceedings Ninth Workshop Geothermal Reservoir Engineering, SGP-TR-74, 331-337, Stanford University, Stanford, California.

Rose, P.E., and Adams, M.C. (1994). The application of rhodamine WT as a geothermal tracer. *Geothermal Resources Council Transactions,* 18, 237-240.

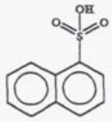
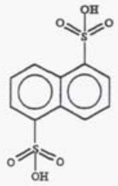
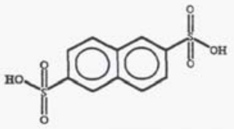
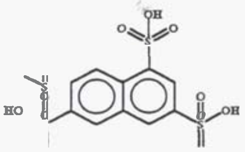
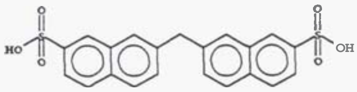
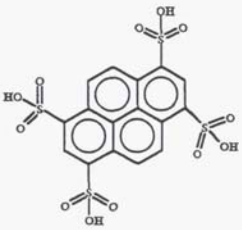
Rose, P.E. and McPherson, P.A. (1997). New fluorescent tracers for use in geothexmal reservoirs. *Geothermal Resources Council Transactions,* 21, 249-253.

Rose, P. E., Apperson, K. D., Johnson, S. D., and Adams, M. C. (1997). Numerical simulation of a tracer test at Dixie Valley, Nevada. *Proceedings, Tweniy-Second Workshop on Geothermal Reservoir Engineering,* Stanford University, 169-176.

Rose, P.E., Benoit, W.R., and Adams, M. C. (1998). Tracer testing at Dixie Valley, Nevada, using pyrene tetrasulfonate, amino G, and fluorescein. *Geothermal Resources Council Transactions,* 22, (in press).

Smart, P.L., Laidlaw, I.M.S. (1977). An evaluation of some fluorescent dyes for water tracing. *Water Resources Research,* 13(1), 15-33.

Table 1. Candidate tracers for use in hydrothermal environments. Although shown as acids, the compounds exist as anions at the reservoir pH.

Compound Name	Chemical Structure	% Decay (1 week at 300°C)	Excitation and Emission Wavelengths (nm)
1-naphthalene sulfonic acid		< 5	217 / 333
1,5-naphthalene disulfonic acid		< 5	218 / 334
2,6-naphthalene disulfonic acid		< 5	228 / 342
1,3,6-naphthalene trisulfonic acid		< 5	228 1342
7-[(7-sulfo-2-naphthyl)-methyl] naphthalene-2-sulfonic acid (Crisotan R5)		15	222 / 340
1,3,6,8-pyrene tetrasulfonic acid (PTSA)		< 5	346(or 280) / 386

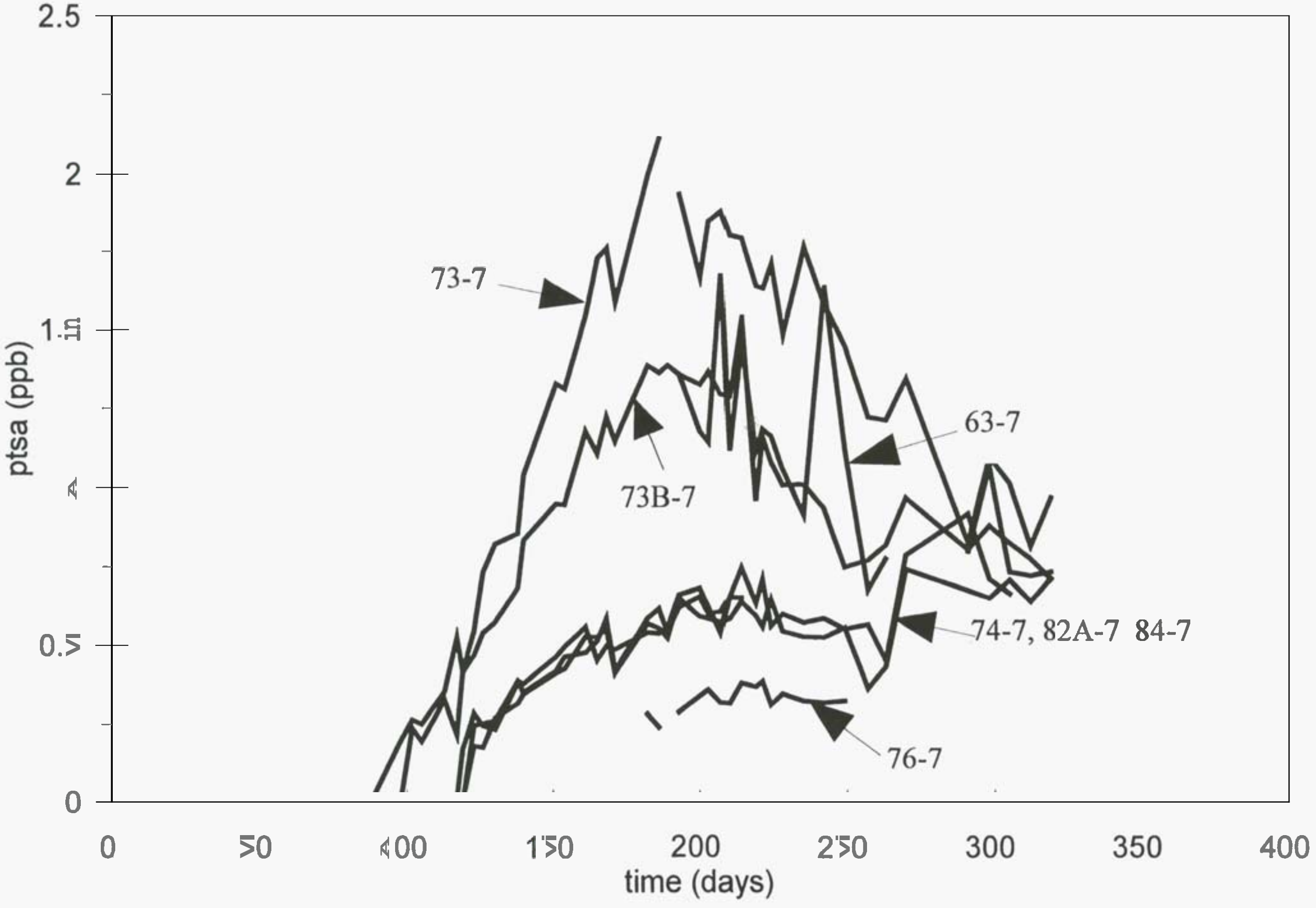


Figure 1. PTSA return curves for seven production wells at Dixie Valley, Nevada.