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THE DEVELOPMENT OF TRACERS FOR USE IN GEOTHERMAL RESERVOIRS

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Project Background and Status

Geothermal energy production involves the flow of large volumes of water through hot fractured rock deep underground, where heat is transferred from the rock to the water. The heated water then flows to the surface through production wells and is used to generate electricity in steam turbines. The cooled water is then reinjected via dedicated injection wells to be recirculated through the reservoir. If the injection wells are located too close to the production wells, there develops a risk of premature thermal breakthrough. If the injectors are placed too far from the producers, then the injectate will not return to the reservoir and the result will be a drop in reservoir pressure. *The use of artificial tracers provides the only expedient, reliable and cost effective means of tracking injection fluids and optimizing injection well placement in geothermal reservoirs.*

Project Objectives

The purpose of this project is to increase the thermal stability and detectability of tracers for use in hydrothermal environments. Operators of geothermal reservoirs claim that many more tracers than are currently available are needed in order to effectively track fluid flow in reservoirs having many injection wells. Such tracers must be environmentally benign, resistant to adsorption on geothermal rock, affordable, thermally stable and very detectable. Whereas all of these qualities are essential, only the latter two are design drivers. Therefore, our primary objectives are:

- to identify and qualify two new thermally stable tracers for use in high-temperature (>300°C) geothermal systems

- to demonstrate an increase in the detectability of fluorescent tracers by a factor of at least 100 for intermediate-temperature (<250°C) applications

Approach

We have focused our attention primarily on a new class of uv-fluorescent compounds that have proven to be excellent candidates for use as tracers in high temperature geothermal reservoirs. These compounds, known as the naphthalene sulfonates, are environmentally benign, very detectable by fluorescence spectroscopy, affordable, and thermally stable. Toxicity studies indicate that the naphthalene sulfonates are neither carcinogenic nor mutagenic (Greim *et al.*, 1994).

Our approach was to study two naphthalene sulfonates candidate tracers, 1-naphthalene sulfonate and 2,6-naphthalene disulfonate, under controlled laboratory conditions to determine their suitability for use in geothermal applications. Next, we set out to verify the laboratory results in a field test at the Dixie Valley geothermal reservoir in west-central Nevada. Shown in Figure 1 are the chemical structures of these two compounds in addition to four other naphthalene sulfonates that have recently been tested and shown to be viable geothermal tracers.

In the area of improved tracer-detectability, our experimental approach was first to design and fabricate an innovative analytical instrument, based upon emerging technologies in laser light sourcing, fiber optics and charge-coupled-device (CCD) spectroscopy (see Figure 2). Using this instrument, we then set out to demonstrate a reduction in the detection limit of fluorescent tracers by a factor of

Compound	Structure	Excitation / Emission (nm)
1-naphthalene sulfonic acid		217 / 333
2-naphthalene sulfonic acid		220 / 336
1,5-naphthalene disulfonic acid		218 / 334
2,6-naphthalene disulfonic acid		225 / 342
2,7-naphthalene disulfonic acid		226 / 339
1,3,6-naphthalene trisulfonic acid		228 / 342

Figure 1. Chemical names, structures, and excitation and emission band maxima of six naphthalene sulfonate geothermal tracers studied in the laboratory and in the field.

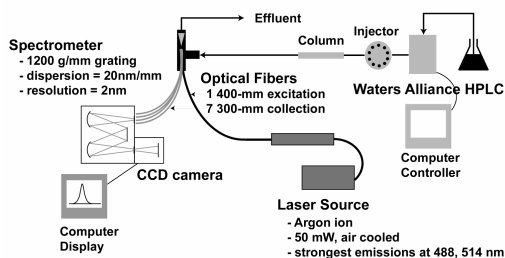


Figure 2. Schematic view of the HPLC/fluorimeter assembly.

100, thereby reducing the quantity of tracer required in a tracer test also by a factor of 100. Second was the evaluation of a family of candidate fluorescent tracer compounds that could be analyzed using the new apparatus. These compounds are not as thermally stable as the naphthalene sulfonates mentioned above. However, they are suitable for use in intermediate-temperature (<250°C) geothermal reservoirs, which constitute a significant fraction of systems in the U.S. In addition, these compounds are sufficiently similar to the geothermal tracer fluorescein that they require the same excitation wavelength as fluorescein, serving to simplify their analysis.

Research Results

This year's results can be summarized as:

- the laboratory demonstration of two new tracers for use in high-temperature (>300°C) reservoirs and verification of those laboratory results in a field test
- the field demonstration of a reduction in the detection limit of fluorescent tracers for intermediate-temperature (<250°C) applications by a factor of 100, resulting in a concomitant reduction in the quantity of tracer required for a tracer test also by a factor of 100.

The high-temperature naphthalene sulfonate tracer candidates were analyzed using High Performance Liquid Chromatography (HPLC) with fluorescence detection (Waters Corporation, Milford, MA). HPLC allows for the separation of the polyaromatic sulfonates not only from each other but also from interferences that occur naturally in the reservoir. Using HPLC, any number of polyaromatic sulfonate tracers can, in principle, be analyzed in each other's presence.

The six naphthalene sulfonate tracers shown in Figure 1 can be analyzed using gradient chromatography in less than 10 minutes, as shown by the chromatogram in Figure 3. The first mobile phase consisted of a solution of 3.17 mM Na₂HPO₄, 6.21 mM KH₂PO₄, and 5.0 mM TBAP in 25%/75% methanol/water. The second mobile phase consisted of the same concentrations of salts in 30% /70% methanol/water.

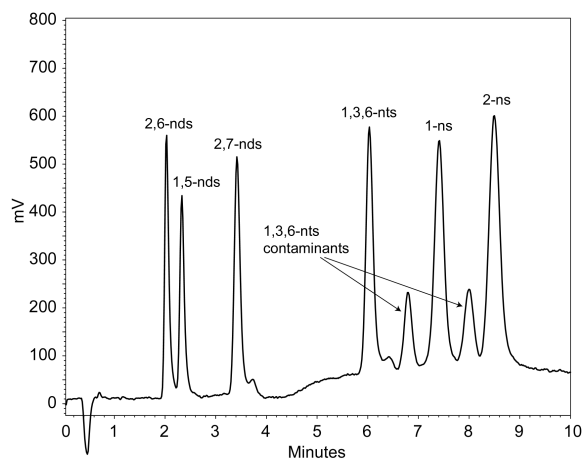


Figure 3. Chromatogram of six naphthalene sulfonate analytes obtained using a gradient method.

The decay kinetics of the two naphthalene-sulfonate tracers was studied using autoclave batch reactors under controlled conditions designed to simulate a geothermal environment.

The naphthalene sulfonate tracers decay according to the first-order differential equation:

$$-dC_n/dt = k_n \cdot C_n \quad (1)$$

where C_n is the concentration of naphthalene sulfonate and k_n is the first-order rate constant. Solution of this equation results in the following relationship between C_n and t :

$$\ln\left(\frac{C_n}{C_n^0}\right) = -k_n \cdot t \quad (2)$$

where C_n^0 is the initial concentration of polyaromatic sulfonate. The temperature dependence of k_n can be described by the Arrhenius relationship:

$$k_n = Ae^{(-E_a/RT)} \quad (3)$$

where A is the pre-exponential factor, E_a is the energy of activation, R is the gas constant and T is absolute temperature.

By solving for the Arrhenius rate-constant coefficients, it is possible to determine the half-life vs. temperature for each compound (see Figure 4). Figure 4 includes data not only for the two naphthalene sulfonate tracers but also for other polyaromatic sulfonate and xanthene-dye tracers that we have studied in our laboratory. No decay was observed for 1-naphthalene sulfonate, 2,6-naphthalene disulfonate, 2-naphthalene sulfonate or 2,7-naphthalene disulfonate upon exposure to simulated geothermal conditions for one week at 330°C. Therefore, we have approximated the half-life data for these four compounds, as shown by the dotted line in Figure 4. We suspect that these compounds are sufficiently stable for use in geothermal reservoirs with fluid temperatures of 330°C or hotter. Since there are no geothermal reservoirs in the U.S. with temperatures that high, these tracers are sufficiently stable to satisfy operator needs.

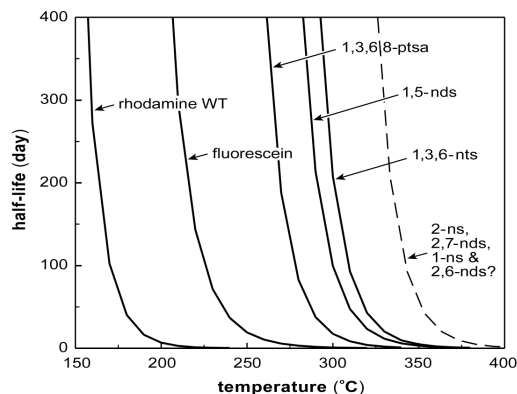


Figure 4. Plots of half-life vs. temperature for several polyaromatic sulfonate tracers as well as for two xanthene dyes as determined from decay kinetics data measured at EGI.

The two naphthalene sulfonates were field tested at the Dixie Valley geothermal reservoir. On July 10, 2001, 143 kg of 1-naphthalene sulfonate (Yick-Vic Chemicals, Hong Kong) was injected into well 45-5, which was flowing at approximately 100 kg/sec. Similarly, on July 10, 2001, 150 kg of 2,6-naphthalene disulfonate (Yick-Vic Chemicals, Hong Kong) was injected into the recently drilled well 38-32, which was flowing at approximately 110 kg/sec. All of the producing wells in the field were subsequently monitored for the two naphthalene sulfonates over the subsequent six months.

A return-curve plot from that test is shown in Figure 5. This represents the return of the candidate tracer 2,6-naphthalene disulfonate that was injected into well 38-32. These return curves show tracer production in the northeast portion of the reservoir only, as no tracer was observed in any of the production wells monitored further to the southwest in section 7. This flow pattern is similar to the one observed from tracer testing of the nearby well 27-32 that was initiated in November 1999 (Rose *et al.*, 2001).

The tracer flow patterns for the two tracers tested this past year, 2,6-naphthalene disulfonate and 1-naphthalene sulfonate, are shown in Figure 6. Also summarized in Figure 6 are the flow patterns of four additional naphthalene sulfonate tracers and one polyaromatic sulfonate tracer (1,3,6,8-pyrene tetrasulfonate) that were recently tested at the Dixie Valley geothermal reservoir. All seven tracers shown in Figure 6 can be analyzed simultaneously by the HPLC methods described in this paper.

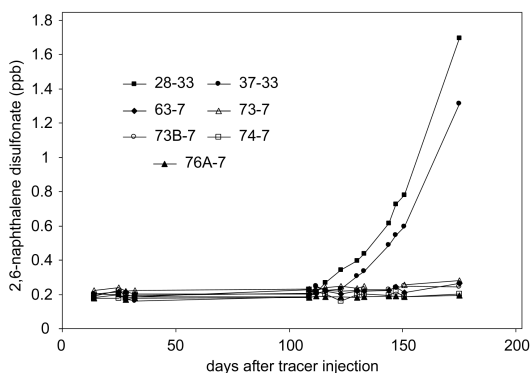


Figure 5. 2,6-naphthalene disulfonate returns observed from the testing of injector 38-32 at the Dixie Valley geothermal reservoir.

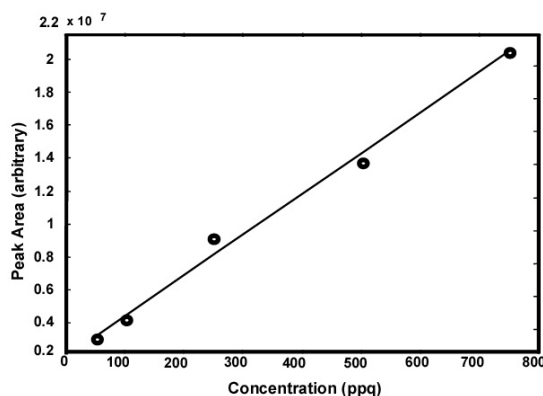


Figure 7. Calibration curve for fluorescein showing a linear relationship between concentration and peak area over the range of interest.

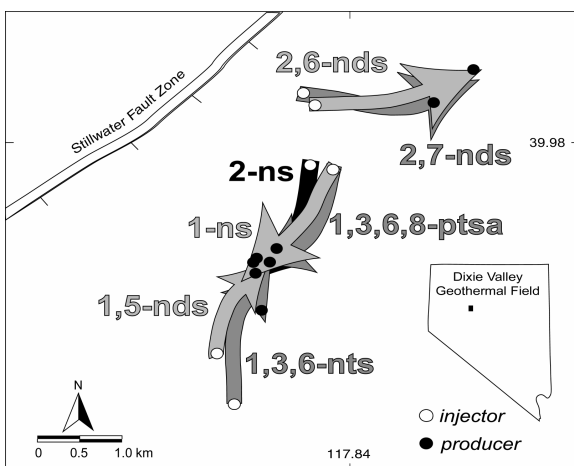


Figure 6. Tracer test results from seven tracer tests recently conducted at the Dixie Valley geothermal reservoir.

The apparatus shown in Figure 2 was used to demonstrate the greatly enhanced detectability of the intermediate-temperature tracer fluorescein in geothermal water. Shown in Figure 7 is a calibration curve for fluorescein between 50 and 750 parts per quadrillion (ppq). The actual limit of detection for fluorescein was 40 ppq, which is the lowest ever reported in the literature for this application and approximately 100-fold lower than what can be obtained by conventional analytical methods.

Having set a new standard for tracer detection in the industry, we then identified a number of tracers that were similar in structure to fluorescein and that, therefore, might possess comparable thermal stability. Shown in Figure 8 are the chemical structures of fluorescein and four similar compounds. The last column in this figure shows the thermal stability of each relative to fluorescein.

The second compound listed in Figure 8, 5-carboxyfluorescein, was chosen for field tests at the Beowawe and Dixie Valley geothermal reservoirs for the purpose of demonstrating in hydrothermal settings the greatly enhanced detectability of the laser fluorimeter over conventional analytical chemistry methods.

Compound	Structure	% Undecayed (2 days at 270°C)
fluorescein		78
5(6)-carboxyfluorescein		83
fluorescein-5-sulfonic acid		59
Oregon Green 488		40
Oregon Green 500 carboxylic acid		30

Figure 8. Compounds of intermediate thermal stability that can be analyzed by the very sensitive laser fluorimeter. The last column lists the percentage of each compound that remains undecayed upon exposure to geothermal conditions for two days at 270°C.

On July 10, 2001, 600 g of 5-carboxyfluorescein was injected into well 38-32 at Dixie Valley as a companion tracer to 2,6-naphthalene disulfonate. The 5-carboxyfluorescein was observed to return to the section 33 wells in similar fashion to the return of 2,6-naphthalene disulfonate as shown in Figure 5. This represents a 150-fold decrease in the quantity of fluorescein tracer used in a previous test at Dixie Valley.

On July 12, 2001, 600 g of 5-carboxyfluorescein was likewise injected into well 85-18 at the Beowawe geothermal field in east-central Nevada. A chemical analysis of returns to the production wells indicated that less than 1 g of 5-carboxyfluorescein would have been sufficient to demonstrate breakthrough at the production wells. This is approximately 100,000 times less than the quantity of tracer used in the previous tracer tests at Beowawe and dramatically illustrates the greatly enhanced detectability of the laser fluorimeter.

Conclusions and Plans for Continued Research

We have made significant progress in identifying and testing a family of tracers for high temperature (>300°C) geothermal applications. These tracers are being used to determine flow processes between injection and production wells within all major U.S. geothermal reservoirs. Since more tracers are needed, however, we plan to continue to identify, test and qualify additional candidates.

We have also made significant progress towards increasing the detectability of geothermal tracers for intermediate temperature (<250°C) tracing applications. We have demonstrated a reduction in the detection limit of these compounds by a factor of 100. We also identified and tested in the laboratory five new intermediate- temperature tracer candidates and demonstrated the greatly enhanced detectability of one of these compounds (5-carboxyfluorescein) in field tests at the Dixie Valley and Beowawe geothermal fields. We plan to continue to demonstrate improved detectability of fluorescent compounds and to use the emerging technologies of laser light sourcing, long pathlength flow cells, fiber optics and CCD spectrometry to implement field deployable detectors for the analysis of fluorescent tracers at the wellhead.

Collaborations, Papers Published and Technology Transfer

The best indication of the utility of technology developed by the R&D community is whether or not that technology gets transferred to the geothermal

industry. Effectively all of the companies operating geothermal reservoirs within the U.S. (and many more companies and institutes internationally) have adopted the use of the naphthalene sulfonate tracers. Shown in Figure 9 is a list of U.S. companies that have either used the new high temperature tracers in their respective reservoirs and/or have developed the ability to chemically analyze the tracers in-house.

Company	In-House Analytical Capability	Field Use
Caithness Energy	yes	yes
Unocal Geothermal	yes	yes
CalEnergy	yes	pending
Far West Capital	no	yes
Puna Geothermal	no	yes
Thermochem	yes	yes

Figure 9. List of U.S. companies that have adopted the use of the high temperature naphthalene sulfonate tracers.

In addition to the direct technology transfer activities summarized in Figure 9, we disseminate our results in peer-reviewed scientific journals and at geothermal conferences and workshops. Listed below are some of our recent publications:

Nimmo, J.R., Perkins, K.S., Rose, P.E., Rousseau, J.P., Orr, B.R., Twining, B.V., and Anderson, S.R., 2001, Kilometer-scale rapid transport of naphthalene sulfonate tracer in the unsaturated zone at the Idaho National Engineering and Environmental Laboratory, submitted for publication.

Rose, P.E., Johnson, S.D., and Kilbourn, P.M., and Kasteler, C. (2002) Tracer Testing at Dixie Valley, Nevada Using 1-Naphthalene Sulfonate and 2,6-Naphthalene Disulfonate: *Proc. Twenty-Sixth Workshop on Geothermal Reservoir Engineering*, Stanford University, SGP-TR-171.

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

- Kleimeyer, J.A., Rose, P.E., and Harris, J.M., 2001, Determination of ultratrace-level fluorescent tracer concentrations in environmental samples using a combination of HPLC separation and laser-excited fluorescence multiwavelength emission detection: application to testing of geothermal well brines: *Applied Spectroscopy*, 55(6), 690-700.
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