The application of the polyaromatic sulfonates as tracers in geothermal reservoirs

Peter E. Rose[a],*, Walter R. Benoit[b], Phaedra M. Kilbourn[a]

[a]*Energy and Geoscience Institute at the University of Utah, 423 Wakara Way, Suite 300, Salt Lake City, Utah 84108, USA*
[b]*629 Jones Street, Reno, NV 89503, USA*

Abstract

Five polyaromatic sulfonate compounds, 1,3,6,8-pyrene tetrasulfonate, 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate, were tested for use as geothermal tracers. They were subjected to a simulated hydrothermal environment in batch autoclave reactors in order to determine their thermal decay kinetics. The decay kinetics study indicated that all of the compounds are suitable for use in reservoirs having temperatures up to 310 °C, whereas some are suitable for use in reservoirs as hot as 350 °C. Methods were developed for the chemical analysis of the poly-aromatic sulfonates and their detection limits were shown to be approximately 200 parts per trillion by conventional high-performance liquid chromatography. The tracers were success-fully tested in a series of field studies at Dixie Valley, Nevada; Steamboat Springs, Nevada; Ohaaki, New Zealand; and Awibengkok, Indonesia. © 2001 CNR. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Tracers; Geothermal reservoirs; Polyaromatic sulfonates; Naphthalene sulfonates; Liquid chromatography; Dixie Valley; Ohaaki; Awibengkok

1. Introduction

Injection of produced fluids is essential to prudent geothermal reservoir-manage-ment strategies, both as a means of disposing of an environmental pollutant as well as a method of maintaining reservoir pressures. The location of the injection wells within the three-dimensional network of fractures that forms the reservoir is crucial

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* Corresponding author. Tel.: +1-801-585-7785; fax: +1-801-585-3540.
  E-mail address: prose@egi.utah.edu (P.E. Rose).

to the successful exploitation of the field. Proper well location leads to increased power production due to enhanced pressures, less reservoir scaling from boiling around the production wells, and reduced thermal breakthrough. Introduction of tracers into the injection-production loops is the fastest and most effective method of obtaining data that reveal the flow patterns of injected fluids.

The xanthene dye fluorescein has been used extensively to trace fluid flow patterns in geothermal reservoirs (Adams et al., 1989; Adams and Davis, 1991; Rose et al., 1995, 1998, 1999). With the exception of rhodamine WT, which has been used only in low-temperature geothermal fields (Gudmundsson et al., 1983; Rose and Adams, 1994), no other visible-fluorescent compounds have been shown to possess sufficient thermal stability to qualify for use as geothermal tracers. Because of the need for simultaneously identifying individual injector/producer flow paths in reservoirs containing multiple injection wells, however, many tracers are needed by the geothermal industry.

The UV-fluorescent polyaromatic sulfonates are excellent candidates for geothermal tracing applications because they are environmentally benign, very detectable by fluorescence spectroscopy, affordable if purchased in bulk quantities, and very thermally stable. In this paper, we report the results of laboratory decay kinetics studies that show that these compounds are suitable for use in reservoirs exceeding 310 °C. We then describe a series of tracer tests wherein the polyaromatic sulfonates were used to determine the injection/production flow patterns in geothermal reservoirs at Steamboat Springs, Nevada; Dixie Valley, Nevada; Ohaaki, New Zealand; and Awibengkok, Indonesia.

2. Concept evolution

Adams et al. (1992) evaluated 39 carboxylic and benzene sulfonic acids for use as hydrothermal tracers. The thermal stability of these compounds was attributed, in part, to their refractory aromatic ring. Since aromatic compounds are strong absorbers of ultraviolet light, they could be readily analyzed by high performance liquid chromatography (HPLC) using uv-absorbance detection. The carboxylic and sulfonic acid groups impart a strong electronegative charge to these compounds, rendering them both water-soluble and resistant to adsorption on negatively charged reservoir rock. Whereas the carboxylic acids possess reasonably good thermal stability (rendering them suitable for use in reservoirs as hot as 275 °C), the benzene sulfonic acids are even more stable. Four aromatic sulfonic acids showed no measurable decay upon exposure to simulated hydrothermal conditions for 2 weeks at 300 °C (Adams et al., 1992).

Smart and Laidlaw (1977) conducted a seminal study of eight fluorescent compounds for application as groundwater tracers. Two of these compounds, amino G and pyranine, were amino- and hydroxyl-substituted polyaromatic sulfonates, respectively, and, due to their structural relationship to benzene sulfonate, were considered to be good candidates for use as geothermal tracers (see Fig. 1). From coal liquefaction and gasification studies, the polyaromatic hydrocarbons (e.g.
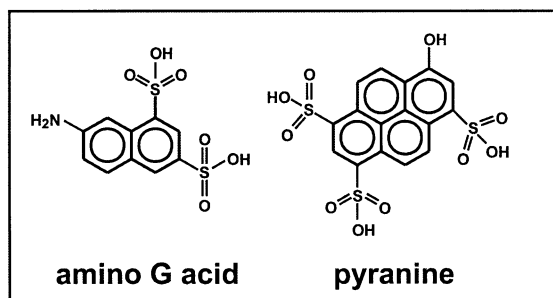
Fig. 1. The chemical structures of two substituted polyaromatic sulfonates, amino G and pyranine.

naphthalene, anthracene, and pyrene) were known to be very thermally stable, due, in large measure, to pi-bonding within the condensed aromatic rings. Given the refractory nature of the polyaromatic hydrocarbon backbone in conjunction with the apparent strength of the aryl-sulfonate bond, the substituted polyaromatic sulfonates were considered to possess sufficient thermal stability for use as geothermal tracers.

In addition to possessing good thermal stability, the substituted polyaromatic sulfonates were known to be detectable at concentrations in the low parts per trillion (ppt) by conventional fluorescence-spectroscopy techniques. Since the detection limit of aromatic acids is in the low parts-per-billion (ppb) range, the substituted poly-aromatic sulfonates are more detectable than the aromatic acids by a factor of approximately 1000.

Adams and coworkers studied the thermal stability of amino G (7-amino-1,3-naphthalene disulfonic acid) under simulated geothermal conditions at temperatures of 210 and 230 °C and found this tracer candidate to be moderately stable and suitable for use in geothermal reservoirs as hot as 250 °C (unpublished results). Rose and coworkers further studied amino G acid and an isomer, sulfotobias acid (2-amino-1,5-naphthalene disulfonic acid), under simulated geothermal conditions between 215 and 245 °C (unpublished results). They confirmed the results of Adams and coworkers that showed that amino G acid was moderately thermally stable and that these two amino-substituted naphthalene sulfonates could be used in reservoirs as hot as 250 °C. They also determined that each of these amino-substituted naphthalene sulfonates reacted to form stable, highly fluorescent compounds of indeterminate structure that showed no thermal decay upon exposure to simulated geothermal conditions at 245 °C (unpublished results). It appears that the naphthalene backbone of these molecules is not destroyed under these reaction conditions, since the products remain highly fluorescent. Given the refractory nature of both the condensed aromatic ring structure and the aryl-sulfonate bond, it is suspected that the labile amino group is responsible for the reactivity of amino G and sulfotobias acid.

Rose and coworkers studied the thermal stability of pyranine by exposing it to simulated geothermal conditions at 215 °C for 1 week (unpublished results). They observed that, like amino G, pyranine reacts to form a stable and strongly fluorescent compound of unknown identity. Pyranine has excitation and emission band maxima at 455 and 510 nm, respectively. The thermal degradation product has

excitation and emission band maxima at 416 and 448 nm, respectively, with an extinction coefficient comparable in strength to that of pyranine. As with amino G, it is probable that neither the condensed aromatic ring structure nor the aryl-sulfonate bonds were altered, but that the labile hydroxyl group was involved in pyranine's reactivity. The acidic hydroxyl group also complicates the analysis of pyranine, since pyranine fluorescence is a strong function of pH over the pH range of interest for hydrothermal waters.

The substituted naphthalene sulfonate, amino G, was successfully tested in the Dixie Valley geothermal reservoir (Rose et al., 1998). With a measured detection limit of approximately 200 ppt using HPLC and UV-fluorescence detection (excitation and emission band maxima at 245 and 445 nm, respectively), amino G concentrations were observed to be well above the detection limit after approximately 250 days in a reservoir with fluid temperatures approaching 250 °C.

The amino- and hydroxyl-substituted polyaromatic sulfonates showed good thermal stability and excellent detectability. The limitations of the substituted polyaromatic sulfonates as tracers, however, appeared to be related to the presence of either the hydroxy or amino groups. Therefore, it was expected that the unsubstituted polyaromatic sulfonates would possess the desirable qualities of the substituted polyaromatic sulfonates, without the problems arising from the presence of amino or hydroxy groups.

3. Experimental methods

Five polyaromatic sulfonates, 1,3,6,8-pyrene tetrasulfonate, 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate were selected for study based upon commercial availability. The structures of these compounds are shown in Fig. 2. The excitation and emission band maxima for each compound indicate that they all fluoresce in the ultraviolet.

When a compound fluoresces, it absorbs radiant light energy at a given wavelength(s) and re-emits that energy at a (usually) longer wavelength. A fluorescence spectrum (see Fig. 3) for one of the polyaromatic sulfonates, 1,5-naphthalene disulfonate, was measured using a Perkin Elmer LS30 spectrofluorometer. The excitation band has two major peaks with maxima at 218 and 285 nm, respectively, and an emission band with a maximum at 334 nm.

The polyaromatic sulfonates were analyzed using HPLC with fluorescence detection (Waters Corporation, Milford, MA). In order to take advantage of the high-resolution capability of a reverse-phase C-18 column (Keystone BetaBasic-18, 30×4.6 mm, 3-μm particles), paired-ion chromatography (PIC) was employed. The mobile phase consisted of a pH-7.5, phosphate-buffered (3.17 mM $Na_2HPO_4 \cdot 7H_2O$, 6.21 mM anhydrous KH_2PO_4), 5 mM solution of tetrabutyl ammonium phosphate (TBAP) in 25% methanol. The flow rate was 1.5 ml/min, ramping to 2.0 ml/min after 1 min. This HPLC method allowed for the chromatographic separation of analytes both from each other and from reservoir interferences. The detection limit for the polyaromatic sulfonates using this approach was approximately 200 ppt.
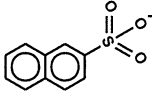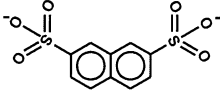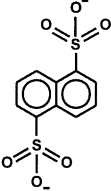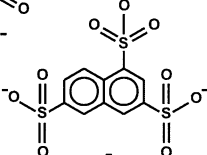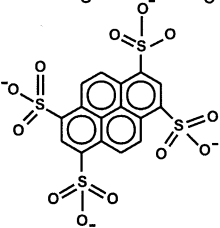
Compound	Structure	Excitation / Emission (nm)
2-naphthalene sulfonate		220 / 336
2,7-naphthalene disulfonate		226 / 339
1,5-naphthalene disulfonate		218 / 334
1,3,6-naphthalene trisulfonate		228 / 342
1,3,6,8-pyrene tetrasulfonate		346 / 386

Fig. 2. Chemical names, structures, and excitation and emission band maxima for the five polyaromatic sulfonates studied in the laboratory and in the field.

The decay kinetics of the five polyaromatic-sulfonate tracer candidates was studied using autoclave batch reactors under controlled conditions designed to simulate a geothermal environment. The compounds were dissolved in buffered aqueous solutions at target concentrations of 25 ppm by weight and adjusted to a room-temperature pH of 6.5. The buffer consisted of 0.747 g/l of KH_2PO_4 and 0.403 g/l of Na_2HPO_4.

Eighteen-milliliter aliquots of the buffered tracer solution were transferred to 30 ml quartz ampules and purged with argon to remove air. The ampules were carefully sealed using an oxymethane flame, while being purged with argon. For each experiment, four ampule-solutions were prepared: three samples and one control.

The sealed vials were transferred to a water-filled, one-liter autoclave (Autoclave Engineers, Philadelphia, PA), which was heated to the target temperature. The time required for the autoclave to attain operational temperature was between 1.5 and 2
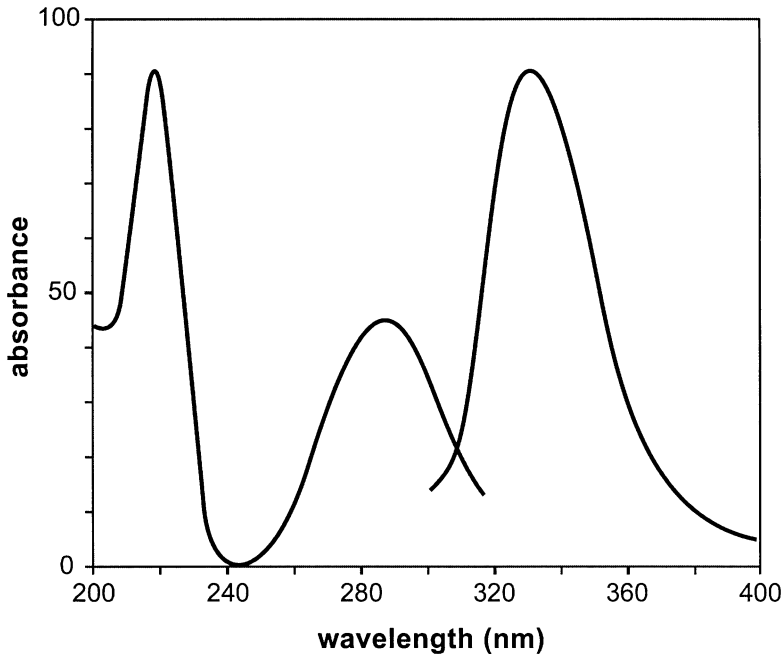
Fig. 3. A fluorescence spectrum for the candidate tracer 1,5-naphthalene disulfonate, consisting of two excitation peaks and one emission peak.

h, whereas the cool-down time was about 4 h. In all cases, the interior of the reactor was maintained within 1 °C of the target temperature for one week. The pressure inside the autoclave was the pressure of steam under saturated conditions at the target temperature. The control ampules were stored at 2 °C for the duration of the autoclave experiments.

The thermal decay data for 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate and 1,3,6,8-pyrene tetrasulfonate are summarized in Table 1. 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate showed modest decay (~20%) upon exposure to simulated geothermal conditions for one week at 330 °C, whereas 1,3,6,8-pyrene tetrasulfonate was almost thoroughly decomposed under similar conditions. No decay was observed for either 2-naphthalene sulfonate or 2,7-naphthalene disulfonate at 330 °C, indicating that these two compounds are the most thermally stable of the five tested.

4. Decay kinetics of the polyaromatic sulfonates

The thermal decay kinetics of the polyaromatic sulfonates was modeled by the first-order differential equation:

$$-\mathrm{d}C_n/\mathrm{d}t = k_n \cdot C_n \tag{1}$$

Table 1
Thermal decay data for three of the polyaromatic sulfonates studied[a]

Reactant	Reaction temp. (°C)	Initial conc. (mg/l)	Average final conc. (mg/l)	Standard deviation (mg/l)
1,5-Naphthalene disulfonate	310	25.00	24.05	0.24
	320	25.00	21.62	0.40
	330	25.00	19.80	–
1,3,6-Naphthalene trisulfonate	310	25.00	23.62	–
	320	25.00	21.81	0.20
	330	25.00	19.56	0.89
1,3,6,8-Pyrene tetrasulfonate	300	24.56	18.675	–
	325	25.00	4.363	0.14
	330	25.00	2.668	0.21

[a] No data are shown for either 2-naphthalene sulfonate or 2,7-naphthalene disulfonate, since no decay was measured for either compound upon exposure to simulated geothermal conditions for 1 week at 330 °C.

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

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

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

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

where A is the pre-exponential factor, E_a is the energy of activation, R is the gas constant and T is absolute temperature. A linearization of the Arrhenius expression results in the following:

$$\ln k_n = \ln A - \frac{E_a}{RT} \tag{4}$$

Fig. 4(a) shows Arrhenius plots of ln k_n vs. inverse temperature between 300 and 330 °C for the three compounds 1,5-naphthalene disulfonate, 1,3,6-naphthalene tri-sulfonate, and 1,3,6,8-pyrene tetrasulfonate. The linear relationship between ln k_n and inverse temperature indicates that the Arrhenius equation provides a good means of expressing the temperature dependence of the decay rate constant.

The straight lines in Fig. 4(a) were determined by linear least-squares fits to the data. The values for the pre-exponential factor, A, and the energy of activation, E_a, obtained from a regressional analysis of each of the three compounds, are listed in Table 2. From these data, the rate constant for the thermal decay of each compound
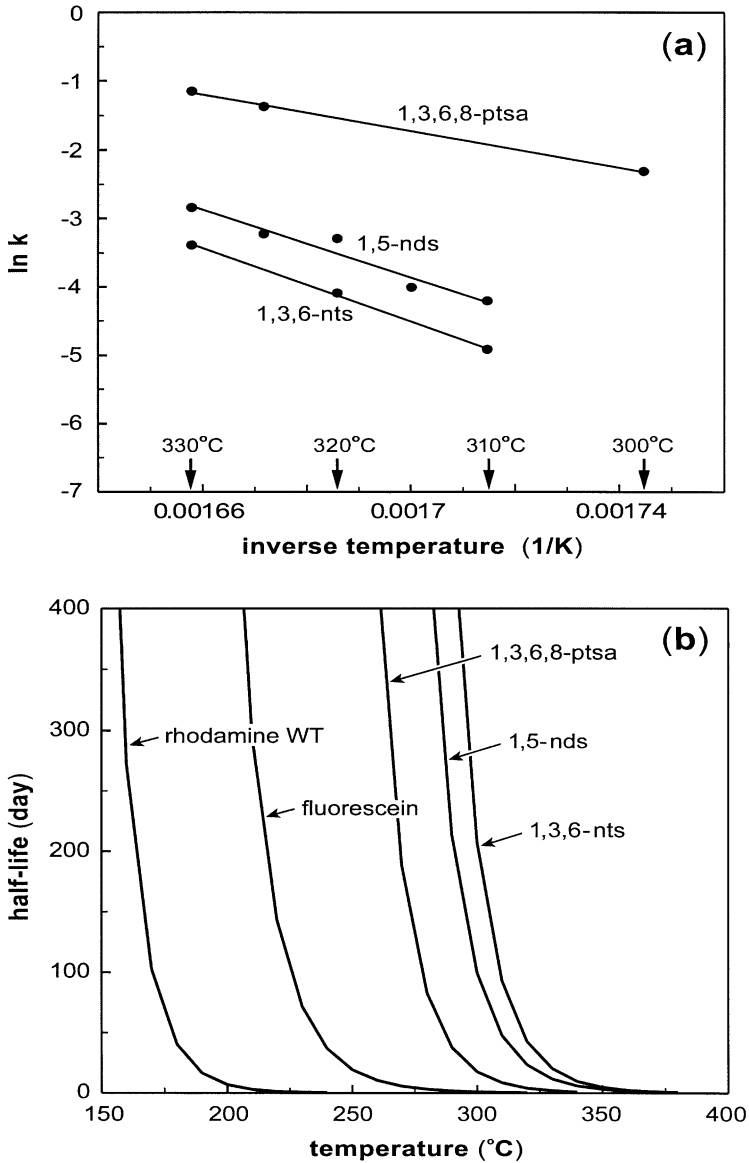
Fig. 4. (a) Arrhenius plots of ln k_n vs. inverse temperature between 300 and 330 °C for the three compounds 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, and 1,3,6,8-pyrene tetrasulfonate. (b) Plots of half-life vs. temperature based upon the Arrhenius decay data shown in (a). Also included is a speculative plot of half-life vs. temperature representing the compounds 2,7-naphthalene disulfonate and 2-naphthalene sulfonate. These latter two compounds were so thermally stable that no decay was measured upon exposure to geothermal conditions for 1 week at 330 °C. Also shown are plots for the lower-temperature geothermal tracers fluorescein and rhodamine WT.

Table 2
Arrhenius constants for three of the polyaromatic sulfonates studied in the laboratory under conditions that simulate a geothermal environment

Compound	Pre-exponential factor, A (day^{-1})	Energy of activation, E_a (J/mol)	Temperature range (°C)	R^2
1,5-Naphthalene disulfonate	3.49E16	205,000	310–330	0.944
1,3,6-Naphthalene trisulfonate	7.12E17	223,000	310–330	0.998
1,3,6,8-Pyrene tetrasulfonate	1.73E17	205,000	300–330	0.998

can be determined at any temperature within the indicated range. Using these data, the half-lives of these three polyaromatic sulfonates are plotted as functions of temperature in Fig. 4b. For comparison, the half-lives of two xanthene dyes that have been used as geothermal tracers, fluorescein and rhodamine WT, are also plotted. No plots are shown for the two compounds 2-naphthalene sulfonate and 2,7-naphthalene disulfonate, since no decay was observed for either compound after exposure to geothermal conditions for 1 week at 330 °C.

5. Tracer testing at Dixie Valley using the polyaromatic sulfonates

The polyaromatic sulfonate candidate tracers were extensively tested in a series of field studies between 1997 and 2000 at the Dixie Valley geothermal field (Rose et al., 1998, 2000, 2001) located in west-central Nevada (Fig. 5). This reservoir is a classical example of a hydrothermal system located along a narrow fault zone. Dixie Valley is an asymmetric basin and range graben that is bounded on the west by the Stillwater range and on the east by the Clan Alpine mountains. The geothermal field is located on the west side of the valley. Benoit (1999) has reviewed the conceptual, structural and numerical models of the Dixie Valley hydrothermal system.

Since the early 1980s, the prevailing structural model for interpreting flow patterns within the Dixie Valley geothermal field was based upon a single range-front fault dipping 52–54° to the SE with a roughly planar geometry to depths of at least 3 km (Benoit, 1995). It assumed that production was controlled primarily by fracture permeability associated with this range-front fault and its related secondary fractures.

A recent reinterpretation based primarily upon Bouguer gravity data and reflection seismic profiles suggests a more complex geometry with a steeper-dipping range front fault that accommodates most of the topographic displacement and a series of steep-dipping piedmont faults that splay off the range front fault and account for most of the displacement at depth (Blackwell et al., 1999). According to this model, the known reservoir is primarily associated with the piedmont faults.

The production wells produce up to 125 kg/s mostly from three to six individual fractures located between depths of 2500 and 3100 m (Barton et al., 1998). Until recently, injection was into three different geologic environments: an areally restricted Miocene basalt aquifer at a depth of approximately 2225 m, a fault zone at a depth of about 1860 m, and the main fault zone between depths of 2700 and 2950 m (Benoit, 1992). In 1999, injection was initiated into well 27-32, which penetrated a
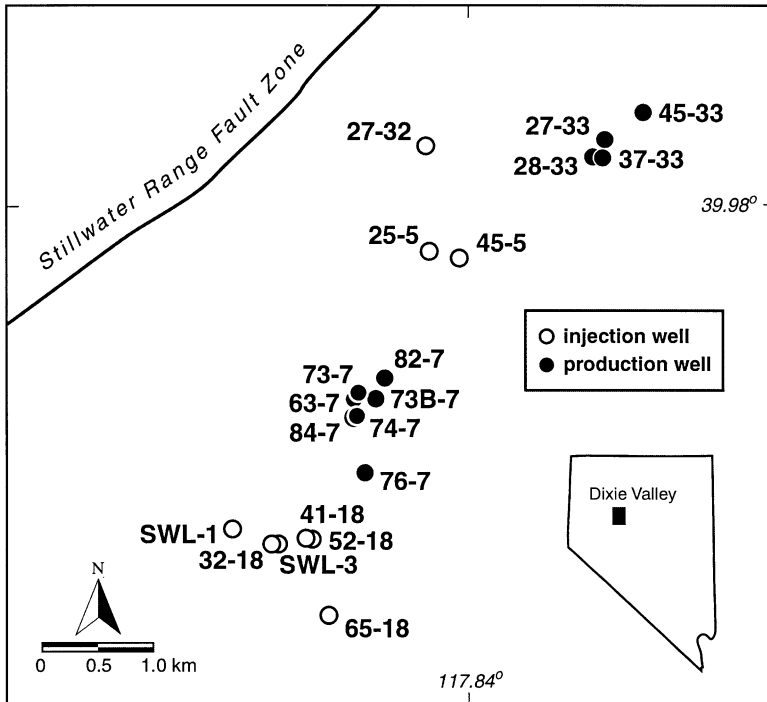
Fig. 5. Map of the Dixie Valley geothermal reservoir, showing the injection and production wellhead locations.

shallow fault zone at approximately 180 m. The reservoir is hosted primarily by metamorphosed Mesozoic sedimentary and mafic igneous rocks (Waibel, 1987).

5.1. 1.3,6,8-Pyrene tetrasulfonate

On 3 September 1997, 1818 kg of a 10 wt.% aqueous solution of 1,3,6,8-pyrene tetrasulfonate (Hilton Davis, Cincinnati) was injected into well 45-5 over a period of about 20 min. The injectate flow rate was approximately 300 kg/s. Nine production wells were sampled twice weekly throughout the subsequent year.

Shown in Fig. 6 are plots of the return curves of 1,3,6,8-pyrene tetrasulfonate that was injected into well 45-5. The tracer first arrived in about 90 days, with the strongest return to well 73-7. The next strongest returns were to wells 73B-7 and 63-7, followed by 82A-7. No 1,3,6,8-pyrene tetrasulfonate was observed in any of the section-33 wells.

5.2. 1,5-Naphthalene disulfonate and 1,3,6-naphthalene trisulfonate

On 14 July 1998, 100 kg of 1,5-naphthalene disulfonate (Konishi Chemical, Japan) was dissolved in approximately 400 l of flashed reservoir water and injected over a
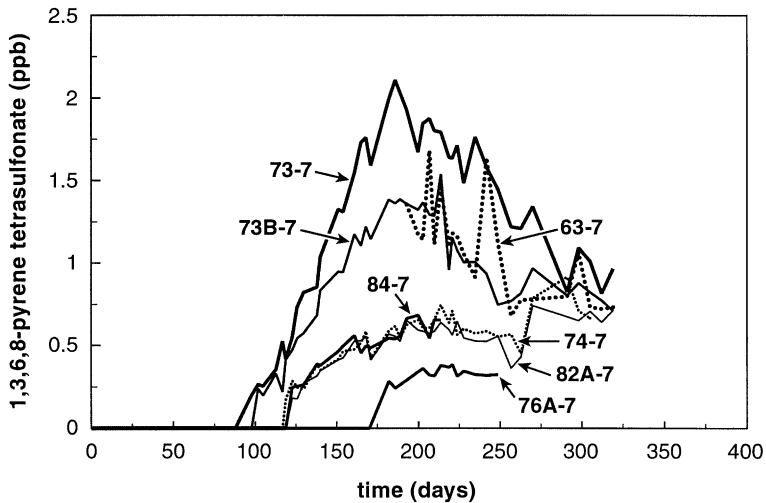
Fig. 6. 1,3,6,8-Pyrene tetrasulfonate returns observed from the testing of injector 45-5 at Dixie Valley.

period of about 15 min into well 41-18 (see Fig. 5). This injector accepts fluids at a rate of approximately 40 kg/s. Similarly, 100 kg of 1,3,6-naphthalene trisulfonate (Konishi Chemical, Japan) was mixed with approximately 300 l of flashed reservoir water and injected over a period of 20 min into injector 65–18 (see Fig. 5), which accepts fluids at a rate of approximately 65 kg/s. All of the producing wells in the field were subsequently monitored for the two tracers over the subsequent 2.5 years.

The return curves for 1,5-naphthalene disulfonate are plotted in Fig. 7. These return curves reflect tracer production in the six wells in Section 7 (see Fig. 5) only, as no tracer was observed in any of the production wells monitored further to the northeast in Section 33. The first arrivals of tracer were between 40 and 54 days for all of the wells except 82A-7, which did not produce tracer until 79 days after injection.

The return curves from the tagging of injector 65-18 with 1,3,6-naphthalene tri-sulfonate are shown in Fig. 8. Like the test that was associated with injector 41-18, tracer was produced in Section 7 only. First arrivals for three of the wells were between 75 and 79 days, although a long sampling hiatus between days 79 and 97 may have obscured the first arrival of tracer to 74-7. Tracer did not arrive in well 73B-7 until day 103, but the slowest arrival of tracer, again, was to 82A-7, which did not show return until 145 days into the test.

There are striking similarities between the return-curve plots for the two injectors tagged with 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate. In both tests, the strongest returns were to producers 63-7, 74-7 and 76A-7. Also, in each test, tracer was measured in well 82A-7 much later than it was measured in any of the other section 7 wells. These similarities suggest a similar path for injectate flowing between the two tagged injectors (41-18 and 65-18) and the Section-7 producers.

In spite of these similarities, a significant difference exists between the return curves for the two tests. The peak concentrations of 1,5-naphthalene disulfonate tracer injected in well 41-18 are approximately 11 ppb, whereas the peak con-
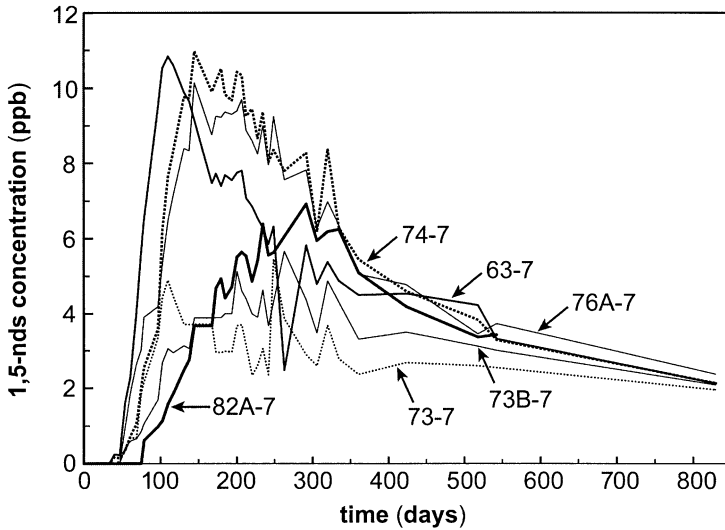
Fig. 7. 1,5-Naphthalene disulfonate returns observed from the testing of injector 41-18 at Dixie Valley.
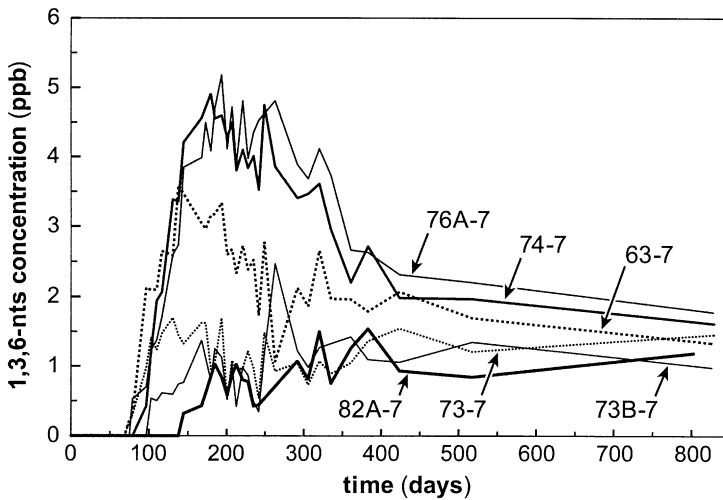

Fig. 8. 1,3,6-Naphthalene trisulfonate returns observed from the testing of injector 65-18 at Dixie Valley.

centrations of 1,3,6-naphthalene trisulfonate are approximately 5 ppb. Since equal quantities of tracer were injected in each injection well and since 65-18 is further away from the Section 7 producers than is 41-18, it is reasonable to assume that the tracer injected in 65-18 was diluted with a greater volume of reservoir water before being produced. The differences in concentration cannot be explained by thermal degradation of tracer, since the reservoirs fluids, whose temperatures measure less than 250 °C, are too cool to cause any measurable decay of 1,3,6-naphthalene tri-sulfonate over such a short duration.

5.3. 2-Naphthalene sulfonate and 2,7-naphthalene disulfonate

On 17 November 1999, 198 kg of 2,7-naphthalene disulfonate (Yick-Vic Chemicals, Hong Kong) was slurried with approximately 400 l of flashed reservoir water and injected over a period of about 4 min into well 27-32 (Fig. 5). Water was continuously injected into the well at a rate of approximately 73 kg/s. Similarly, on 18 November 1999, 199 kg of 2-naphthalene sulfonate (Yick-Vic Chemicals, Hong Kong) was dissolved into approximately 400 l of flashed reservoir water and injected over a period of 2 min into injector 25-5 (Fig. 5), which was flowing at a rate of approximately 310 kg/s. All of the producing wells in the field were subsequently monitored for the two naphthalene sulfonates over the subsequent year.

The return curves for the 2,7-naphthalene disulfonate that was injected into well 27-32 are plotted in Fig. 9. These return curves show tracer production in three producers in Section 33 only (Fig. 5), as no tracer was observed in any of the production wells monitored further to the southeast in Section 7. This represents the first observation of tracer production ever to Section 33. The tracer first arrived at two producers (28-33 and 37-33) approximately 135 days after tracer injection. This is the longest measured duration before first arrival of tracer in any tracer tests conducted at Dixie Valley.
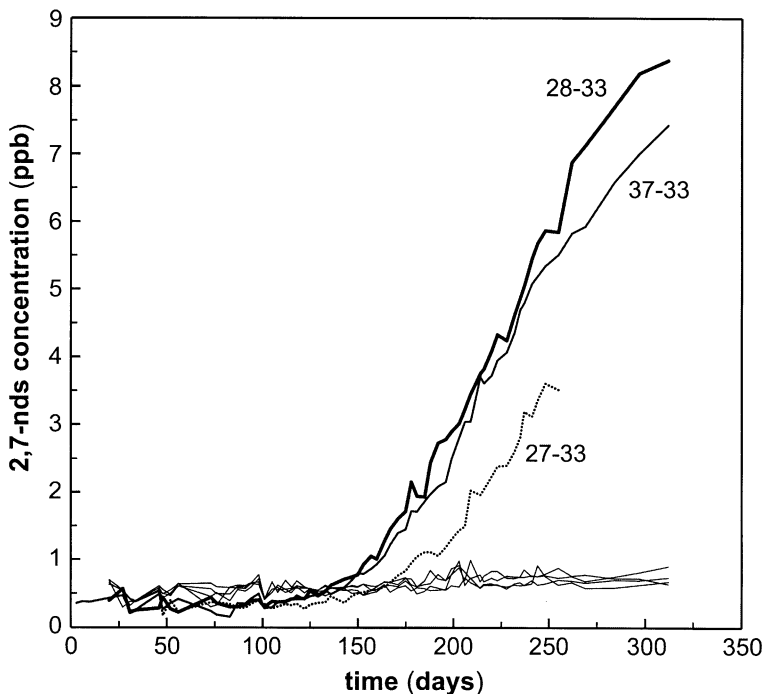

Fig. 9. 2,7-Naphthalene disulfonate returns observed from the testing of injector 27-32 at Dixie Valley.

The return curves for the 2-naphthalene sulfonate that was injected into well 25-5 are plotted in Fig. 10. These return curves show tracer production in all of the operating producers in Section 7 except well 76A-7 (Fig. 5). No tracer was observed in any of the production wells monitored further to the northeast in Section 33. The tracer first arrived to two producers, 63-7 and 73B-7, approximately 100 days after tracer injection.

A plot of the return curves of 2,7-naphthalene disulfonate show a significant background concentration of approximately 0.5 ppb in all of the wells monitored during the test (Fig. 9). The identity of this background contaminant is not known, although it is possible that it is 2,7-naphthalene disulfonate, which was created as either an isomerization product or partial decomposition product of other naphthalene sulfonates injected in previous tracer tests. There is also a significant background concentration between approximately 2 ppb and 3.8 ppb of an apparent contaminant that is chromatographically indistinguishable from 2-naphthalene sulfonate (Fig. 10). Again, the identity of this compound is not known. And, again, it is possible that it is either 2-naphthalene sulfonate or a similar compound that co-elutes with 2-naphthalene sulfonate.

Neither 2,7-naphthalene disulfonate nor 2-naphthalene sulfonate had ever been used as tracers at Dixie Valley prior to the two tests described here. The existence of strong background contaminant concentrations that are chromatographically indistinguishable from these two compounds is therefore somewhat troubling. Since nearly all of the water produced at the Dixie Valley reservoir is reinjected and since
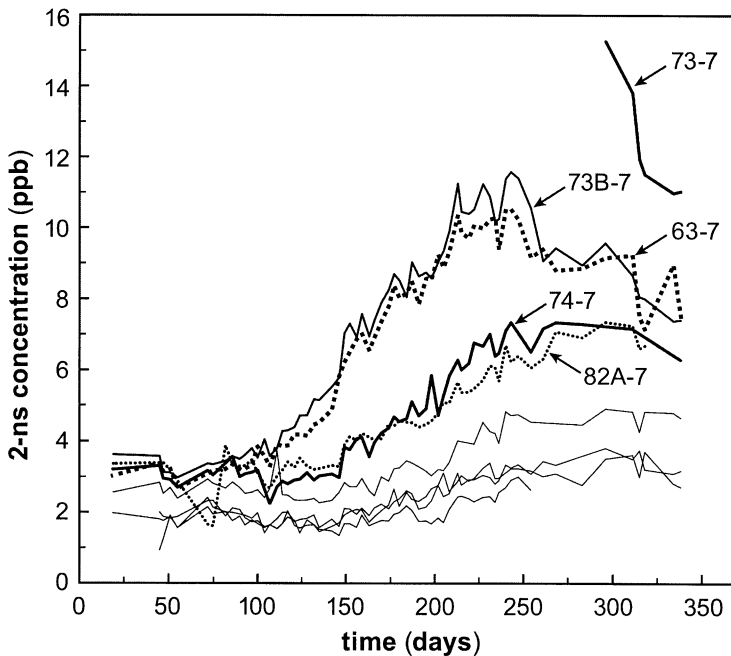

Fig. 10. 2-Naphthalene sulfonate returns observed from the testing of injector 25-5 at Dixie Valley.

the production wells within the reservoir are underpressured relative to the surrounding aquifers, thermally stable tracers such as the naphthalene sulfonates remain in the reservoir until they decay. The result is that tracers tend to remain in solution in the reservoir for a long time. In addition to the four naphthalene sulfonate tracers tested in the Dixie Valley reservoir and reported here (1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate), an amino-substituted naphthalene disulfonate (amino G) and a dimerized naphthalene sulfonate (Crisotan R5) were also recently tested (Rose et al., 1998). Therefore, the background concentrations may be attributed to a combination of isomerization and/or partial decomposition of a number of naphthalene sulfonates and an amino-substituted naphthalene disulfonate tested at the Dixie Valley reservoir over the past several years. These examples illustrate the result of using conservative tracers in reservoirs where all of the produced fluids are reinjected and where there is very little natural fluid leakage into surrounding aquifers.

6. Tracer testing at Steamboat Springs using 1,5-naphthalene disulfonate

The Far West Capital (FWC) Steamboat Springs geothermal field is located approximately 14 km south of Reno, Nevada. Fig. 11 shows the location of production, injection and exploratory slim holes drilled on the FWC Steamboat Springs geothermal operations area. Average geothermal fluid production temperature is approximately 160 °C. The combined production flow rate to the SB 1/1A and SB 2/3 power plants is approximately 1370 kg/s. The combined electrical power output from these two plants is approximately 31 MW.

Fractured granodiorite underlies the volcanic sequence and comprises the geothermal reservoir system at Steamboat Springs (Rose et al., 1999). The permeability of the fractured granodiorite is very high. The total thickness of the granodiorite is unknown. The deepest hole drilled in the area (GTH 87-29) encountered granodiorite to a depth of 1220 m.

The tracer test at Steamboat Springs was designed to compare the performance of the candidate tracer 1,5-naphthalene disulfonate with the well-characterized geothermal tracer, fluorescein. On 24 July 1998, 91 kg of uranine (sodium salt of fluorescein) was mixed with 100 kg of the disodium salt of 1,5-naphthalene disulfonic acid in a tank with approximately 3.8 m^3 of water (Rose et al., 1999). Upon dissolution of the tracers, the solution was injected over a period of approximately 45 min into slim hole GTH 87-29. Brine was then injected continuously into GTH 87-29 at a rate of 9 kg/s.

The 1,5-naphthalene disulfonate return curves for selected wells are shown in Fig. 12. The strongest return is to well HA-4, which is located only 10 m from the tagged slim hole GTH 87-29. The distance separating the completion intervals of the two wells is much greater, since producer HA-4 has a total depth of only 220 m, whereas the slim hole injection well is completed in a deeper region of the reservoir below a depth of about 670 m.

Fig. 13 shows the normalized fluorescein and 1,5-naphthalene disulfonate return curves for production well HA-4. Each return curve has been normalized for the
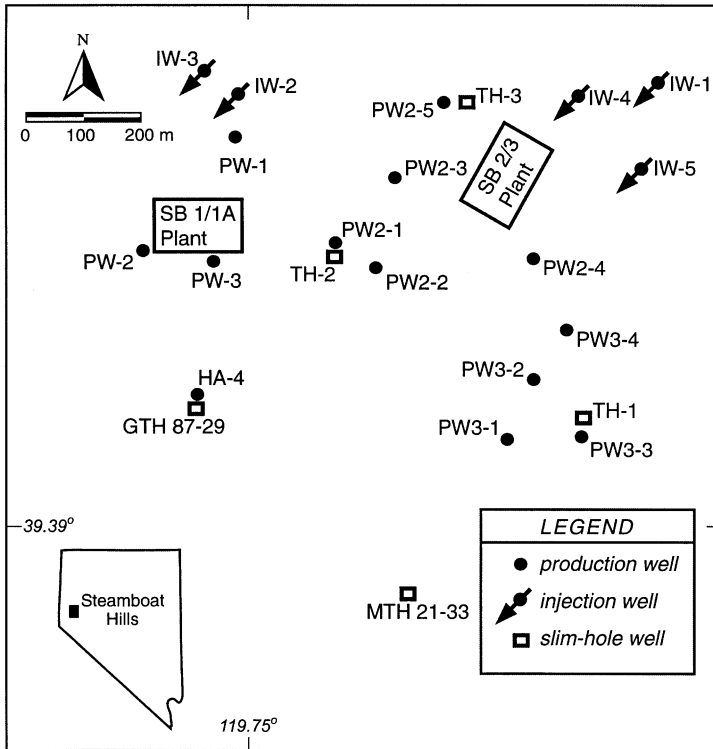
Fig. 11. Location map of production, injection and exploratory slim holes drilled in the Far West Capital Steamboat Springs geothermal operations area.

quantity of tracer injected, and the fluorescein plot has been corrected for the initial background concentration of approximately 200 ppt. It is evident from this figure that the normalized return-curve concentrations are nearly identical. In a tracer test at Dixie Valley, Nevada, Adams and coworkers (1989) showed that fluorescein did not adsorb on reservoir rock when its normalized return curve was compared to that of the tracer benzoic acid, which was assumed to behave conservatively. Since 1,5-naphthalene disulfonate was shown to have a normalized return curve that was essentially identical to that of fluorescein (Fig. 13), it is unlikely that either 1,5-naphthalene disulfonate or fluorescein adsorbed on the reservoir rock at Steamboat Springs.

7. Tracer testing at Ohaaki, New Zealand using 1,5-naphthalene disulfonate

The Ohaaki geothermal field is located 30 km northeast of Lake Taupo on either side of the Waikato river (Fig. 14). The geology at Ohaaki represents about 750,000 years of accumulation of rhyolitic and sedimentary rocks in a subsiding basin at the eastern margin of the Taupo Volcanic zone (Clotworthy et al., 1995). The basement
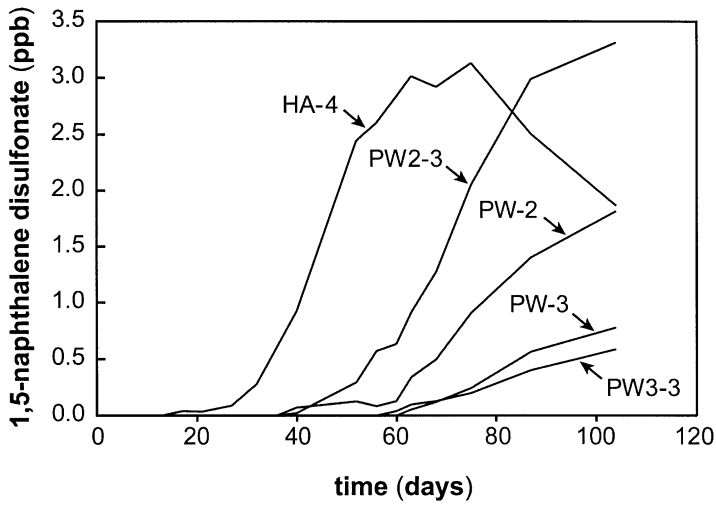
Fig. 12. 1,5-Naphthalene disulfonate returns observed from the testing of injector GTH 87-29 at Steamboat Springs.
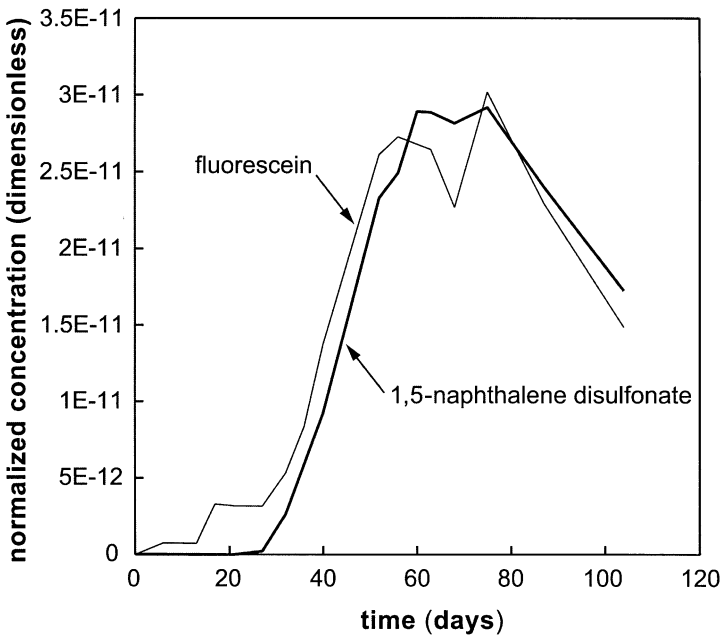

Fig. 13. Normalized fluorescein and 1,5-naphthalene disulfonate returns from injection well GTH 87-29 to production well HA-4.

comprises mainly greywacke sandstones of the Mesozoic Torlesse Terrane to the depths currently explored, or about 2.5 km. Above the basement, the Waikora Formation greywacke conglomerates are interbedded with undifferentiated Ohakuri
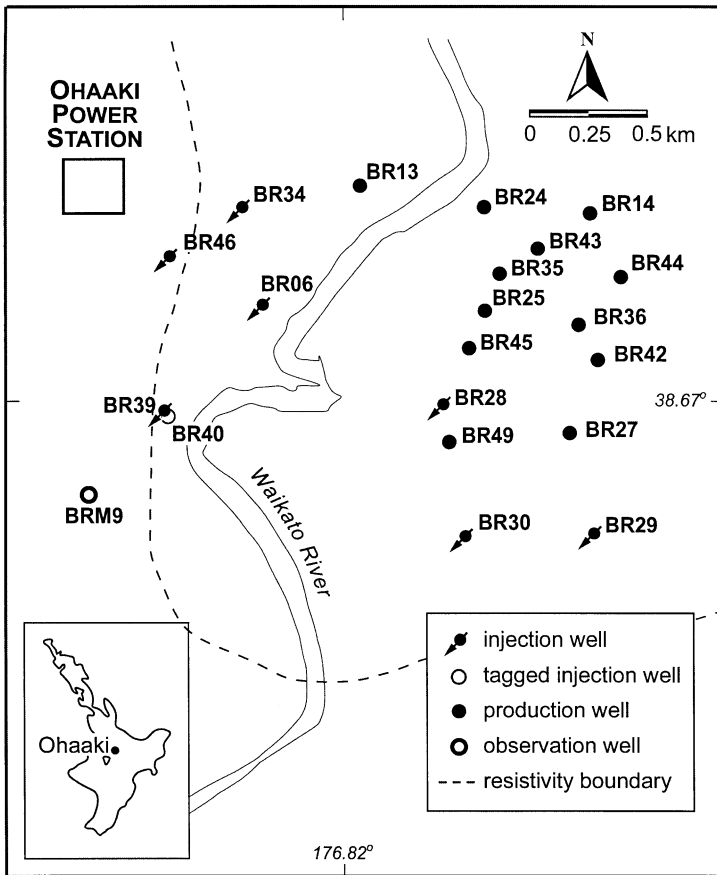
Fig. 14. Map of the southwest portion of the Ohaaki, New Zealand, geothermal field showing the injection and production wellhead locations.

Group volcanics, forming a wedge of rocks of poorly known production potential. The 330,000-year-old Rangitaiki ignimbrite forms a thick, field-wide marker horizon above which are 800–1000 m of variable deposits which include lacustrine sediments (lower siltstone, Huka Falls Formation), lava domes (east Broadlands rhyolite, Broadlands dacite, Broadlands rhyolite, Ohaaki rhyolite), and bedded volcanics (Rautawiri breccia, Waiora formation) (Clotworthy et al., 1995).

The thick, ubiquitous, pumiceous tuffs of the Rautawiri breccia and the more restricted Waiora Formation are generally permeable and productive. The Broadlands rhyolite has good fracture permeability, and occurs only near the western margin of the field where it is used for reinjection. The Ohaaki rhyolite is present in the western and central parts of the field. It has fracture permeability where it is thickest, west of the Waikato River. Prior to field development, it acted as a mixing aquifer for cooler shallow waters and hot geothermal fluids originating from depth. Unlike the two large rhyolite domes (Ohaaki and Broadlands rhyolites), the similar-

sized Broadlands dacite dome in the southeastern part of the field has low permeability. The inner rhyolite overlying the west-bank production wells is poorly connected to the outer Ohaaki rhyolite to the south (Clotworthy et al., 1995).

On 25 May 1999, 150 kg of 1,5-naphthalene disulfonate (Pfaltz and Bauer, USA) was injected into well BR-40 at the Ohaaki geothermal reservoir (see Fig. 14). Various production and monitoring wells were sampled and analyzed for tracer over several subsequent months (Rose et al., 2000).

Shown in Fig. 15 are the returns of the 1,5-naphthalene disulfonate tracer within and adjacent to the Ohaaki reservoir. The strongest returns were to the observation well BRM-9, which is in close proximity to BR-40 and just outside of the resistivity boundary for the field. Modest returns were also observed to wells BR-25, BR-36, BR-44, and BR-45 within the field, with first arrivals approximately 140 days into the test. These two producers are among the closest to the tagged injector. It is evident, however, that the tracer returns to the wells within the field are much weaker than the returns to the observation well, which is just outside of the field, indicating that most of the injectate into BR40 flows away from the field.

8. Tracer testing at Awibengkok, Indonesia using 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate

The Awibengkok geothermal field is located in West Java, Indonesia, approximately 60 km south of Jakarta. The resource is liquid-dominated, containing relatively benign
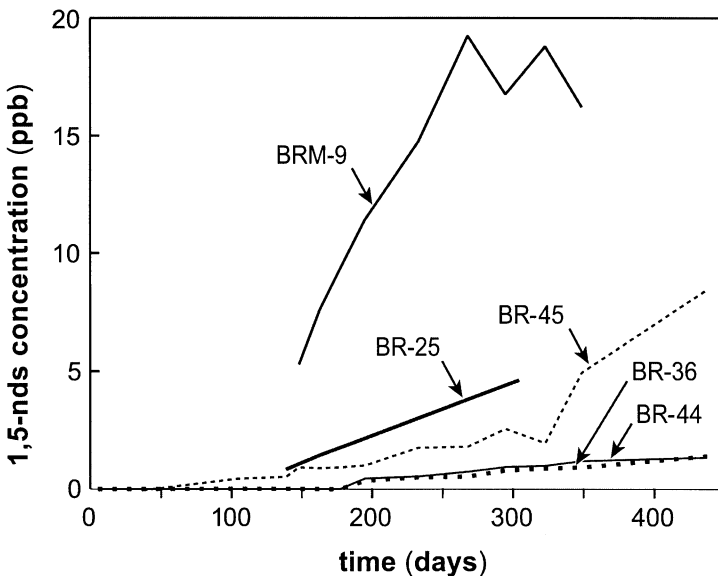

Fig. 15. 1,5-Naphthalene disulfonate tracer returns observed from the testing of injector BR-40 at Ohaaki.

fluid with reservoir temperatures ranging from 221 to 312 °C. It is a highly fractured reservoir set in andesitic rocks. Within the reservoir, the matrix rocks are propylitically altered.

The first tracer tests at Awibengkok were conducted in 1994 using fluorescein. These tests successfully identified good hydraulic connections between closely spaced injection and production wells (Murray et al., 1995). Because of the better thermal stability offered by the naphthalene sulfonates, these compounds were chosen for use in hotter parts of the reservoir and where the hydraulic connections between injection wells and production wells appear to be weak or the flow paths relatively long.

In the eastern part of the field where the naphthalene sulfonates tracers were injected (Fig. 16), there are 19 production wells on three locations (AWI-1, AWI-13 and AWI-16). The total mass production rate of these 19 wells averages approximately 1400 kg/s. There are seven injection wells in the area grouped on two locations (AWI-14 and AWI-15) that accept approximately 1390 kg/s of separated brine, which is about 50% of the total brine injected at Awibengkok.

On 6 November 1998, 150 kg of 1,5-naphthalene disulfonate and 150 kg of fluorescein were dissolved in approximately 2400 l of fresh water and injected over a period of about 6 min into AWI 15-2, which was accepting about 110 kg/s of brine (Rose et al., 2000). This resulted in a final concentration of 3600 ppm for each tracer. On 8
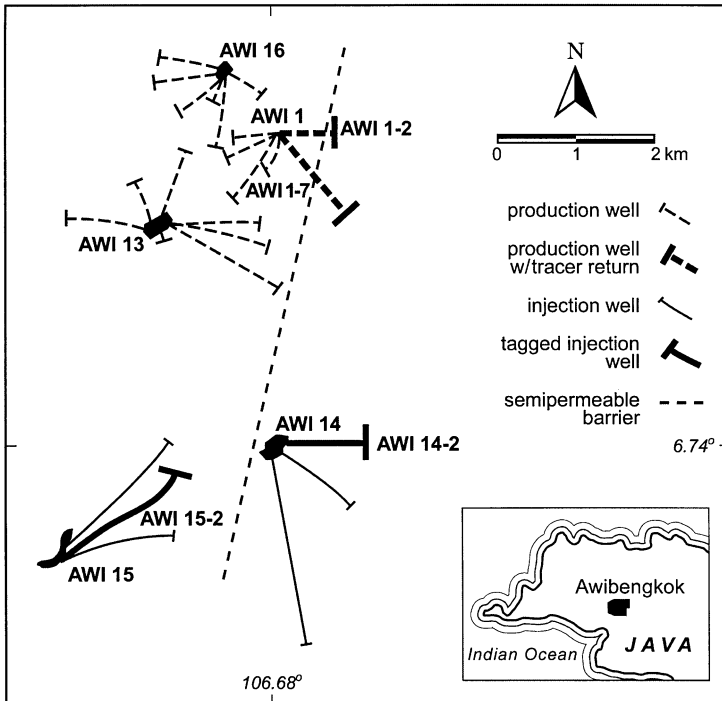

Fig. 16. Map of the eastern portion of the Awibengkok, Indonesia, geothermal field showing the injection and production wellhead locations.

November 1998, 150 kg of 1,3,6-naphthalene trisulfonate was dissolved in approximately 1500 l of fresh water and injected over a period of about 5 min into AWI 14-2, which was accepting about 90 kg/s of brine. This resulted in a final tracer concentration of 5200 ppm. All production wells in the field were subsequently monitored for the three tracers for approximately 8 months.

Neither 1,5-naphthalene disulfonate nor fluorescein was detected in any of the production wells. 1,3,6-naphthalene trisulfonate was observed in two production wells, AWI 1-2 and AWI 1-7 (Fig. 17). That returns of the 1,3,6-naphthalene trisulfonate injected at AWI 14-2 were observed in only two producers supports the existence of a semi-permeable barrier separating AWI 14-2, AWI 1-2 and AWI 1-7 from the rest of the field (Fig. 16). This barrier was first proposed to explain pressure interference tests conducted prior to commercial operations (Murray et al., 1995). The tracer tests reported here, however, offer the most conclusive evidence to date of the existence of this barrier. That no returns of 1,5-naphthalene disulfonate or fluorescein injected at AWI 15-2 were detected in any of the producing wells may be explained by the fact that the fluid injected into this well exits the wellbore below a thick rhyodacite unit that extends over the entire field, while most eastern production wells
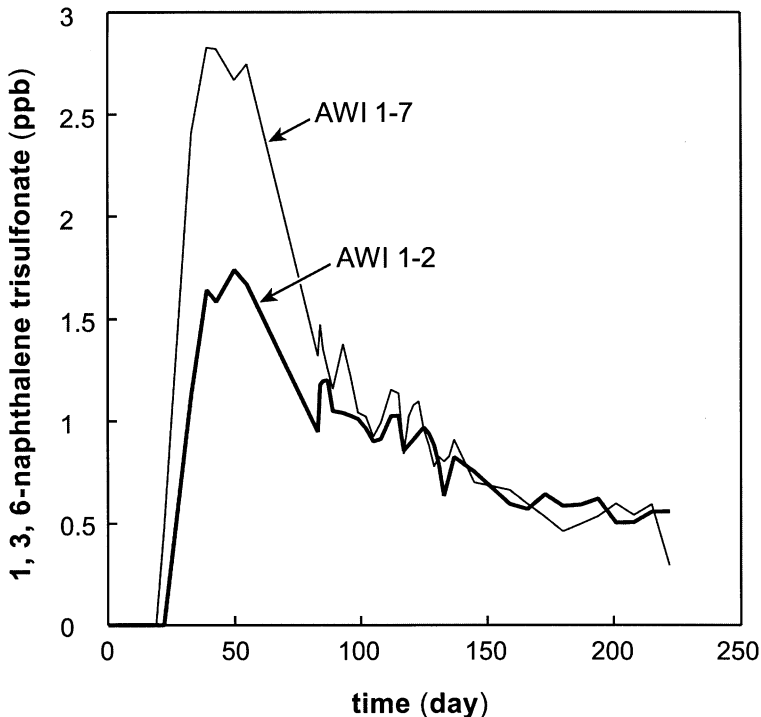

Fig. 17. 1,3,6-Naphthalene trisulfonate tracer returns observed from the testing of injector AWI 14-2 at Awibengkok.

have entries above this unit. Clay-rich tuffs associated with the rhyodacite unit may act as semi-permeable barriers impeding vertical flow in the reservoir.

9. Conclusions

The polyaromatic sulfonates were successfully tested in laboratory and field studies and shown to be robust geothermal tracers. In addition to being environmentally benign and very affordable, these fluorescent compounds have detection limits of approximately 200 ppt using conventional HPLC analysis. Decay kinetics studies indicate that the five polyaromatic sulfonates tested (1,3,6,8-pyrene tetrasulfonate, 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate) possess excellent thermal stability and are suitable for use in high-temperature, liquid-dominated geothermal reservoirs. An Arrhenius model was used to determine the temperature dependence of the decay rate constants on temperature. Using this model, we showed that 1,3,6,8-pyrene tetrasuflonate can be used in reservoirs as hot as 310 °C, 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate in reservoirs as hot as 340 °C, and 2-naphthalene sulfonate and 2,7-naphthalene sulfonate in reservoirs having fluid temperatures of 350 °C or hotter.

In a series of tracer tests at the Dixie Valley geothermal reservoir, all five polyaromatic sulfonate tracers were successfully tested. The tests revealed that Section-18 and Section-5 injectate flows to the Section-7 production wells. Injection into the newly drilled 27-32 injector flows to the Section-33 producers.

In a tracer test at Steamboat Springs, Nevada, 1,5-naphthalene disulfonate was tested in combination with fluorescein. Normalized return curves of the two tracers showed that 1,5-naphthalene disulfonate does not adsorb relative to fluorescein at a reservoir-fluid temperature of 160 °C, indicating that the naphthalene sulfonates are suitable for use in low-temperature geothermal reservoirs.

A tracer test at the Ohaaki geothermal reservoir using 1,5-naphthalene disulfonate revealed that most of the water injected via well BR-40 flows away from the reservoir. A small fraction of the injectate returns to some of the production wells in the southwest portion of the field.

In a field test at the Awibengkok geothermal reservoir, both naphthalene sulfonate tracers were used. The lack of tracer response from well AWI 15-2, which was tagged with 1,5-naphthalene disulfonate, indicates that this well is not immediately connected with any production wells. Tracer returns show, however, that well AWI 14-2, which was tagged with 1,3,6-naphthalene trisulfonate, is connected to two producers in the eastern portion of the reservoir.

The polyaromatic sulfonates that we tested for this study are all sufficiently stable to be used in liquid-dominated geothermal reservoirs with temperatures exceeding 310 °C. Two of them (2-naphthalene sulfonate and 2,7-naphthalene sulfonate) are sufficiently stable for use in reservoirs whose temperatures exceed 350 °C. Whereas none of the reservoir waters in which the polyaromatic sulfonates were tested possess such high temperatures, the field tests nevertheless showed that these com-

pounds can serve as conservative tracers to simultaneously tag injection wells in a variety of geothermal settings.

Acknowledgements

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