TESTING THE NAPHTHALENE SULFONATES AS GEOTHERMAL TRACERS 
AT DIXIE VALLEY, OHAAKI, AND AWIBENGKOK

Peter Rose¹, Dick Benoit², Sang Goo Lee³, Bagus Tandia⁴, and Phaedra Kilbourn¹

¹Energy and Geoscience Institute at the University of Utah
423 Wakara Way suite 300
Salt Lake City, Utah, 84108

²Oxbow Power Services
9790 Gateway Drive suite 220
Reno, Nevada 89511

³Contact Energy
Wairakei Power Station
State Highway 1, Taupo, New Zealand

⁴Unocal Geothermal of Indonesia, Ltd.
Sentral Senayan I Office Tower 11th Fl.
Jl. Asia Afrika No. 8, Jakarta 10270, Indonesia

ABSTRACT
The decay kinetics of the candidate tracer 1,3,6-naphthalene trisulfonate was studied under conditions that simulate a hydrothermal environment. It was shown to possess sufficient thermal stability to qualify for use in reservoirs as hot as 340°C. In a series of field tests at Dixie Valley, Nevada; Ohaaki, New Zealand; and Awibengkok, Indonesia, 1,3,6-naphthalene trisulfonate and the closely related 1,5-naphthalene disulfonate were successfully used to trace injection-production flow patterns. In addition to being environmentally benign, affordable and very thermally stable, these compounds were shown to have excellent detection limits of approximately 200 parts per trillion by standard HPLC and fluorescence detection methods.

INTRODUCTION
The xanthene dye fluorescein has been used extensively to trace fluid flow patterns in geothermal reservoirs. With the exception of rhodamine WT, which has been used only sparingly in low-temperature geothermal reservoirs (Gudmundsson et al., 1983; Rose and Adams, 1994), no other visible-fluorescent compounds have been shown to be sufficiently thermally stable to qualify for use as geothermal tracers.

The uv-fluorescent polyaromatic sulfonates are excellent candidates for geothermal tracing applications because they are environmentally benign, very detectable by fluorescence spectroscopy, affordable, and thermally stable. The first successful use of the polyaromatic sulfonates as geothermal tracers occurred in recent tracer tests at Dixie Valley (Rose et al., 1998). In one of these tests, the amino-substituted naphthalene disulfonate, 7-amino-1,3-naphthalene disulfonate (amino G), was shown to have a detection limit of approximately 500 parts per trillion and to possess reasonably good thermal stability. Tracer concentrations were observed to be well above the detection limit after approximately 250 days of exposure to geothermal fluids approaching 250°C. In a subsequent test, 1,3,6,8-pyrene tetralsulfonate was shown to have a detection limit of approximately 200 parts per trillion and to possess sufficient thermal stability for use in 250°C geothermal systems.

A sub-class of the polyaromatic sulfonates that has shown particular promise for geothermal tracing applications is the naphthalene sulfonates. Two compounds from this category, 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate, have been investigated in the laboratory and in the field and have been shown to be suitable for both low-temperature and high-temperature geothermal reservoirs (Rose et al., 1999). In this paper, we report the continued laboratory and field study of these candidate tracers. The application of the naphthalene sulfonates to monitor the movement of subterranean fluids in multiple injection wells has been patented by Unocal (Hutchins and Saunders, 1992).
DECAY KINETICS OF 1,3,6-NAPHTHALENE DISULFONATE

The decay kinetics of 1,3,6-naphthalene trisulfonate was determined under controlled laboratory conditions using autoclave batch reactors. Our experimental approach has been described elsewhere (Rose et al., 1999).

The thermal decay of 1,3,6-naphthalene trisulfonate can be modeled by the first-order differential equation:

\[-dC_n/dt = k_n \cdot C_n\]  \hspace{1cm} (1)

where \(C_n\) is the concentration of 1,3,6-naphthalene trisulfonate and \(k_n\) is the first-order rate constant. Solution of this equation results in the following relationship between \(C_n\) and \(t\):

\[\ln \left( \frac{C_n}{C_0} \right) = -k_n \cdot t\]  \hspace{1cm} (2)

where \(C_0\) is the initial concentration of 1,3,6-naphthalene trisulfonate. The temperature dependence of \(k_n\) can be described by the Arrhenius relationship:

\[k_n = A e^{-E_a/(RT)}\]  \hspace{1cm} (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:

\[\ln k_n = \ln A - \frac{E_a}{RT}\]  \hspace{1cm} (4)

Figure 1 shows a fairly linear relationship between \(\ln k_n\) and inverse temperature, indicating that the Arrhenius equation provides a reasonable means for expressing the temperature dependence of the decay rate constant.

The straight line in Figure 1 was determined by a linear least-squares fit to the data. Solving for the slope and intercept results in the following expression that can be used to determine the decay constant at any temperature between 310°C and 330°C:

\[\ln k_n = 39.3 - \frac{214,000 \, J/mol \cdot \frac{1}{T}}{R} \]  \hspace{1cm} (5)

TRACER TESTING AT DIXIE VALLEY

The Dixie Valley geothermal field, located in west-central Nevada, is perhaps the classical hydrothermal system located along a narrow fault zone (Figure 2). 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. For a review of conceptual, structural and numerical models of the Dixie Valley hydrothermal system see Benoit (1999).

Sibson (1977) and Chester and Logan (1986) developed a conceptual fault zone model consisting of a fault core and damage zone surrounded by relatively undeformed protolith (see also Caine et al., 1996). In any individual fault zone segment, the fault core and damage zone can be spatially heterogeneous, and either may be absent. Fault cores, which accommodate most of the fault displacement, typically consist of fine-grained gouge and cataclasite. Associated damage zones are typically faulted and fractured.

Fractures and faults in the damage zone oriented subparallel to the main fault increase the permeability in the plane of the fault (Forster and Evans, 1991). As Caine et al. (1996) suggest, permeability in the fault core may be limited by the fine grain size, whereas it is the hydraulic properties of faults and fractures in the damage zone which control permeability there.

The prevailing structural model for interpreting flow patterns within the Dixie Valley geothermal field is based upon a single range-front fault dipping 52°-54° to the SE with a roughly planar geometry to depths of 3 km (Benoit, 1995). According to this model, it is assumed that production is controlled primarily by fracture permeability associated with this range-front fault and its related secondary fractures or faults.
A recent study based primarily upon Bouguer gravity data suggests a more complex model with a steep-dipping range front fault that accommodates most of the topographic displacement and a series of steep-dipping piedmont faults that account for most of the displacement at depth within the reservoir (Blackwell et al., 1999). According to this model, the reservoir is primarily associated with the piedmont faults.

Most production wells produce up to 125 kg/sec from three to six individual fractures located between depths of 2500 and 3100 m (Hickman and Zoback, 1998). Injection is into three different environments (Benoit, 1992): an areally restricted basalt aquifer at a depth of 2225 m, the main fault zone at a depth of about 1860 m, and the deep fault zone between depths of 2700 and 2950 m.

The first tracer tests at the Dixie Valley, Nevada, geothermal reservoir were conducted in 1989 (Adams et al., 1989; Benoit, 1992). These tests were largely unsuccessful, however, due to poor tracer detectability and an underestimation of the length of time required for tracer breakthrough.

A series of tracer tests was conducted at Dixie Valley between 1996 and 1999 using fluorescein, 7-amino-1,3-naphthalene disulfonate (amino G), and 1,3,6,8-pyrene tetrapsulfonate (Rose et al., 1997; Rose, 1998; Rose et al., 1998). In addition, two tests using 1,5-naphthalene disulfonate and 1,3,6-naphthalene trisulfonate were initiated in 1998 and are reported here.

On 14 July, 1998, 100 kg of 1,5-naphthalene disulfonate (Konishi Chemical, Japan) was dissolved in approximately 400 liters of flashed reservoir water and injected over a period of about 15 minutes into well 41-18 (see Figure 2). This injector accepts fluids at a rate of approximately 40 kg/sec. Similarly, 100 kg of 1,3,6-naphthalene trisulfonate (Konishi Chemical, Japan) was mixed with approximately 300 liters of flashed reservoir water and injected over a period of 20 minutes into injector 65-18 (see Figure 2), which flows at a rate of approximately 65 kg/sec.

All of the producing wells in the field were subsequently monitored for the two naphthalene sulfonates over the subsequent 1.5 years.

The return curves for the candidate tracer 1,5-naphthalene disulfonate are plotted in Figure 3. These return curves reflect tracer production in the six wells in section 7 (see Figure 2) 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 trisulfonate are shown in Figure 4. Like the test that was associated with injector 41-18 (see Figure 2) 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 tagged injectors. 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 common 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 concentrations 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.

**TRACER TESTING AT OHAAKI**

The Ohaaki geothermal field is located 30 km northeast of Lake Taupo on either side of the Waikato River (see Figure 5). The geology at Ohaaki represents about 750,000 years of volcanic and sedimentary accumulation in a subsiding basin at the eastern margin of the Taupo Volcanic Zone.

The basement 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 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).

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.

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 Figure 5). Various production and monitoring wells were sampled and analyzed for tracer over several subsequent months.

**Figure 4.** 1,3,6-naphthalene trisulfonate returns observed from the 1998 tracer testing of injector 65-18 at the Dixie Valley geothermal reservoir.

**Figure 5.** Map of the southwest portion of the Ohaaki geothermal field showing the principal flow paths from the tagged injector BR40.
Shown in Figure 6 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 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 is flows away from the field.

TRACER TESTING AT AWIBENGKOK

The Awibengkok geothermal field is located in West Java, Indonesia, approximately 60 km south of Jakarta. The resource is liquid-dominated, containing relatively benign fluid with reservoir temperatures ranging from 221°C to 312°C. It is a highly fractured reservoir set in andesitic volcanic rocks. Within the reservoir, the matrix rocks are propylitically altered.

In the eastern part of the field where the naphthalene sulfonates tracers were injected (Figure 7), there are 19 production wells on three locations (Awi 1, 13 and 16). The total mass production rate of these wells averages 1390 kg/sec. There are seven injection wells in the area grouped on two locations (Awi 14 and 15) that accept approximately 1390 kg/sec of separated brine, which is about 50% of the total brine injected at Awibengkok.

The first tracer tests at Awibengkok were conducted in 1994 using fluorescein. These tests were successful in identifying injection wells that have good hydraulic connections with production wells (Murray et al., 1995). Because of the better thermal stability offered by 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.

On 6 November 1998, 150 kg of 1,5-naphthalene disulfonate and 150 kg of fluorescein were dissolved in approximately 2,400 liters of fresh water and injected over a period of about 6 minutes into Awi 15-2 which was accepting about 110 kg/sec of brine. This resulted in a final concentration of 3,600 ppm for each tracer. On 8 November 1998, 150 kg of 1,3,6-naphthalene trisulfonate was dissolved in approximately 1,500 liters of fresh water and injected over a period of about 5 minutes into Awi 14-2 which was accepting about 90 kg/sec of brine. This resulted in a final tracer concentration of 5,200 ppm. All production wells in the field were subsequently monitored for the three tracers for several months.

No 1,5-naphthalene disulfonate or fluorescein was ever detected in any of the production wells. However, 1,3,6-naphthalene trisulfonate was observed in two production wells, Awi 1-2 and 1-7. Shown in Figure 8 are the return curves for those two wells. The first arrival of the tracer was at Awi 1-7 after 20 days followed by Awi 1-2 after 32 days. The peak concentration reached 2.8 ppb at Awi 1-7 compared to 1.7 ppb at Awi 1-2. Both the arrival times and the peak concentrations correlate with the distance between producer and injector.

That returns of the 1,3,6-naphthalene trisulfonate injected at Awi 14-2 were observed in only two
producers, Awi 1-2 and 1-7, supports the existence of a semi-permeable barrier separating Awi 14-2 and the two production wells from the rest of the field (see Figure 7). This barrier was first proposed to explain pressure interference tests conducted prior to commercial operations (Murray et al., 1995). Geologic data subsequently obtained during drilling and surface reconnaissance also support the existence of this barrier. The tracer tests reported here, however, offer the most conclusive evidence to date.

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 which extends over the entire field while most eastern production wells 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.

CONCLUSIONS

The naphthalene sulfonates show excellent potential for use as tracers in geothermal reservoirs. In addition to being environmentally benign and very affordable, these fluorescent compounds have detection limits of approximately 200 parts per trillion.

A decay kinetics study in the laboratory indicates that the candidate tracer 1,3,6-naphthalene trisulfonate, like the closely related 1,5-naphthalene disulfonate, possesses excellent thermal stability and is suitable for use in reservoirs as hot as 340°C.

A tracer test at the Dixie Valley geothermal reservoir using both tracers confirms that water injected in two deep wells in section 18 flows towards the main production area in section 7. Similarities between the sets of return curves for each tracer indicate that injectate from these two injectors takes a similar flow path over much of the distance to the production wells.

A tracer test at the Ohaaki geothermal reservoir using 1,5-naphthalene disulfonate reveals that most of the water injected via well BR40 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 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 14-2, which was tagged with 1,3,6-naphthalene trisulfonate, is connected to two producers in the eastern portion of the reservoir.

ACKNOWLEDGEMENTS

We thank Oxbow Power Services, Contact Energy, and Unocal Geothermal of Indonesia for their participation in this project. The support of these companies in providing access to their reservoirs and in conducting the field tests has been essential for the successful testing of these candidate tracers. We also acknowledge the continued support of the Department of Energy (under contract number DE-HC07-90ID12929), without which this project could not have been accomplished. Such support does not constitute an endorsement by the U.S. Department of Energy of the views expressed in this publication.

REFERENCES


