The Thermal Stability of the Naphthalene Sulfonic and Naphthalene Disulfonic Acids under Geothermal Conditions: Experimental Results and a Field-Based Example

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ABSTRACT

The thermal stability of six naphthalene sulfonic acid tracers (2,6-NDS, 2,7-NDS, 1,5-NDS, 1,6-NDS, 1-NSA, 2-NSA) was investigated using a one-pass, continuous flow, fluid - rock interaction simulator. The pore fluid utilised was pH modified, low pressure separator brine from Nga Awa Purua power station at Rotokawa with 100 µg/kg of the six tracers added. The simulator contained crushed and clean fragments of greywacke sourced from well RK24. The temperature range investigated was 270°C – 390°C

Results show that 2,6 and 2,7-NDS remain stable to about 340°C while 1,5-NDS begins to degrade as early as 280°C. 1,6-NDS shows degradation beginning at 330°C. For the NSA, the concentration of 1-NSA increases until 330°C after which, it begins to degrade while 2-NSA concentration increases until 380°C. The results are interpreted using three reaction mechanisms: desulfonation, isomerisation and naphthalene pyrolysis.

A field-based example of tracer degradation is described from the Rotokawa geothermal field. A suite of NDS tracers was injected and returns were not found after a monitoring period of one year. Reanalysis, in light of the experimental results, showed the presence of 2-NSA which was not one of the original tracers injected.

These results provide field-based evidence of the thermal degradation of naphthalene sulfonic acid tracers and imply the use of tracer mixtures for use as geothermometers.

1. INTRODUCTION

The use of chemical tracers for the measurement of enthalpies and the decipherment of reservoir properties is a standard technology utilised widely in the geothermal industry. Tracers are used in well discharges to determine mass flows and enthalpies and in reservoir tracer re-injection tests used to determine subsurface properties and injection breakthrough behaviour.

For reservoir modelling and re-injection breakthrough, suitable tracers require certain properties. These include thermal stability, non-absorptivity, low detection limit, low natural background concentration, low cost, and low toxicity. Naturally occurring chemical tracers such as bromide are not suitable because of the large amounts of material that must be injected due to the relatively high detection limit. Radioactive tracers, including I^{131} and I^{125} have a suitably low detection limit, however, the half-lives of these isotopes are eight days and 60 days respectively, limiting their longer term usage (McCabe et al., 1998).

An alternative is the use of non-naturally occurring organic compounds. For example, fluorescein and rhodamine have been used for many years as tracers of fluid flow at ambient temperatures; however, these chemicals have limited thermal stability and are not suitable for use in high enthalpy geothermal systems (cf. Adams et al., 1992). One group of organic compounds that have proved to be suitable at geothermal conditions is the polyaromatic sulfonates (Rose et al., 2001, 2002). These include the naphthalene sulfonic acids (NSA), naphthalene disulfonic acids (NDS), naphthalene trisulfonic acids (NTS), and pyrene tetrasulfonic acid (PTS). These compounds are currently being used in tracer studies throughout the world and have become an industry standard.

Rose et al. (2001) conducted laboratory experiments to test the thermal stability of a selection of the polyaromatic sulfonates (2-NSA, 1,5-NDS, 2,7-NDS, 1,3,6-NTS, 1,3,6,8-PTS). These experiments used pH-buffered solutions containing the tracer compound sealed in quartz glass ampoules and heated to temperature in stainless steel autoclaves. Their results showed modest thermal decay of the 1,5-NDS and 1,3,6-NTS over a period of one week at 330°C while 1,3,6,8-PTS was almost thoroughly decomposed under the same conditions. No decay was found for 2-NSA or 2,7-NDS at 330°C. These two compounds were concluded to be the most thermally stable of those tested.

The above experiments provided valuable data on the thermal stability of the polyaromatic sulfonates allowing some guidelines to be implemented in their use. However, three questions arise that remain unanswered and have important implications to the usefulness of these compounds in high enthalpy geothermal environments:

a) What are the thermal stabilities of the more temperature-stable polyaromatic sulfonates?

b) What is the effect of mineral surfaces on the stability of the polyaromatic sulfonates?

c) What are the breakdown products of the polyaromatic sulfonates and can they be used as tracers themselves?

In our study, laboratory simulations are being performed using a one-pass, continuous flow, fluid - rock interaction simulator to measure the thermal stability of six naphthalene sulfonic acids (2,6-NDS, 2,7-NDS, 1,5-NDS, 1,6-NDS, 1-NSA, 2-NSA) in the presence of rock material between the temperature range of 270 – 390°C.

2. METHOD

Figure 1 shows a schematic diagram of the experimental apparatus. Continuous flow is achieved by a computer-controlled double-piston pump with a flow rate range of

0.001 – 15 ml/min. The pump injects distilled water into a titanium separator containing a movable diaphragm. The experimental fluid is located above the diaphragm. As the pump injects distilled water below the diaphragm, this forces the experimental fluid through the pressure vessel. This set-up allows corrosive and/or saline fluids to be used without damage to the pump. The rock material is contained in a titanium pressure vessel that is externally-heated in an insulated oven. Temperature is monitored by a thermocouple inserted in the top of the pressure vessel. The pore fluid pressure is maintained by a digitally-controlled back pressure regulator. The exit valve and effluent path are heated to approximately 160°C using heating tape to minimise silica precipitation. All components wetted by the pore fluid are composed of titanium except for the Teflon diaphragm in the back pressure regulator. The sample was collected in a standard luer lock disposable syringe. A computer is connected to the equipment and regularly records pressure, temperature and pumped volume.

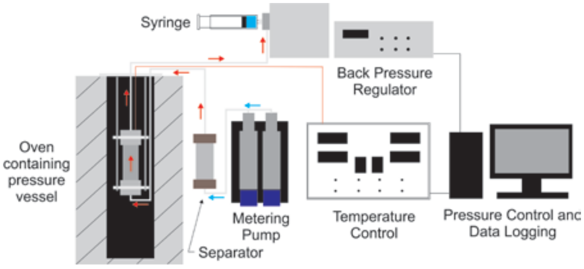

Figure 1: Schematic diagram of the one-pass, continuous flow, fluid-rock interaction simulator. Arrows show the flow path of the fluid (blue for distilled water, red for the pore fluid).

The rock used was a cuttings composite of greywacke from well RK24 (2178 m – 2575 m CHF) at Rotokawa. The cuttings were crushed and sieved, and cleaned with distilled water for one hour in an ultrasonic bath to remove highly reactive fine particles. The pressure vessel (15 cm^3) was filled with approximately 25 g of greywacke fragments of 1-2 mm in diameter. The pore fluid used was pH-modified (pH 6.1), low pressure separator brine from Nga Awa Purua power station located in the Rotokawa geothermal field. The brine was spiked with the six naphthalene sulfonic acid tracers to attain a concentration of 100 μg/kg.

Fluid flow was commenced at room temperature and 14 bar pressure. After three days, to remove air from the pressure vessel, the temperature and pressure were increased to 270°C and 60 bar. Four samples were collected at each subsequent temperature using three different flow rates (2 x 1.0 ml/hr, 1 x 0.5 ml/hr, 1 x 0.1 ml/hr). The temperature was increased incrementally after each set of four samples to a final temperature and pressure of 390°C and 250 bar. For all temperatures, experimental pressure was maintained above saturated water vapour pressure to avoid boiling. Samples for tracer analysis were untreated until analysis.

Naphthalene sulfonic acids were analysed by high performance liquid chromatography (HPLC) with a Shimadzu Prominence HPLC using fluorescence detection. The excitation wavelength was 222 nm and the emission wavelength was 338 nm. The mobile phase was 5 mM tetrabutyl ammonium phosphate in 25% methanol/water. Eluent flow was isocratic. Detection limits were 0.04 and 0.4 μg/kg for NDS and NSA, respectively. Samples were pre-filtered before analysis. Figure 2 shows the HPLC chromatogram results for the six naphthalene sulfonic acids in the unreacted starting solution.

3. EXPERIMENTAL RESULTS

Figure 3 shows the normalised fluorescence versus temperature results at the three different flow rates for the four NDS and two NSA. The six tracers respond to temperature as follows: 2,6 and 2,7-NDS are thermally stable until approximately 340°C above which there is noticeable degradation at 0.5 and 0.1 ml/hr and this rate increases with temperature; 1,5-NDS begins to degrade at a temperature as low as 280°C and there is complete loss of 1,5-NDS by 370°C; 1,6-NDS shows degradation beginning at 330°C and increasing with temperature; 1-NSA begins to increase in concentration at 310°C (at 0.5 and 0.1 ml/hr) and reaches peak concentration between 330 - 350°C, depending on the flow rate, after which it begins to decay; and 2-NSA shows a continual increase with temperature reaching about eight times its original emission and begins to degrade at 370°C.

The isomers of the NDS and NSA are separated chromatographically because of the differing positions of the sulfonate groups (-SO_3) on the naphthalene backbone (the naphthalene moiety); however, it is the naphthalene moiety that is fluorescing. The differing peak heights in the chromatogram (Fig. 2) are due to differing intensities of the fluorescence at 338 nm for each isomer. The intensities are different because the sulfonate groups interact with the electrons in the naphthalene moiety that are excited to cause the fluorescence. The different positions result in different effects on the fluorescing electrons and hence differing response to excitation.

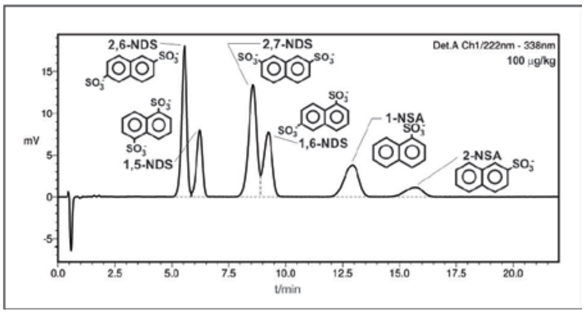

Figure 2: HPLC chromatogram showing the fluorescence emission at 338 nm for the four NDS isomers and two NSA isomers.

As the naphthalene moiety is the origin of the fluorescence emission, total fluorescence is a measure of the total concentration of this moiety. Figure 4 shows the total fluorescence normalised to the total fluorescence of the starting solution. At 340°C there is a significant decrease in total fluorescence at a flow rate of 0.1 ml/hr while at 1.0 ml/hr total fluorescence begins to drop at about 360°C. Decreases in total fluorescence are an indication of degradation of the naphthalene moiety itself.

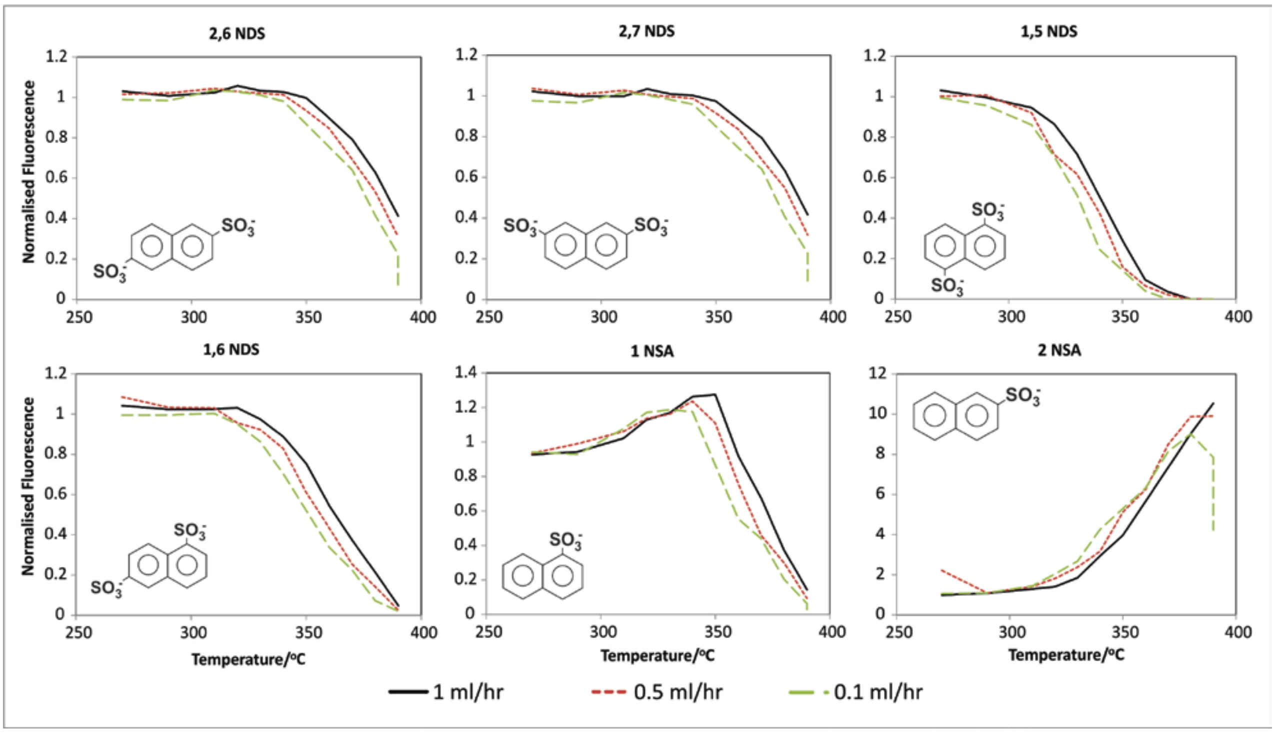

Figure 3: Normalised fluorescence of six naphthalene sulfonic acids versus temperature at three different flow rates. Fluorescence was normalised using peak response at 25°C. Light horizontal line represents no change in concentration.

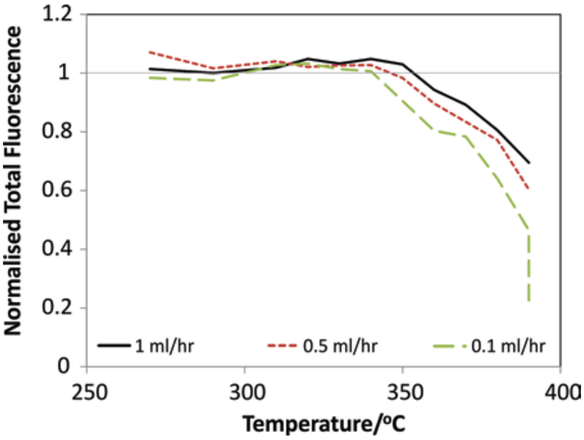

Figure 4: Normalised total fluorescence versus temperature at three flow rates. Peak response was normalised using total fluorescence at 25°C. Light horizontal line represents no change in total fluorescence.

4. DISCUSSION

4.1 Experimental Results

According to the HPLC results there are no new peaks found, at least until 22 minutes of the chromatogram (Fig. 2). This indicates that there are three possible mechanisms occurring to explain the changes in the concentration of the four NDS and two NSA. These are: desulfonation (the loss of one or more sulfonate groups); isomerisation (the switching of the sulfonate group position); and napthalene pyrolysis (the breakdown of the napthalene moiety).

Figure 5 depicts the possible reactions for single stage desulfonation of the four NDS isomers. Both 2,6 and 2,7-NDS desulfonate to form 2-NSA due to the two-fold rotation symmetry in 2,6-NDS and a mirror plane in 2,7-NDS. 1,5-NDS also has a two-fold rotation symmetry and desulfonates to 1-NSA while 1,6-NDS has no symmetry axis so can desulfonate to either 1-NSA or 2-NSA.

Figure 6 shows the isomerisation of 1-NSA to 2-NSA. In this case the position of the sulfonate switches position to form a more stable molecule.

The third possible mechanism is the pyrolysis of the napthalene moiety to reactions products that are unknown but are assumed to be non-fluorescent.

The normalised fluorscence vs temperature results can be interpreted based on the above mechanisms. Both 2,6 and 2,7-NDS do not show any increase or decrease in concentration until they begin to breakdown at around 330°C (Fig. 3). This suggests that no isomerisation was occurring between the 6 and 7th position on the naphthalene moiety. For 1,5-NDS, degradation begins at lower temperature by desulfonation as reflected in the increase in 1-NSA concentration while for 1,6-NDS, which can desulfonate to form either 1-NSA or 2-NSA, desulfonation appears to be occurring to form both of these molecules. The concurrent response of 1-NSA and 2-NSA (note differing scales) shows that there is no evidence for isomerisation of 1-NSA to form 2-NSA or vice versa. It is evident from the data that 2-NSA is the most thermally stable of the six sulfonic acids. The reason for this stability is unknown but could be investigated using *ab initio* calculations of molecular stability.

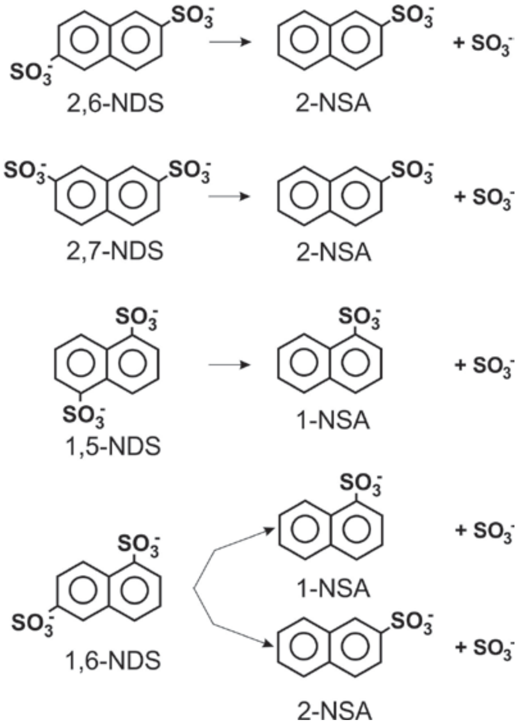

Figure 5: Single step desulfonation reactions for the four NDS isomers.

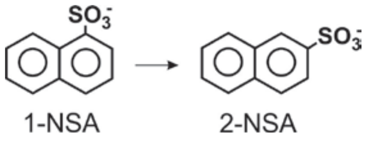

Figure 6: Isomerisation reaction forming 2-NSA from 1-NSA.

The preliminary implications of our results indicate that for a system dosed with either 2,6 or 2,7-NDS, tracer returns should show no change in isomer below about 330^{o}C. Above this temperature, 2-NSA would be the only isomer returned (Fig. 5). Injection of 1,5-NDS is not recommended for systems above about 270^{o}C but if it were injected into such a system one would expect 1-NSA (270 – 330^{o}C) and no returns above 330^{o}C assuming no isomerisation of 1-NSA to 2-NSA (Fig. 6). Dosing with 1,6-NDS would result in a mixture of 1-NSA and 2-NSA until about 340^{o}C after which only 2-NSA would be found. Above 350^{o}C only 2-NSA would be expected for any tracer injection and above 380^{o}C no NDS or NSA tracer returns would be found. Note that this does not preclude the appearance of as yet unknown fluorescent breakdown products above 380^{o}C.

All the above interpretations are speculative because the catalytic effects of mineral surfaces have not been investigated so far in our study. The experiment described used greywacke as the rock material and it is uncertain as to whether differing proportions of rock-forming minerals would change the kinetics of the breakdown due to sorption effects on the sulfonic acids. This is currently under investigation. Also, the surface of the titanium reaction cell may provide a catalytic effect so in order to properly investigate the fluid phase degradation reactions, experiments should be conducted in gold-lined cells. This is also planned.

In our experiment, the residence time of the fluid is short (estimated to be between 1 and 10 hours depending on the flow rate). In a natural system, the residence time would be much longer and thus any degradation found in the experiment should be expected in the natural system. Figure 3 shows degradation at three differing flow rates and hence residence times; however, the response curves are very similar. The vertical distance between the curves at any one temperature shows the effect of residence time. This effect is most evident in the degradation of 1,6-NDS above 340^{o}C and in 2-NSA above 380^{o}C. The fact remains that temperature is the most important parameter determining isomer stability due to the exponential dependence of the degradation rate on temperature.

4.2 Tracer Injection at Rotokawa

In 2011, about one year following the commissioning of the 140 MW triple flash Nga Awa Purua power station, Mighty River Power Ltd conducted a reservoir tracer injection test as part of its comprehensive best-practices reservoir management program. The purpose of the test was to understand the dynamics of fluid movement within the Rotokawa geothermal reservoir in response to the increased production fluid take.

The same four NDS tracers discussed herein (1,5-NDS, 1,6-NDS, 2,6-NDS, 2,7-NDS) were injected into dedicated re-injection wells, and production fluids were subsequently monitored for returns of the tracer compounds for at least one year post-injection. The selection of the NDS tracers was made on the basis of their successful application at other geothermal fields around the world (e.g. Ohaaki, New Zealand; Negros, Philippines; Awibengkok, Indonesia; and Dixie Valley, USA) and on the assumption that these compounds would be stable at reservoir temperatures (Gunderson et al., 2002; Maturgo et al., 2010; Rose, et al., 2001). However, it should be noted that Rotokawa is among one of the hottest geothermal reservoirs in production anywhere. Measured well temperatures in some areas of the current injection field are as high as 337°C.

During the entire monitoring period of one year, no detectable NDS tracers were observed from any of the monitored production wells. Other reservoir monitoring data, including production fluid geochemistry, tracer flow test mass-flow and enthalpy determinations, and regular down-hole surveys suggested that some production wells may be experiencing chemical breakthrough from injection, but with no measurable impact to reservoir enthalpies. To-date, production from the Rotokawa reservoir to both the 34 MW Rotokawa A binary plant and the 140 MW Nga Awa Purua triple flash power station has continued with >98% plant availability, and on-going reservoir monitoring has not shown any thermal degradation of production wells resulting from injection (no thermal breakthrough).

Following the initial results of the laboratory experiments, which demonstrate that some of the NDS compounds decompose at the temperatures of the reservoir, Mighty River Power began a program of re-analysing the reservoir tracer samples looking for the presence of 1-NSA and 2-NSA. It is important to note that no 1-NSA or 2-NSA compounds were ever injected in Rotokawa as part of any prior reservoir tracer test. If these compounds were detected, their presence at Rotokawa could only have come from the thermal decomposition of the injected NDS tracers. This re-analysis program is currently underway, and initial results have confirmed the presence of 2-NSA in wells consistent with the indications of very minor injection fluid chemical breakthrough based on geochemistry monitoring. Tracer first arrivals were detected on the order of 1.5-3 months post-injection. When normalised to production and injection rate data, these results demonstrate injection fluid contributions of less than <0.5%.

5. CONCLUSIONS

A laboratory simulation of the interaction between re-injection brine containing six naphthalene sulfonic acid tracers (2,6-NDS, 2,7-NDS, 1,5-NDS, 1,6-NDS, 1-NSA, 2-NSA) with greywacke sourced from RK24 at Rotokawa have been conducted. This experiment investigated the thermal stability of the NDS and NSA between 270 and 390°C in the presence of rock material. The results show the following:

a) 2,6 and 2,7-NDS are thermally stable until approximately 340°C above which there is noticeable degradation;

b) 1,5-NDS begins to degrade at a temperature as low as 280°C and there is complete loss of 1,5-NDS by 370°C;

c) 1,6-NDS shows degradation beginning at 330°C;

d) 1-NSA begins to increase in concentration at 310°C and reaches peak concentration between 330 - 350°C, depending on the flow rate;

e) 2-NSA shows a continual increase in temperature reaching about eight times its original emission at 370°C after which it begins to rapidly degrade.

Total fluorescence, reflecting the total concentration of the naphthalene moiety, begins to decrease at 340°C indicating the commencement of the degradation of the naphthalene backbone itself.

The results are interpreted according to three reactions mechanisms: desulfonation of the NDS; isomerisation of the NSA; and thermal pyrolysis of the naphthalene moiety. Preliminary results allow predictions of tracer returns based on system temperature; however, the results are speculative at this time due the unknown effects of rock properties.

A field example is described were tracer injection was undertaken at the Rotokawa geothermal field using a mixture of NDS. At Rotokawa measured temperatures have reached as high as 337°C in areas of current re-injection and therefore thermal degradation of any injected NDS should be expected. After one year of monitoring, no detectable NDS returns were found. Due to the results of our experiments, samples were re-analysed for the NSA (which have never been used at Rotokawa). The re-analyses have confirmed the presence of 2-NSA on the order of 1.5 - 3 months post-injection consistent with the degradation of the NDS originally injected. These results provide field-based evidence of the thermal degradation of naphthalene sulfonic acid tracers and suggest the use of tracer mixtures for use as geothermometers.

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