EXPERIMENTAL EXAMINATION OF ADSORPTION OF THE NAPHTHALENE SULFONATES UNDER GEOTHERMAL CONDITIONS

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ABSTRACT

Naphthalene sulfonates (NDS and NSA) are widely used in the geothermal industry as reservoir tracers. However, there is little experimental data on the adsorption of these compounds under geothermal conditions. Knowledge of the adsorption effect is essential to correctly interpret tracer test results. In this preliminary study, we have investigated the possibility of tracer adsorption onto rock surfaces under geothermal conditions.

Six tracers: 2-naphthalene sulfonate, 1-naphthalene sulfonate, 1,5-naphthalene disulfonate, 1,6- naphthalene disulfonate, 2,6- naphthalene disulfonate and 2,7-naphthalene disulfonate were used. A continuous flow-through apparatus was used in which a small amount of the six tracer mixture was injected into the flow of geothermal brine. The pressure vessel was filled with either quartz or greywacke material. The experiments were conducted at three temperatures: 22°C, 100°C and 250°C. Samples were collected every hour after injection. Samples were analysed for tracers by high performance liquid chromatography (HPLC) using fluorescence detection.

The results show the following:

- no observable difference in breakthrough time for different tracers;
- decrease in breakthrough time with increased temperature;
- possible weak adsorption of tracers in the greywacke experiments;
- decrease of integrated tracer concentration at 250°C suggests the onset of thermal decay.

1. INTRODUCTION

The efficiency of geothermal energy production is improved by evaluating geothermal reservoir properties allowing better planning of wells. Tracer tests are the best tool to provide data on the flow of fluid from re-injection to production wells. The examination of tracer returns reveals reservoir properties, such as permeability, providing important input data to numerical models.

The naphthalene sulfonic acids are one group of compounds that are used as tracers in the geothermal industry. Suitable tracers must meet basic criteria, including thermal stability, low detection limit, low natural background concentration, non-absorptivity, non-toxicity and low-cost. The naphthalene sulfonic acids appear to satisfy these criteria, however, a better understanding of their thermal stability and adsorptivity is needed.

The different isomers of naphthalene sulfonates can be used simultaneously during one test. They can be easily differentiated and detected by high performance liquid chromatography (HPLC). Numerous tests have been conducted worldwide, including in New Zealand (e.g. Addison et al., 2015; Buscarlet et al., 2015).

The thermal stability of aromatic compounds used for geothermal tracers has been the subject of research during the last two decades. This includes: unsubstituted and substituted benzene sulfonic acids (Adams, 1992); naphthalene sulfonic acids (NSA); naphthalene disulfonic acids (NDS); and naphthalene trisulfonic acids (NTS) (Rose et al., 1999; Rose et al., 2001; Mountain and Winick, 2012). However, few studies on adsorption on naphthalene sulfonates at geothermal conditions have been reported

The possibility of adsorption of tracers on the surface of minerals can have an influence on the interpretation of tracer test results. For example, 1,5-NDS and 1,6-NDS were used as conservative tracers in a sorption test by Peter Rose (2014). Some work has been done on transport behavior of other soluble organic compounds like alkylphenols (Licha and Sauter, 2002a). Nevertheless, it is unclear if previously obtained data on soluble organic substances or ionic compounds adsorption will apply to naphthalene sulfonates.

Adsorption of organic molecules is mainly controlled by surface area, surface properties of the adsorbent, solubility of the organic molecule in water, salinity, pH, co-solvents and temperature (Licha and Sauter, 2002b). Generally, adsorption effects decrease with temperature increase. Surface area increase will increase adsorption. Change of pH can change surface charge. Solvent – solute competition is significant in underground systems. Silicates and oxide rock constituents have abundant hydroxyl sites, which strongly attract water. Adsorption of an organic molecule would require replacement of the water molecule to exchange with it.

Adsorption is complex and requires extensive controlled experimental work to decipher. This paper presents the results of an experimental study that explores the multifaceted problem of adsorption of naphthalene sulfonates under geothermal conditions.

It is important to look at the tracer's adsorption processes at elevated temperatures in context of thermal stability of tracers. Additional experiments, to examine the pH dependence of the thermal stability of 1,5-NDS and 2-NSA at higher temperatures, have been done using sealed glass ampoules (Sajkowski et al., 2017). Sets of ampoules with varying pH value and with ionic strengths (I) of 0.001 and 0.05 M were exposed for 40 hours to 200°C and 300°C. Results show that the stability of 1,5-NDS and 2-NSA increases, with increasing pH and the ionic strength. 1-NSA appears as a breakdown product at 300°C, pH = 5.2 - 7.2. Its increase in concentration is independent of ionic strength.

2. METHOD

2.1 Analytical method

The naphthalene sulfonic acids are analysed using HPLC by fluorescence detection (Shimadzu Prominence RF-20Axs). To protect the column from particulates, all samples are filtered through a 0.2 µm Minisart® NML surfactant-free cellulose acetate filters. The mobile phase is 5 mM tetrabutylammonium phosphate (Sigma-Aldrich) in 29:71% methanol:water. Methanol is HPLC grade from ThermoFisher Scientific. Ultrapure water with a conductivity of 0.055 µS cm^{-1} (18.2 MΩ cm^{-1}) is produced by Arium® pro-Ultrapure water system. Detection limits are 0.04 µg kg^{-1} for NDS and 0.4 µg kg^{-1} for NSA. The column is kept at 35°C. Sample injection volume is 50 µL and a 50 µL ultrapure water blank is run between each standard/sample.

2.2 Experimental method - adsorption

Four preliminary experiments were conducted. The experimental apparatus is shown in Figure 1. The pressure vessel containing the rock material has an internal volume of 19.3 cm^3. Three experiments used 22 g of crushed greywacke (180-220 um) and one experiment used 21.6 g of crushed quartz (180-220 um). The pressure vessel was exposed to 25°C, 100°C and 250°C. The metering pump creates the flow of geothermal brine (Table 1) through the pressure vessel at a rate of 2 ml hr^{-1}. The rock materials were saturated with geothermal brine within the pressure vessel for 24 hours prior to each experiment. A six-tracer mix (0.025 ml of 200 – 400 ppb; 2,6-NDS, 2,7-NDS, 1,5-NDS, 1,6-NDS, 1-NSA and 2-NSA) was injected to the system through an injection valve (Fig. 1). Samples were collected every hour for 20 hours from the collection syringe.

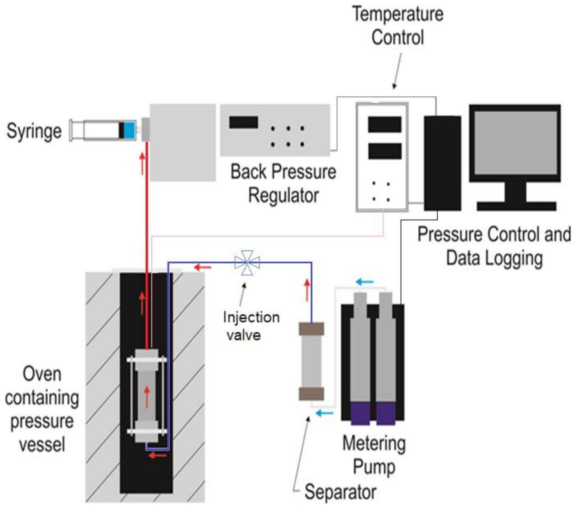

Figure 1. Experimental setup.

Table 1. Composition of geothermal fluid used (mg kg^{-1}).

Na	681	**SiO_2**	340
K	70	**B**	45
Ca	30	**Li**	4
Mg	4	**Al**	2

The fluid was measured for tracer content before each experiment. Due to the previous field tracer studies, the brine contained several tracers with up to 1.5 ppb of 2,7-NDS. These results were subtracted from the experimental results.

2.3 Experimental method - thermal stability

Eight sets of tubes were used representing different pH values. Each set includes the two ionic strengths (0.001 M, 0.05 M). The solutions were prepared using ultrapure water. HCl and NaOH were used to fix pH and NaCl to adjust ionic strength. To each tube, 1,5-NDS and 2-NSA were added to obtain a concentration of 0.02 mg kg^{-1} and 0.01 mg kg^{-1} respectively. The tubes were heated to 200°C and 300°C for 10, 20, 40, 60 and 166 hours (Fig. 2). Details of the method are explained in the other proceedings paper (Sajkowski et al., 2017).

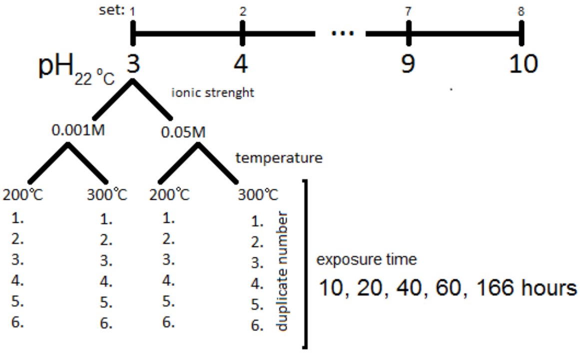

Figure 2. Experimental protocol.

3. RESULTS

3.1 Results - adsorption

Figure 3 shows the concentration of each tracer after injection versus time. Figure 5 shows the cumulative concentration of injected tracers versus time.

The experiment using quartz at room temperature was design to provide a comparison with the multi-mineralic rock (Fig 3A). The tracers arrived 6 hours after injection and by hour 16 after injection all tracers were returned. The results show that the injected tracers returned over the same time period and hence there is no evidence of tracer-dependent adsorption

The experiment using greywacke at room temperature shows comparable results to quartz (Fig 3B). The first detectable tracers appeared after six hours similar to the quartz and fell below detection limit by hour 16 after injection. The amplitude of the tracer returns is higher as twice the amount of tracers was injected in the greywacke experiments in order to increase the resolution. At 100°C and 250°C the first tracer returns arrived after 4.5 and 4 hours, respectively (Fig 3C and D). The last detectable tracer returns were found after nine hours at 250°C and eleven hours at 100°C.

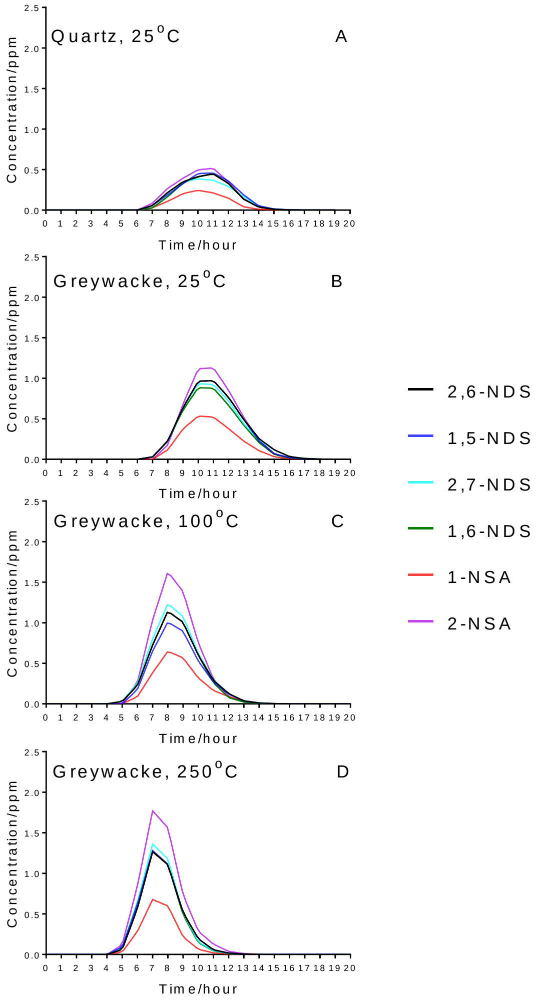

Figure 3. Tracer concentrations (mg kg^{-1}) as measured every hour after injection. A. 25°C, quartz, B. 25°C, greywacke, C. 100°C, greywacke, D. 250°C, greywacke.

3.2 Results - thermal stability

Figure 4 shows the rate constant k(day^{-1}) versus experimental pH for ionic strength 0.05 and 0.001 M at 200°C and 300°C. At 200°C, I = 0.05 M, k decreases from pH = 3 down pH = 6 after which k increases with increasing at pH = 8. At 200°C, I < 0.001 M, the relationship between k and pH is less conclusive, however, below pH = 4 the rate is clearly faster than at higher pH values. At 300°C, I = 0.05 M, the rate constant decreases from at pH = 4 down at pH = 8. At 300°C, I < 0.001 M, k decreases with increase of pH.

4. DISCUSSION

The physical processes controlling the adsorption will depend on the materials involved. The greywacke used in the experiment is composed of quartz, plagioclase, albite, K-feldspar, chlorite, illite with trace amounts of calcite, epidote, oxide and sulfide (Table 2). Different minerals have different surface properties.

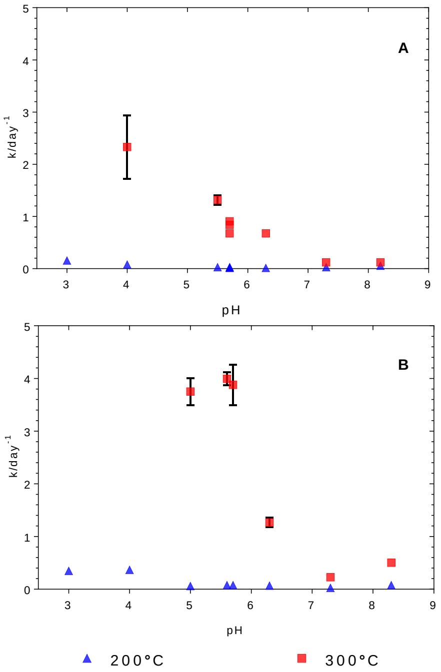

Figure 4: Rate constant k/day^{-1} versus experimental pH for the decay of 1,5-NDS at 200°C and 300°C for (A) I = 0.05 M and (B) I = 0.001 M.

Tabele 2. Mineral composition of the greywacke used.

Minerals	Abundance vol%
Quartz	20
Plagioclase	5
Albite	5
K-Feldspar	5
Calcite	<5
Epidote	<5
Oxide -sulfide	<5
Chlorite	10
Illite	40

Within each individual experiment, no detectable differences were detected between the return times of each tracer. This suggests that all tracers interact with the rock to a similar degree (Fig. 3). Tracer breakthrough time decreases with increasing temperature (Fig. 5). Cumulative tracer returns curves have half-widths that narrow with increased temperature. This can be explained by changes in water density and perhaps increased diffusivity with increased temperature.

Peak area is similar for 25°C and 100°C but is noticeably smaller for 250°C. This can be explained by the onset of thermal breakdown of the tracers at this higher temperature. The slight asymmetry in the return curves with the greywacke experiment suggest a limited rock-tracer interaction that is not observed with quartz alone.

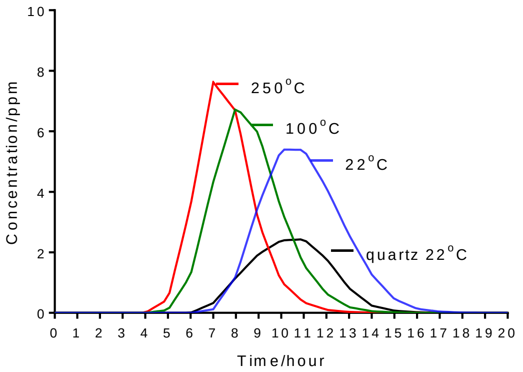

Figure 5: Cumulative tracer concentration versus time after injection.

Future experiments are planned where a conservative tracer will be added to the injection mixture to test possible weak interactions between NDS and the rock. In addition, decreasing the average grain size of the rock particles will increase the available surface area and thus adsorptive capacity of the rock.

The solution pH influences the stability of the tracers and is also expected to also influence adsorption processes. Future experiments will test pH influence on adsorption. The mechanism of pH influence on naphthalene sulfonate thermal stability is described in Sajkowski et al. (2017).

5. CONCLUSIONS

An experimental study of 2,6-NDS, 2,7-NDS, 1,5-NDS, 1,6-NDS, 1-NSA and 2-NSA adsorption in contact with greywacke and quartz, at 25°C, 100°C and 250°C and pH dependence on stability of 1,5-NDS and 2-NSA have been conducted.

The results show the following:

- no observable difference in breakthrough time for different tracers;
- decrease in breakthrough time with increased temperature;
- possible weak adsorption of tracers in the greywacke experiments;
- decrease of integrated tracer concentration at 250°C suggests the onset of thermal decay

Previous thermal stability work found that

- 1,5-NDS thermal stability depends on the composition of the solution;
- 1,5-NDS is not stable at 200°C - 300°C, pH = 3.0 – 8.3, I = 0.001 M, 0.05 M;
- 1,5-NDS breakdown rate increases with decreasing pH and decreasing ionic strength;
- 2-NSA is stable at 200°C pH: 3.0 – 6.3, I = 0.05 M;
- 2-NSA is not stable at 300°C pH 3.0 – 4.2 and 6.3 – 8.2, I = 0.05 M.

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REFERENCES

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

Mountain, B.W., Winick, J.A.: The thermal stability of the naphthalene sulfonic and naphthalene disulfonic acids under geothermal conditions: Experimental results and a field-based example. *Proc. New Zealand Geothermal Workshop*, Auckland, New Zealand 19-21 November (2012).

Licha T. and Sauter M.: Use of short chained alkylphenols (SCAP) in analysis of transport behavior of oil contaminated groundwater. Journal of Agricultural and Marine Sciences, 7(2), 29-38. (2002a).

Licha T. and Sauter M.: Short-chained alkylphenols (SCAP) as reactive tracers. DECHEMA, European Conference on Natural Attenuation, Heidelberg, 49-51. (2002b).

Rose, P.E., Harris J., Pruess K., Xu T., Mella M., Leecaster K., Fayer S., Olsen S., Norman R., Petty S.,: Tracer methods for characterizing fracture creation in engineered geothermal systems. Department of Energy, USA, Award Number DE-GO18193 (2014).

Rose, P.E., Benoit, D., Kilbourn, P.: The application of the polyaromatic sulfonates as tracers in geothermal reservoirs. *Geothermics* 30, 617 – 640. (2001).

Rose, P. E., Goranson, C., Salls, D., Kilbourn, P.: Tracer testing at Steamboat Hills, Nevada, using fluorescein and 1,5-naphthalene disulfonate. *Proc. 24th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA.* (1999).

Sajkowski, L., Mountain, B.W., Terry M. Seward.: Experimental determination of the thermal stability of the organic tracers 1,5-nds and 2-nsa under geothermal. *Proc. New Zealand Geothermal Workshop*, Rotorua, New Zealand 21-25 November (2017).