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The Use of Amino G as a Thermally Reactive Tracer for Geothermal Applications

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ABSTRACT

A thermally reactive tracer can be used in combination with a conservative tracer within a geothermal reservoir to determine the effective temperature along an injection-production pathway. The thermal decay kinetics of the uv-fluorescent optical brightener 7-amino-1,3-naphthalenedisulfonate (Amino G) was measured under simulated geothermal conditions using a high-temperature laboratory batch reactor. The decay product was shown to be a fluorescent, water-soluble compound (2-naphthol), possessing greater thermal stability than the parent compound. Amino G and its daughter product thus represent a new tracer pair for use in geothermal reservoirs, suggesting that other amino-substituted or even hydroxy-substituted naphthalene sulfonates might be used as geothermal tracers. A tracer test demonstrated the successful use of Amino G at the Dixie Valley geothermal field.

1. INTRODUCTION

The uv-fluorescent polyaromatic sulfonates have proven to be excellent tracers in high temperature geothermal reservoirs 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 involved 1,3,6,8-pyrene tetrasulfonate at the Dixie Valley, Nevada geothermal system (Rose *et al.*, 1998).

The naphthalene sulfonates, a subset of the polyaromatic sulfonates, have been used extensively as tanning agents, cement dispersants, and intermediates in the synthesis of dyes. Studies on surfactant toxicity indicate that the naphthalene sulfonates are neither carcinogenic nor mutagenic (Greim *et al*., 1994). We have studied eight naphthalene sulfonates and one pyrene sulfonate in the laboratory and have found them to be suitable for use as conservative tracers in high temperature (>300^oC) reservoirs (Rose *et al.,* 2001). Field tests in a number of geothermal reservoirs with temperatures sometimes exceeding 300^oC further confirm the thermal stability of these chemicals (Rose *et al.,* 2001).

Amino G is the common name for an amino-substituted naphthalene sulfonate (7-amino-1,3-naphthalenedisulfonic acid monopotassium salt) that is used in the detergent industry as an optical brightener. It is reasonably nontoxic, environmentally benign, affordable in bulk quantities and very detectable by fluorescence spectroscopy. In this paper we present data on the thermal stability of Amino G and its thermal decay product, 2-naphthol. We then present results of a tracer test at the Dixie Valley, Nevada geothermal field using Amino G that further confirms the utility of the Amino G/2-naphthol pair for use as geothermal tracers. In reservoirs wherein the temperature is below the threshold for thermal decomposition, Amino G can serve as a conservative tracer. In hotter reservoirs, the relative concentrations of Amino G and 2-Naphthol can be used to calculate the effective temperature along the injection/production pathway. Some structurally related amino- and hydroxy-substituted naphthalene sulfonates that are also commercially available in bulk include 2-amino-5-hydroxynaphthalene-1,7-disulfonate; 6-amino-1,3-naphthalene disulfonate; 2-naphthylamine-4,6,8-trisulfonate; and 4,5-dihydroxy-2,7-naphthalene disulfonate (personal communication Victor Leung, Yick-Vic Chemicals and Pharmaceuticals, 2013). These compounds are being investigated as candidates for use as either conservative or thermally reactive geothermal tracers, depending on the target-reservoir temperature and the thermal decomposition product(s) at that temperature.

2. THERMAL DECAY KINETICS OF AMINO G

The decay kinetics of Amino G was studied using autoclave batch reactors under controlled conditions designed to simulate a geothermal environment. Amino G was dissolved in buffered aqueous solutions at target concentrations of 25 ppm by weight and adjusted to a room-temperature pH of 6.8. The buffer consisted of 0.747 gm/l of KH_2PO_4 and 0.403 gm/l of Na_2HPO_4.

Eighteen-ml aliquots of the buffered tracer solution were transferred to 30-ml quartz ampules and purged with argon to remove elemental oxygen. 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 hours, whereas the cool-down time was about 4 hours. The pressure inside the autoclave was the pressure of steam under saturated conditions at the target temperature. The control sample was stored at 2^oC in the dark before being analyzed with the reacted samples.

Amino G decays according to the following pseudo-first-order expression:

$$-dC_{AG} \big/ dt = k_{AG} \cdot C_{AG} \qquad (1)$$

where C_{AG} is the concentration of Amino G and k_{AG} is the pseudo-first-order rate constant. Solution of this equation results in the following relationship between C_{AG} and t:

$$\ln\left(\frac{C_{AG}}{C^0_{AG}}\right) = -k_{AG} \cdot t \tag{2}$$

where C^0_{AG} is the initial concentration of Amino G. The temperature dependence of k_{AG} can be described by the Arrhenius relationship:

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

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 expression 3 results in:

$$\ln k_{AG} = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \tag{4}$$

A plot of ln k_{AG} vs. 1/T for the thermally reactive tracer Amino G is shown in Figure 1. The data show excellent fit to expression 4, indicating that the Arrhenius equation is a good model for representing the temperature dependence of the decay rate constant between 240°C and 260°C.

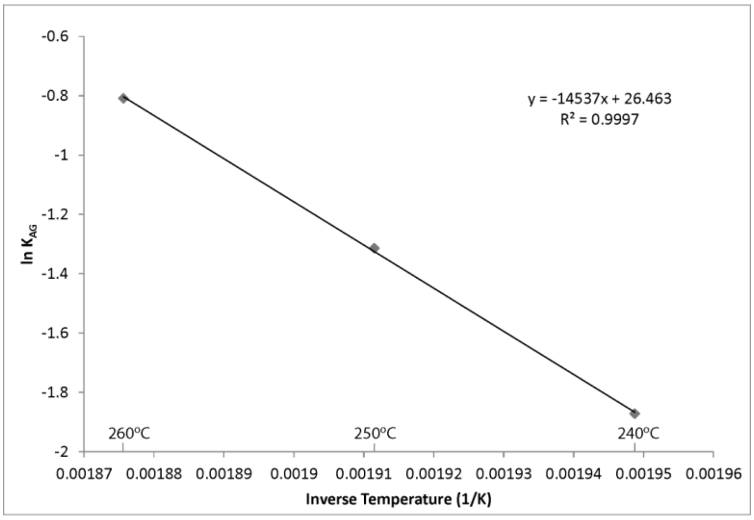

Figure 1. A plot of ln k_{AG} vs. inverse temperature for the pseudo-first-order decay of Amino G under reducing geothermal conditions.

By solving for the Arrhenius rate constant coefficients, it is possible to determine the half-life vs. temperature relationship for Amino G (see Figure 2). Also shown for comparison in Figure 2 are the half-life vs. temperature plots for the two xanthene dyes fluorescein and rhodamine WT, as well as for three polyaromatic sulfonates.

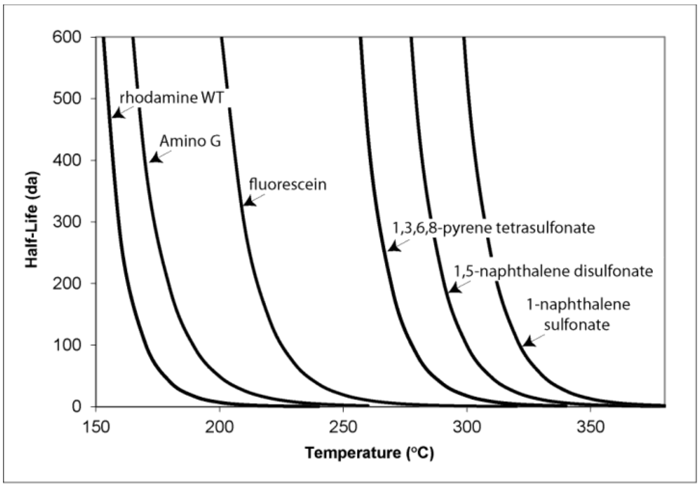

Figure 2. Plot of half-life vs. temperature for Amino G. Shown for comparison are similar plots for three polyaromatic sulfonate tracers as well as two xanthene dyes, rhodamine WT and fluorescein.

3. DETERMINATION OF THE THERMAL DECOMPOSITION PRODUCT(S) OF AMINO G

High resolution liquid chromatography/mass spectrometry (LC/MS) analysis was used in order to determine the major high-temperature degradation product(s) of Amino G. A Waters Acquity H-Class Ultra Performance Liquid Chromatograph (UPLC) equipped with photodiode array (PDA) detection and a Waters Acquity tandem quadrupole detector (TQD) mass spectrometer using electrospray ionization were used for this analysis. The column was a Waters BEH C18 2.1 x 50mm with 1.7 µm particle size. Mobile phases used for the LC/MS analysis were mixtures of filtered deionized water and HPLC-grade methanol.

Solutions of 1.0 part-per-thousand (ppth), unbuffered, Argon-sparged Amino G were sealed in pyrex ampoules and baked for 24 hours at 250°C. Upon cooling, the ampoules were opened in order to analyze the contents by LC/MS. The measured mass of 143.0510 gm/mol of the primary decay product was very close to the mass of 2-naphthol (chemical formula $C_{10}H_7O$), which is calculated as 143.0497 gm/mol. The only other possible candidates within +/- 0.002 mass units contain fewer than 10 carbon atoms. Since it is known that the naphthalene backbone structure persists and contains ten carbon atoms, it is extremely unlikely that the decay product is not $C_{10}H_7O$. This chemical formula corresponds to the conjugate base of either of the two isomers of naphthol, 1-naphthol and 2-naphthol. In order to determine the correct isomer, samples of 1-naphthol and 2-naphthol were procured and run via UPLC with fluorescence detection against the Amino G autoclaved sample, showing that Amino G degrades into 2-naphthol.

In order to determine the effect of pH buffering, the 250°C 24-hour experiment was repeated, this time with Amino G at a concentration of 17.7 parts per million (ppm) and the pH-6.8 phosphate-buffered solution as described in the previous section. The Amino G decayed but no 2-naphthol was observed. A subsequent phosphate-buffered solution that was run for 3 days at 300°C showed that Amino G did decay at the higher temperature into 2-naphthol. Apparently, the presence of the phosphate buffer had inhibited its formation at 250°C. Figure 3 shows an HPLC chromatogram confirming the decay of Amino G to 2-naphthol in a buffered solution at 300°C, with a rapidly eluting, minor decay product. Further analyses will be required to determine the identity of the unknown minor product, as well as to determine whether it is an unreacted intermediate to the final 2-naphthol product.

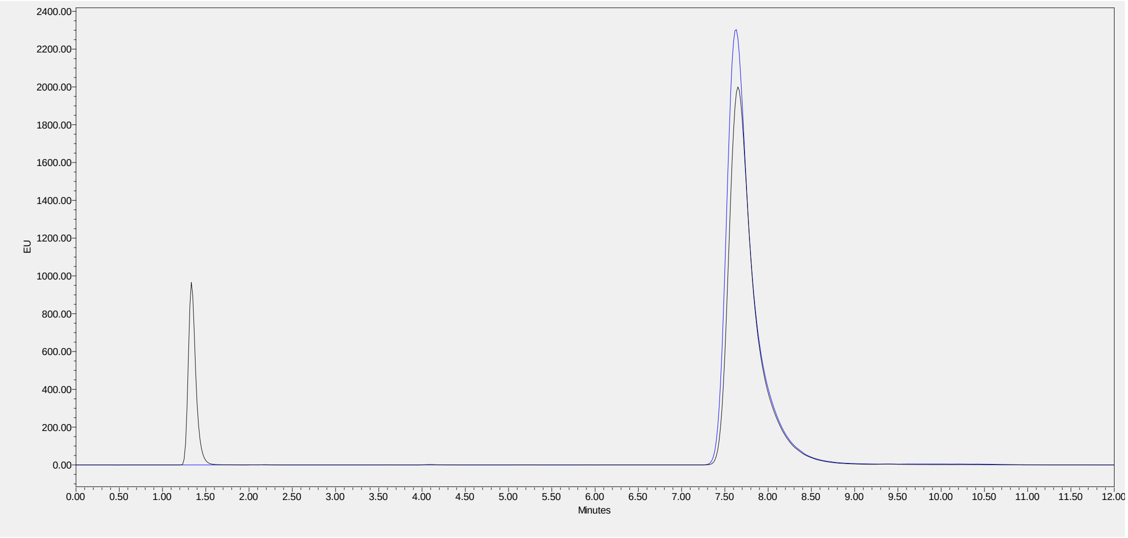

Figure 3. HPLC confirmation of the 2-naphthol decomposition product of Amino G. The black line represents the contents of the buffered Amino G ampoule that was held at 300°C for three days. The blue line represents a standard solution of 2-naphthol. The trace of 1-naphthol is not shown since its presence was barely detectable.

At sufficiently high temperature under simulated, reducing geothermal conditions, Amino G reacts to form 2-naphthol. The reaction is summarized in Figure 4. It is certain that the decomposition does not proceed in just one step. As described above, in the 24-hour reaction at 250°C, Amino G decayed, but no 2-naphthol was observed. It is likely that one or more intermediate steps are involved before the release of both sulfonate groups and the replacement of the amino substituent by a hydroxyl group. Although the chemical structure of Amino G is shown in its acid form in Figure 4, it is fully deprotonated in solution to its anionic form.

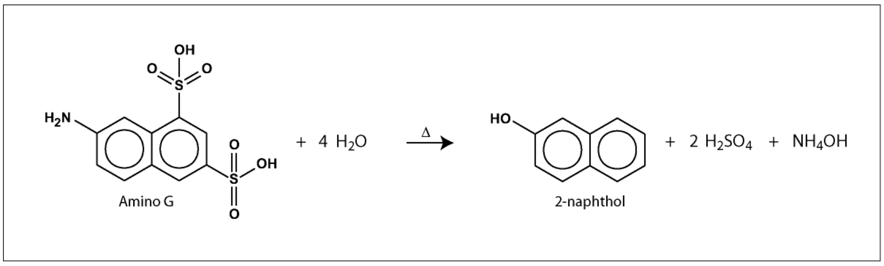

Figure 4. Amino G reacts under reducing hydrothermal conditions to form 2-naphthol.

4. THE PHOTO-STABILITY OF AMINO G

Some fluorescent geothermal tracers, such as fluorescein, display good or even excellent thermal stability but very poor photo-stability. Fluorescein degrades photolytically at ambient temperature under either natural sunlight or artificial light.

In order to test the photostability of Amino G, a sample of known concentration was sealed in a glass bottle and placed on a window shelf, where it was exposed to both indirect sunlight and artificial fluorescent light for a period of 10 days. At the end of the test period, the samples were analyzed by HPLC to determine residual concentration. The Amino G solution showed a 12% reduction in concentration relative to a control sample that was stored in the dark. Amino G samples and standards should therefore be stored in opaque bottles, either glass or Nalgene, in order to avoid photodegradation.

5. THE TRACER TEST AT THE DIXIE VALLEY GEOTHERMAL FIELD

5.1 The Geologic Setting of Dixie Valley

The Dixie Valley geothermal field, located in west-central Nevada, is a classical hydrothermal system located along a narrow fault zone (Figure 5). 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.

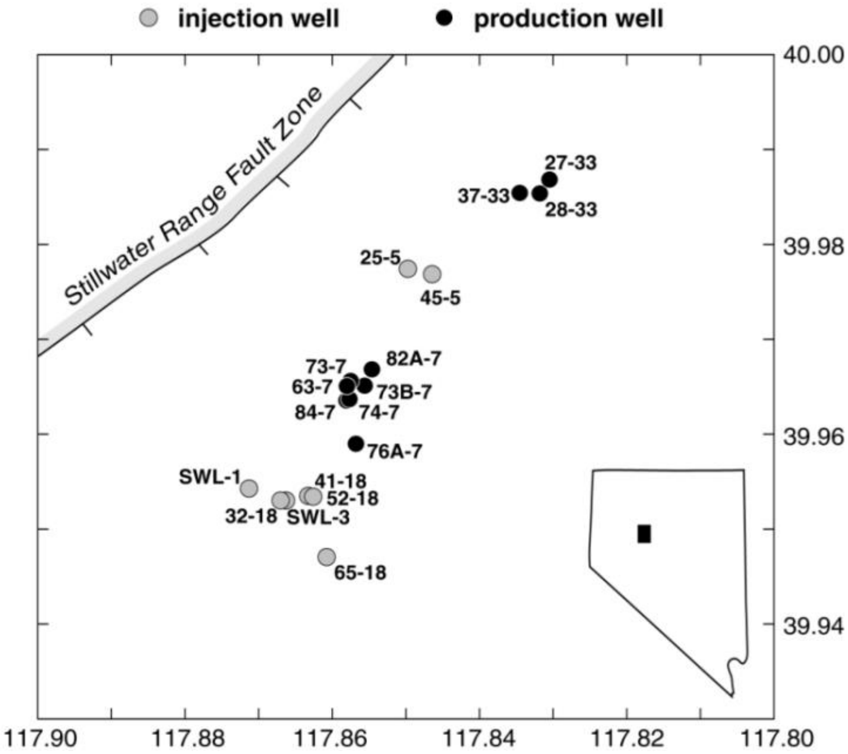

Figure 5. A plan view showing wellhead locations at the Dixie Valley geothermal field.

Production in the Dixie Valley geothermal field is defined primarily by fracture permeability associated with the Stillwater range-front fault and related secondary fractures or faults (see Figure 5). In the vicinity of the geothermal field, the Stillwater range-front fault is known to dip 52^o-54^o to the SE with a roughly planar geometry to depths of 3 km (Benoit, 1995). Most production wells produce up to 2,000 gpm from three to six individual fractures located between depths of 2500 and 3100 m. Injection is into three different environments: 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 (Benoit, 1992).

5.2 The Tracer Test

The first successful test of Amino G as a geothermal tracer was conducted at the Dixie Valley geothermal field. On July 15, 1997, 100 kg of powdered Amino G was mixed with approximately 1 m^3 of produced reservoir brine and injected into well 65-18 over a period of approximately one hour (Rose et al., 1998). Ten production wells were sampled twice weekly over the subsequent several months. The samples were sent to the EGI Tracer Development Laboratory for analysis by HPLC with fluorescence detection.

A plot of the return of Amino G is shown in Figure 6. The first arrival of tracer to section 7 occurred approximately 100 days after injection. The strongest return is to well 74-7, which showed only weak returns from the other tagged wells. Slightly weaker concentrations were measured in wells 63-7, 73-7, 76A-7, and 73B-7. Still weaker but significant tracer concentrations were measured in wells 82A-7 and 84-7. No Amino G was observed in any of the section-33 production wells in the northeast compartment of the field.

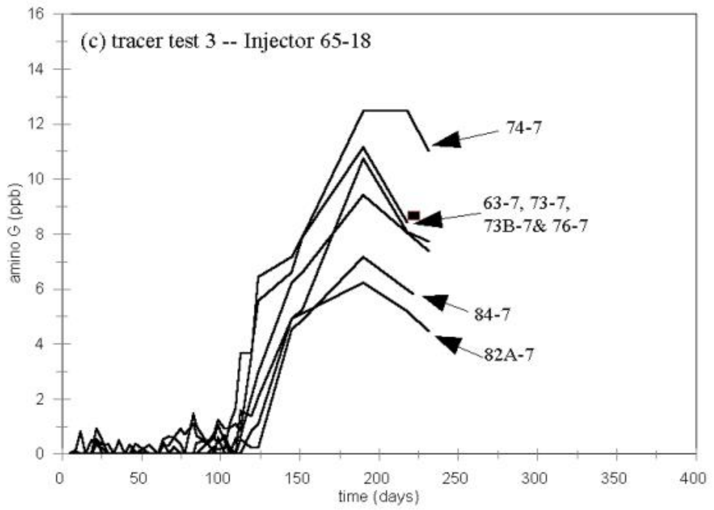

Figure 6. Plots of the return of the decay product of Amino G to several wells at the Dixie Valley geothermal field. The decay product was subsequently determined to be 2-naphthol. Figure borrowed from Rose et al., (1998).

In Rose et al. (1998), it was acknowledged that the identity of the compound plotted in Figure 6 was not known—only that it was a thermally stable decay product of Amino G. As described above, that compound was determined to be 2-naphthol.

6. CONCLUSIONS

The thermal decay kinetics of Amino G was studied in the laboratory under simulated geothermal conditions. These studies reveal that Amino G decays at moderate reservoir temperatures according to an Arrhenius model and that its concentration relative to that of a non-degrading tracer can therefore be used to determine the effective temperature along an injection/production pathway (Rose and Adams, 1994). Using UPLC and high-resolution mass spectrometry, the decay product was shown to be 2-naphthol. In a tracer test conducted at the Dixie Valley geothermal field in 1997, no Amino G was detected in any of the produced water, but an apparent decomposition compound with shifted excitation and emission wavelengths was observed. From the current study, we have determined that decomposition product to be 2-naphthol.

Under sufficiently harsh conditions of time and temperature, Amino G decomposes to 2-naphthol. It is likely, however, that there are intermediate products along the reaction pathway. These intermediates have not yet been identified, but are probably include partially de-sulfonated and/or partially amino-exchanged naphthalenes. Caution should therefore be taken in the interpretation of 2-naphthol as a quantitative decay product of Amino G unless those sufficiently harsh conditions of time at temperature have been met.

7. ACKNOWLEDGEMENTS

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