PROCEEDINGS, 42nd Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 13-15, 2017
SGP-TR-212

The Use of Amino-Substituted Naphthalene Sulfonates as Tracers in Geothermal Reservoirs

Peter Rose and Scott Clausen

Energy and Geoscience Institute at the University of Utah, 423 Wakara Way suite 300, Salt Lake City, Utah, 84103

prose@egi.utah.edu

Keywords: geothermal, tracers, thermally reactive tracers, Amino C, Amino E, Amino G, Amino J, Amino R, substituted naphthalene sulfonates

ABSTRACT

A family of eight commonly available, uv-fluorescent naphthalene sulfonate compounds have proven to be excellent tracers for use in high temperature geothermal reservoirs because they are environmentally benign, very detectable by HPLC with fluorescence detection, affordable, and thermally stable. An amino-substituted naphthalene sulfonate, Amino G (7-amino-1,3-naphthalene disulfonate), has likewise been used as a conservative geothermal tracer. Several isomers of Amino G, including Amino C, Amino E, Amino J, and Amino R, are commercially available. The thermal decay kinetics of each compound was determined from experiments under simulated geothermal reservoir conditions using laboratory autoclaves. Three of the four compounds were determined to have thermal stabilities intermediate to those of rhodamine WT and fluorescein, whereas one was found to be less stable than rhodamine WT. They are all suitable for use as either reactive or conservative geothermal tracers, depending on the temperature of the resource. The use of Amino G as a reactive tracer to determine the effective temperature along an injection-production pathway was demonstrated in a field experiment at the site of the Desert Peak, Nevada EGS Demonstration Project.

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 reservoirs (Rose *et al.,* 2001). Field tests in a number of geothermal reservoirs with temperatures sometimes exceeding 300^{o}C further confirm the thermal stability of these chemicals (Rose *et al.,* 2001).

If a tracer is sufficiently stable at geothermal reservoir temperatures, it will not decompose as it is advected through a reservoir. Furthermore, if its absorptivity and diffusivity are not significantly different from those of water, then the tracer will behave conservatively in that its flow through the reservoir will be indistinguishable from that of water. Conversely, if a tracer is not sufficiently stable then it will decompose as it is advected through the reservoir and its rate of decomposition will be a direct function of reservoir temperature. If the decay kinetics of a thermally reactive tracer is known, then it is possible to measure the effective reservoir temperature along an injection/production pathway so long as a conservative tracer is injected simultaneously with the thermally reactive tracer.

Adams and Davis (1991) first recognized the utility of a thermally reactive tracer for measuring the reservoir temperature along an injection-production pathway. In a tracer test at the Dixie Valley geothermal field, the thermally reactive tracer fluorescein was co-injected with the conservative tracer benzoic acid in injection well 32-18. From an analysis of the tracers produced at well 76-7, a value of 230^{o}C was calculated as the effective temperature for the flow path between the two wells. Adams and Tripp (1991) showed that the ‘effective’ temperature was a geometric mean and not an arithmetic average. Rose and Adams (1994) used fluorescein as a conservative tracer and rhodamine WT as a thermally reactive tracer to calculate an effective reservoir temperature of 163^{o}C at the Steamboat Springs geothermal field. In these two tests, fluorescein was first used as the thermally reactive tracer and subsequently as the conservative tracer, showing that the same tracer can behave either conservatively or reactively depending on reservoir temperature.

Amino G is the common name for an amino-substituted naphthalene sulfonate (7-amino-1,3-naphthalenedisulfonate) that is used in the detergent industry as an optical brightener. It is reasonably nontoxic, environmentally benign, affordable in bulk and very detectable by fluorescence spectroscopy. It has been used as a conservative tracer in groundwater aquifers and in geothermal reservoirs (Rose and Clausen, 2014) and as a thermally reactive tracer (this study). Several isomers of Amino G have been developed for industrial applications but have never before been investigated for use as geothermal tracers. They include Amino C (2-Amino-4,8-naphthalenedisulfonate), Amino E (8-amino-1,6-naphthalene disulfonate), Amino J (6-amino-1,3-naphthalene disulfonate), and Amino R (3-amino-2,7-naphthalene disulfonate). The chemical structures of these amino-substituted naphthalene sulfonates are shown in Figure 1. We present the thermal decay kinetics of all five amino-substituted naphthalene sulfonates and discuss their potential for use as either conservative or thermally reactive geothermal tracers.

2. THERMAL DECAY KINETICS

The decay kinetics of the amino-substituted naphthalene sulfonates was studied using autoclave batch reactors under controlled conditions designed to simulate a geothermal environment. Each was dissolved in a buffered aqueous solution (0.8 g/L Na_2HPO_4, 0.8 g/L KH_2PO_4) at a target concentration of 1 ppm by weight and adjusted to a room-temperature pH of 7.0.

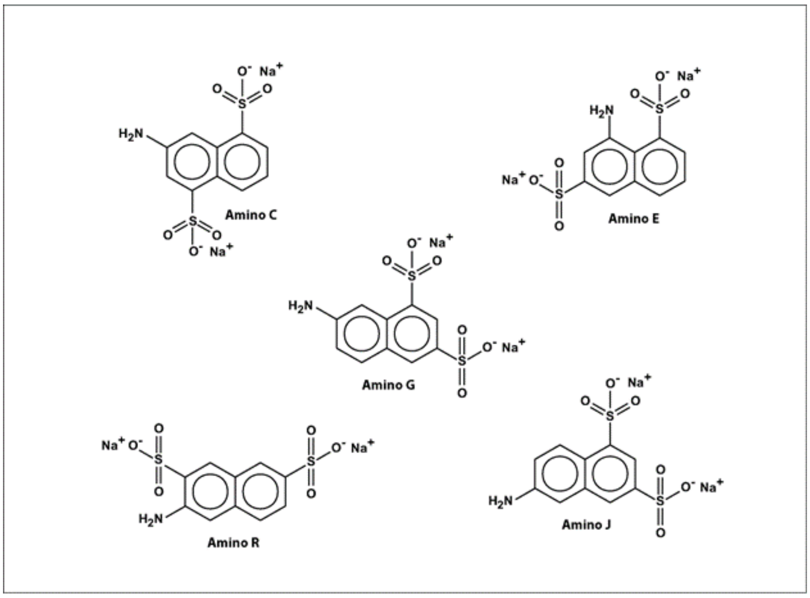

Figure 1. Chemical structures of selected amino-substituted naphthalene sulfonates.

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 ampules 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°C in the dark before being analyzed with the reacted samples.

The amino-substituted naphthalene sulfonates decay according to the following pseudo-first-order expression:

$$-dC_A/dt = k_A \cdot C_A \qquad (1)$$

where C_A is the concentration of the compound and k_A is the pseudo-first-order decay-rate constant. Solution of this equation results in the following relationship between C_A and t:

$$\ln\left(\frac{C_A}{C_A^0}\right) = -k_A \cdot t \qquad (2)$$

where C^0_A is the initial concentration. The temperature dependence of k_A can be described by the Arrhenius relationship:

$$k_A = Ae^{(-E_a/RT)} \qquad (3)$$

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:

$$\ln k_A = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \qquad (4)$$

Plots of ln k_A vs. 1/T for all of the amino-substituted naphthalene sulfonates is shown in Figure 2. In most cases, the data show good fit to expression 4, indicating that the Arrhenius equation is a good model for representing the temperature dependence of the decay rate constant.

By solving for their Arrhenius rate constant coefficients, it is possible to determine the half-life vs. temperature relationships for the amino-substituted naphthalene sulfonates (see Figure 3). Also shown for comparison in Figure 3 are the half-life vs. temperature plots for two xanthene dyes, fluorescein and rhodamine WT, as well as for two polyaromatic sulfonates—1,3,6,8-pyrene tetrasulfonate (ptsa) and 1,5-naphthalene disulfonate (1,5-nds). This plot shows that none of the amino-substituted naphthalene sulfonates are as thermally stable as fluorescein but that four of the five are more thermally stable than rhodamine WT.

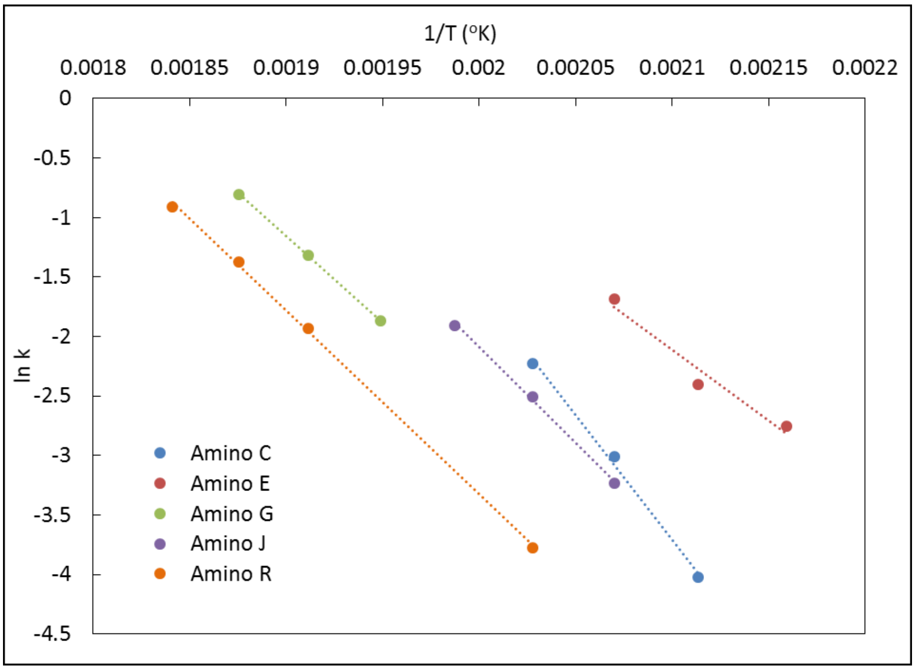

Figure 2. A plot of ln k_A vs. inverse temperature for the pseudo-first-order decay of the amino-substituted naphthalene sulfonates under reducing geothermal conditions.

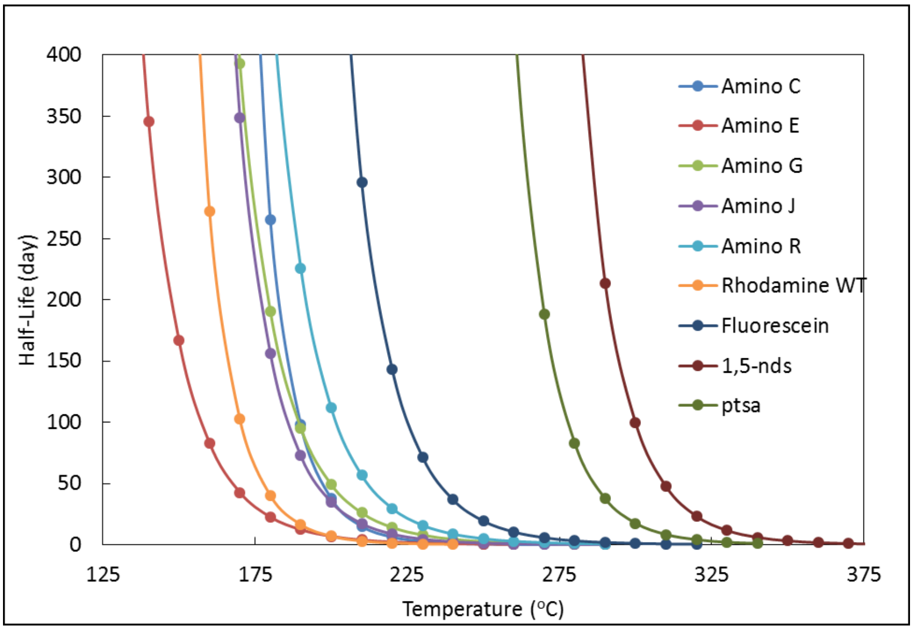

Figure 3. Plot of half-life vs. temperature for the amino-substituted naphthalene sulfonates. Shown for comparison are similar plots for other polyaromatic sulfonate tracers as well as two xanthene dyes, rhodamine WT and fluorescein.

4. THE PHOTO-STABILITIES OF THE AMINO-SUBSTITUTED NAPHTHALENE SULFONATES

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. Amino G was also shown to be subject to thermal degradation (Rose and Clausen, 2014). Therefore, addition studies should be undertaken to determine the photostabilities of the other amino-substituted naphthalene sulfonates. Until those studies are undertaken, it is advisable to store their solutions in opaque bottles, either glass or Nalgene, in order to avoid photo-degradation.

5. TRACER TESTING AT THE DESERT PEAK EGS DEMONSTRATION PROJECT

5.1 A 2008 Tracer Test Using Conservative Tracers

Extensive research funded by EERE/DOE was conducted by multiple agencies between 2007 and 2012 to design and create an EGS at the Desert Peak, Nevada geothermal reservoir through hydraulic and chemical stimulation (e.g. Davatzes and Hickman, 2009). Prior to any stimulations, a tracer test was conducted in 2008 in order to determine the fate of fluids injected into two major injectors 21-2 and 22-22—just to the south of the EGS target injection well 27-15 (Rose et al., 2009). Shown in Figure 4 are the return curves plotted for each of the wells in which tracer was observed. Notably, very large concentrations were observed almost immediately at the producer 74-21—just to the south of the two injectors. But significant concentrations were also observed in well 67-21, the next well to the south of 74-21.

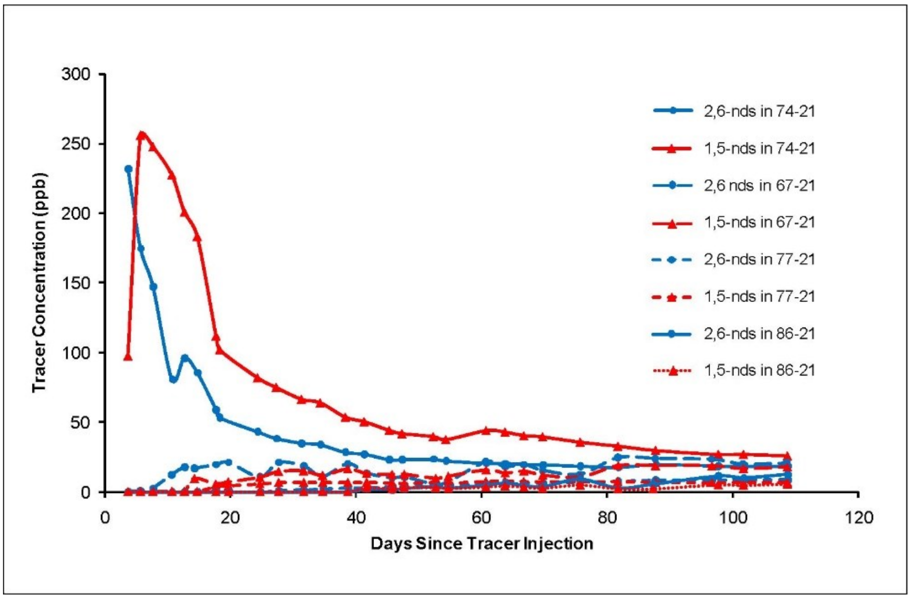

Figure 4. Return curves to all of the producers in which tracer was observed during a 2008 tracer test at the Desert Peak field.

A map showing wellhead locations and interpreted flow patterns for the 2008 Desert Peak tracer test is shown in Figure 5. The order of return to each of the wells is shown by the purple and green arrows.

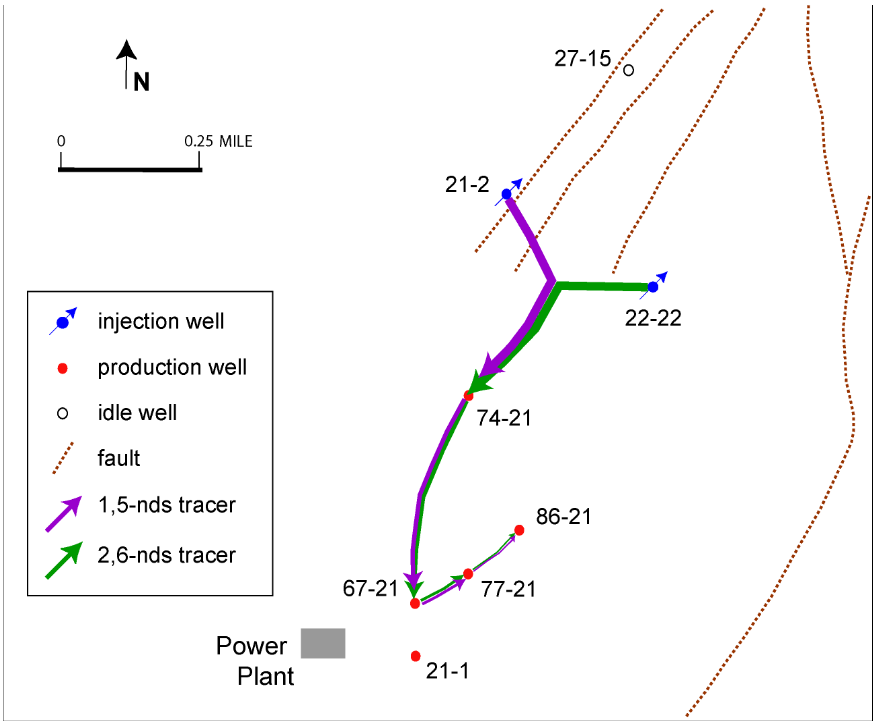

Figure 5. Flow pattern between injectors and producers as determined by a tracer test at the Desert Peak field in 2008.

The project resulted in the claimed successful creation of an EGS at Desert Peak with significantly enhanced electrical output at the power plant. As a result, it was possible to initiate a DOE-funded project to study the evolution of fracture-flow processes following a hydraulic stimulation.

5.2 A 2015 Tracer Test Using a Conservative Tracer in Combination with a Thermally Reactive Tracer

On September 15 2015, 150 kg of the reactive tracer 7-amino-1,3-naphthalene disulfonate (Amino G) and 80 kg of the conservative tracer 2-naphthalene sulfonate (2-ns) were injected into well 27-15 at the Desert Peak EGS site. All of the wells in the field were subsequently sampled with the objective of measuring interwell connectivity and the relative degree of thermal degradation of the reactive tracer.

Shown in Figure 6 are the returns of the tracers Amino G and 2-ns to well 67-21. Since well 74-21 is no longer in service, the first (and only) well in which tracer returns were measured in the 2015 tracer test is 67-21. This is consistent with the 2008 tracer-test findings, since in that test 67-21 was the second well after 74-21 in which tracers were observed. However, the tracer concentrations are much lower in the 2015 test than those observed in any of the wells tested during the 2008 test.

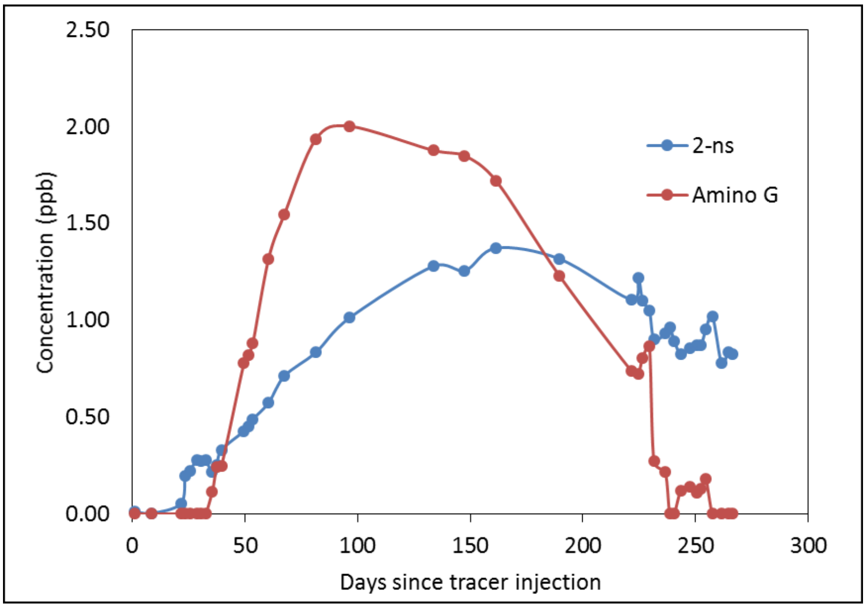

Figure 6. Return curves showing the concentrations of the conservative tracer 2-ns and the thermally degrading tracer Amino G returning to Desert Peak well 67-21 during the 2015 test.

By integrating the area under the curve for the conservative tracer 2-ns in well 67-21 after approximately 270 days following injection and multiplying by the flow rate to 67-21, one can calculate the mass of tracer produced. That calculation revealed that only 0.925% of the mass of tracer injected was produced—implying that only 0.925% of the water injected into 27-15 was produced at this closest production well. No tracer was observed in any of the other producers. This of course means that more than 99% of the water injected into 27-15 was either on the path to production, had flowed to other stagnant regions of the reservoir, or had flowed out of the reservoir during these nine months following tracer injection.

The masses injected were different for each tracer for the 2015 test—150 kg of Amino G and 80 kg of 2-ns. Therefore the produced concentrations of tracers in well 67-21 were normalized to their injected masses. Figure 7 shows the normalized plots that reveal that, as expected, the concentration of Amino G continuously diminished over time relative to that of 2-ns. The normalized concentration of Amino G exceeds that of 2-ns between about day 50 and day 90. However, this may be due to analytical error, given that the concentrations of both tracers are near their respective detection limits. Alternatively, this apparent error may be due to the possibility that the mass of Amino G injected was underestimated. Another possibility is that 2-ns reversibly adsorbed, delaying its arrival slightly, relative to that of Amino G.

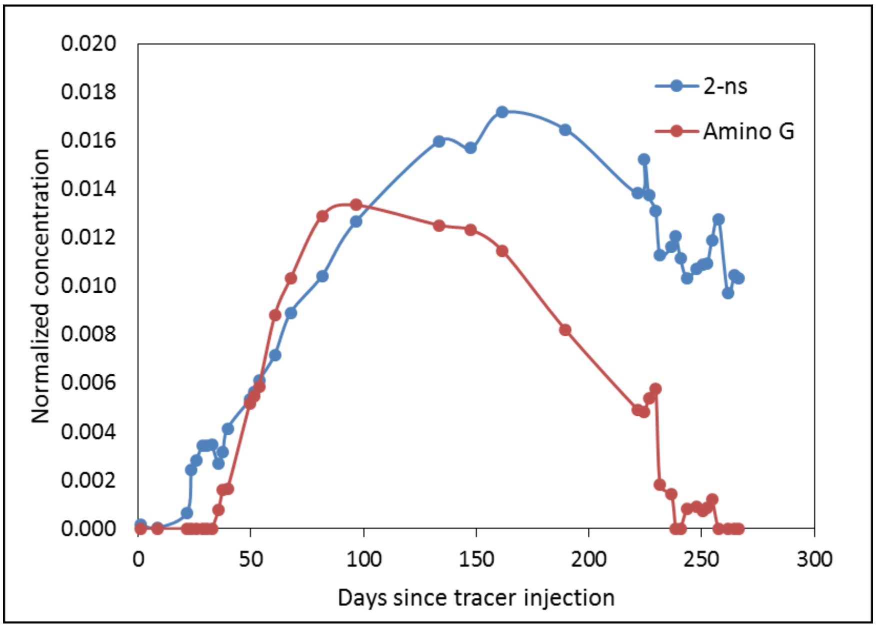

Figure 7. Return curves showing the normalized concentrations of the conservative tracer 2-ns and the thermally reactive tracer Amino G returning to Desert Peak well 67-21.

Through trial and error, a value was found for T in equation 3 that allows for the calculated concentration of Amino G in equation 1 to overlap that of the conservative tracer 2-ns in Figure 7. That 'effective' temperature was determined to be 175°C (see Figure 8). The reconstituted return curve overlaps that of the conservative tracer imperfectly for reasons suggested above. Likewise, this value for the effective temperature must be used with caution, since the data for Amino G decay kinetics were determined between 240°C and 260°C. Since 175°C is outside this range, a more detailed kinetics study is needed wherein data are obtained in a range that encompasses 175°C. For the purposes of this study, however, this extrapolation is acceptable.

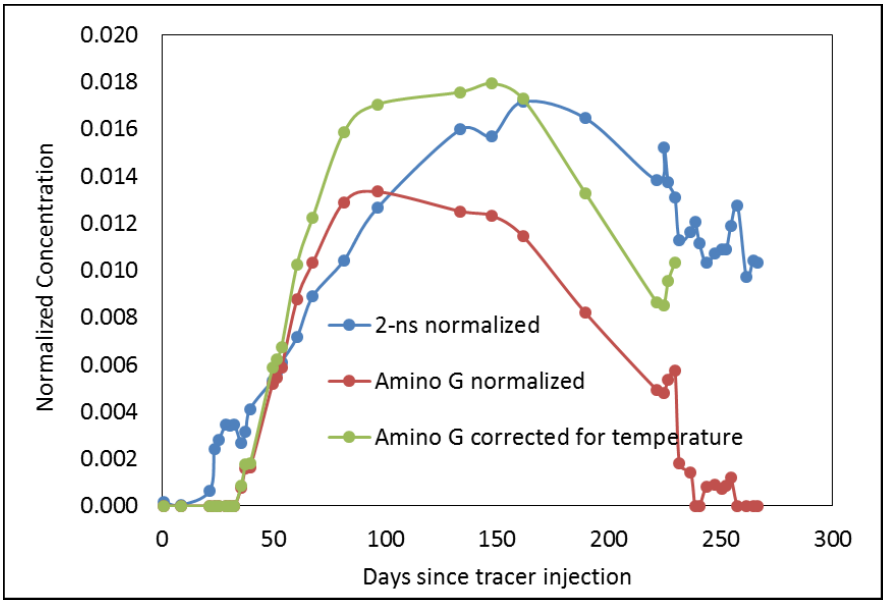

Figure 8. Return curves showing the normalized concentrations of the conservative tracer 2-ns and the thermally reactive tracer Amino G returning to Desert Peak well 67-21. It also shows (in green) the return curve for Amino G—as corrected for a reservoir temperature of 175°C. This is the return curve that the Amino G would have had if Amino G had not thermally decayed.

6. CONCLUSIONS

Of the five new compounds that were studied for use as either conservative or reactive tracers—depending on reservoir temperature—four (J, G, C and R) were found to be intermediate in thermal stability between rhodamine WT and fluorescein and one (E) was determined to be less thermally stable than rhodamine WT. They can each be used in combination with a conservative tracer to measure an effective reservoir temperature along an injection-production pathway. In an example at the Desert Peak EGS project using the reactive tracer Amino G, the effective reservoir temperature along the pathway between wells 27-15 and 67-21 was estimated to be 175°C. Subsequent tracer testing using this or another of the amino-substituted naphthalene sulfonates in conjunction with a conservative tracer could serve to determine the rate at which this portion of the reservoir is cooling.

But even if the amino-substituted naphthalene sulfonates are used without companion conservative tracers in reservoirs wherein they experience significant but not complete thermal decay, their return concentrations can be corrected for thermal decay since their decay kinetics are known. In this manner, thermally reactive tracers can be used as stand-alone conservative tracers.

7. ACKNOWLEDGEMENTS

We thank John Akerley and Lara Owens of Ormat Technologies for their roles in coordinating the tracer testing at the Desert Peak geothermal field.

REFERENCES

Adams, M.C. and Davis, J. (1991) Kinetics of fluorescein decay and it application as a geothermal tracer, *Geothermics*, **20(1/2),** 53-66.

Davatzes, N. C. and Hickman, S. H. (2009) Fractures, stress, and fluid flow prior to stimulation of well 27-15, Desert Peak, Nevada, EGS Project, *Proceedings, 34th Workshop on Geothermal Reservoir Engineering*, Stanford University SGP-TR-187.

Greim H., Ahlers, R., Bias, R., Broecker, B., Hollander, H., Gelbke, H.P., Klimisch, H.J., Mangelsdorf, I., Paetz, A., Schon I., Stropp, G., Vogel, R., Weber, C., Ziegler-Skylakakis, K., and Bayer, E. (1994) Toxicity and Ecotoxicity of Sulfonic Acids: Structure-Activity Relationship: *Chemosphere*, **28(12)**, 2203-2236.

Leung, V. (2013) Yick-Vic Chemicals and Pharmaceuticals, yickvic@hkstar.com

Rose, P.E. and Adams, M.C. (1994) The application of rhodamine WT as a geothermal tracer: *Geothermal Resource Council Transactions*, **18**, 237-240.

Rose, P.E., Benoit, W.R., and Adams, M.C. (1998) Tracer testing at Dixie Valley, Nevada, using pyrene tetrasulfonate, amino G, and fluorescein: *Geothermal Resource Council Transactions*, **22**, 583-587.

Rose, P.E., Benoit, W.R., and Kilbourn, P.M., (2001) The application of the polyaromatic sulfonates as tracers in geothermal reservoirs: *Geothermics*, **30(6),** 617-640.

Rose, P.E., Leecaster, K., Drakos, P., and Robertson-Tait, A. (2009) Tracer Testing at the Desert Peak EGS Project, *Geothermal Resource Council Transactions.*

Rose, P.E. and Clausen, S. (2014) The Use of Amino G as a Thermally Reactive Tracer for Geothermal Applications, *Proceedings, 39th Workshop on Geothermal Reservoir Engineering*, Stanford University SGP-TR-202.

Tripp, A. C., and Adams, M. C., (1991), Estimation of effective flow-path temperature using reactive tracers, University of Utah Research Institute, Earth Science Laboratory.