# MODELLING TRACER BREAKDOWN UNDER GEOTHERMAL CONDITIONS

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#### **ABSTRACT**

Geothermal tracer tests are widely used in the industry to identify flow pathways between production and reinjection zones. The results of these tests are often used to predict the potential for thermal breakthrough of cooler reinjection fluids. This is usually done by using the tracer test data to constrain the flow paths through which reinjection fluids travel in numerical reservoir models.

Recent experimental studies by Mountain and Winnick, and Sajkowski et al have shown that naphthalene sulfonates that are widely used in the geothermal industry as tracers have temperature limits. These studies have measured the rates of the thermal breakdown reactions that these compounds undergo. These breakdown rates have been shown to depend on temperature and pH.

This paper presents work to model the breakdown of different types of geothermal tracers and incorporate the reactions into transport models of tracer flow in a geothermal reservoir. The ultimate purpose is to estimate temperatures along the paths that tracers flow within the reservoir. We will present models of the reaction kinetics of some naphthalene sulfonate and alcohol tracers and the findings of incorporating these reactions into numerical models of reservoir tracer tests.

#### 1. INTRODUCTION

Tracers are used in geothermal developments to understand pathways between production and reinjection wells (Axelsson et al., 2001, Axelsson, 2013). Information from these tests is used to estimate the potential for returns of cooled reinjection fluids to production wells by providing calibration data for numerical reservoir models (Burnell et. al., 2016). Recent experiments by Mountain and Winnick (2012) and Sajkowski et al. (2021) have shown that the commonly used naphthalene sulfonates (Rose et al., 2001 and Ayling and Rose, 2013) breakdown at temperatures greater than 200 °C under acidic conditions.

#### 1.1. Rotokawa Tracer Test

Rotokawa is a geothermal system in New Zealand's Taupō Volcanic Zone that has been well documented in the geothermal literature (e.g. Addison et. al. 2015, Hernandez et. al. 2015, Sewel et. al., 2015). Rotokawa has been under development since 1997. In 2010, take from the reservoir increased from around 15,000 t/day to approximately 60,000 t/day with the commissioning of the 138 MWe Nga Awa Purua geothermal power plant. In 2011, after nearly one year of Nga Awa Purua operations, a tracer test was conducted at the Rotokawa geothermal system using four naphthalene disulfonic acid NDS tracers (Addison et al., 2015). Production wells and surface features were monitored for one year. During that time, none of the injected tracer isomers were detected.

As a consequence of this unusual result, a study was undertaken to investigate the stability of the tracers under temperatures representative of Rotokawa (Mountain et al, 2012). The results showed that at higher reservoir temperatures the tracers breakdown completely. This provided the motivation for subsequent studies by Sajkowski and the current paper.

# 1.2. Arrhenius Behaviour

Tracer breakdown can be assessed by measuring rates of the reactions that occur when they breakdown. An example of this behaviour is shown in Figure 1 which shows the reaction rate at different temperatures for 1,5-NDS tracers at two different pH conditions. This shows there are orders of magnitude difference in the reaction rate as the temperature increases from 200 and 330 °C and provided an explanation as to why no tracer returns were detected at Rotokawa.

The dependence of the reaction rate with temperature can be obtained by fitting the Arrhenius equation to this data. That is the reaction rate is given by equation (1)

$$k = Ae^{-\frac{E_a}{RT}} \tag{1}$$

Where k is the reaction rate (units of 1/time), A is the pre-exponential factor (1/time),  $E_a$  is the activation energy (kJ/mol), R is the universal gas constant (J/mol/K) and T is temperature in deg. K. For the data shown in Figure 1, the Arrhenius coefficients are given in Table 1.

Table 1: Estimated Arrhenius coefficients corresponding to the data in Figure 1

pН	A (1/day)	E <sub>a</sub> (kJ/mol)
5.6	$3.7x10^{10}$	114
6.4	8.7x10 <sup>12</sup>	160

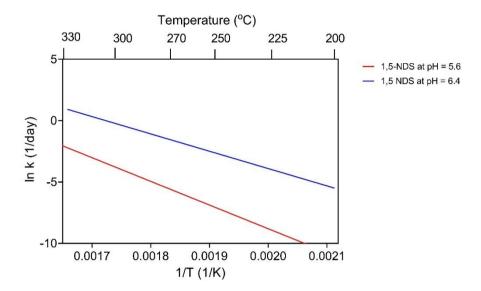


Figure 1: Reaction rates of 1,5-NDS tracers for different temperatures and pH conditions, from Sajkowski et al 2021.

## 2. MODELLING FLOWS AND BREAKDOWN

To calculate the effects of tracer breakdown new software was developed that modelled both the transport and reactions of tracers in a geothermal reservoir. The software was coupled with a modified version of TOUGH2 (Pruess, 1999), that recorded the fluid state and flows between model cells at specified times in a format suitable for rapid processing.

Equation (2) describes the transport and reaction of a tracer with concentration C that exists in either liquid or vapour phases

$$\frac{\partial \varphi S_p \rho_p C}{\partial t} = \nabla \cdot \left( C \rho_p \boldsymbol{u}_p \right) - k(T) C \tag{2}$$

Where the subscript p represents the phase (liquid or vapour),  $\varphi$  is the porosity,  $S_p$  is the volume saturation,  $\varphi_p$  is the fluid density  $(kg/m^3)$ ,  $\mathbf{u}_p$  is the fluid velocity (m/s) and k is the reaction rate (1/s).

The reaction rates for NDS tracers were calculated from the experimental data obtained by Sajkowski and colleagues (Sajkowski et al, 2020). That data was collected at different temperatures allowing the coefficients of the Arrhenius equation (Arrhenius, 1889) to be fitted.

A new software programme was developed to solve the advection equation of equation (2). It used an implicit Crank-Nicolson time discretisation (Chock, 1991) together with the same method of upwinding for the advection term used by TOUGH2 (Pruess, 1999). The velocities in the advection term were taken directly from the TOUGH2 simulation output. The software was tested against simulations of synthetic tracer tests made with TOUGH2 and Volsung (Franz et al, 2018) using brine as a tracer. These tests showed good matches to the output of the simulators. There are a few advantages to using a separate program to model the transport: it removes the need to include a brine component in natural state and history matching calculations, when a tracer test may only cover 1 or 2 years; it allows more complex tracers to be considered – such as vapour phase tracers; and it allows easier development and testing of new components of the analysis such as tracer breakdown.

#### 1.2 Rotokawa-like Model

To test this software, we have constructed a model with similar conditions to the Rotokawa test. A reservoir model based on descriptions of the Rotokawa reservoir given in Hernandez et al., 2015 and Sewel et al, 2015 was constructed. The model was developed using the EOS1 module and using MINC for dual porosity. Model parameters were adjusted until temperatures of over 300 °C were reproduced in the south-east of the reservoir. Production from Nga Awa Purua, starting in 2010, was simulated with production rates of 60,000 t/d and reinjection rates of 40,000 t/d. The model grid and simulated temperatures are shown in Figures 2

and 3. These show southern reservoir temperatures of more than 310 °C which are approximately consistent with the observed Rotokawa temperatures (Hernandez et al.).

Two variants of the 2011 tracer test at Rotokawa were simulated in this model to understand the potential effect of tracer breakdown at Rotokawa. For both variants, 300 kg of tracer was injected at the start of 2011 after one year of Nga Awa Purua operations. In the first version the tracer was considered to be non-reactive and did not breakdown. In the second version, tracer breakdown rates shown in Figure 1 were applied to equation (2).

The first version of this test corresponds to the Iodine-125 tests conducted in 2013 (Addison et al, 2015, and Addison and Clearwater, 2017). Iodine-125 is a known thermally stable tracer with a half-life of 59 days. This test corresponds to a non-reactive tracer, that showed initial returns in the central field wells of approximately 80 days and the tracer peak was not conclusively observed after 300 days. The modelled concentration corresponding to this test is shown in Figure 4(a) and is approximately consistent with the field observations from the Iodine-125 test. This demonstrates that the flow model is reproducing the connectivity between production and reinjection wells.

In the second version of the model, measured breakdown rates from Figure 1 and Table 1 for pH 5.6 were applied to the tracer test. This corresponds to the 2011 tracer test that used NDS isomer tracers. The results of this model are shown in Figure 4(b) and are consistent with observations that the levels of tracer from production wells are below detectible limits (Addision et al., 2015).

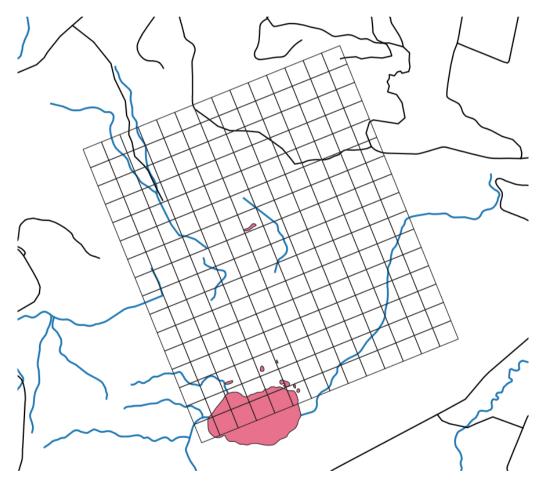


Figure 2: Model grid for Rotokawa-like numerical reservoir model, the blue lines are streams, the black lines are roads, and the magenta polygon is Lake Rotokawa.

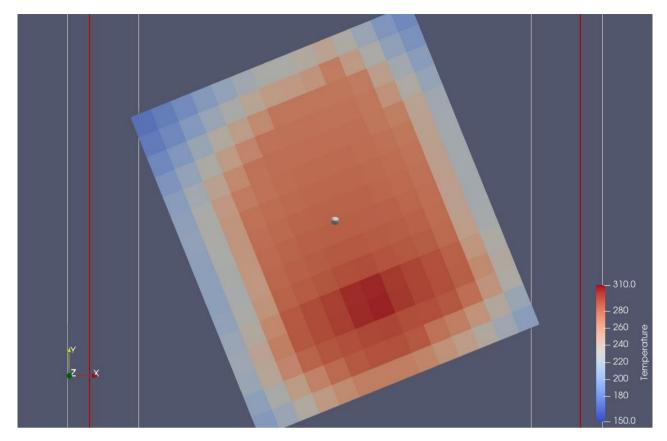


Figure 3: Simulated reservoir model temperatures at production levels from the Rotokawa-like model.

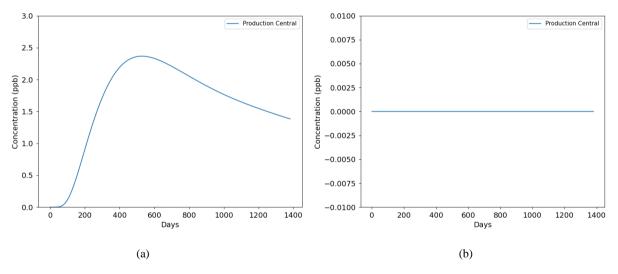


Figure 4: Calculated tracer returns at a central field production well for the Rotokawa-like model. For (a) the tracer is assumed to be non-reactive and for (b) it breaks down as 1,5 NDS at a pH of 5.6.

### 3. MODELLING ALCOLHOL TRACERS

The NDS tracers discussed above partition into the liquid phase and are useful for understanding connections between production and reinjection wells. However, these tracers have limited to no value in two-phase or vapour phase conditions respectively. Alcohol and sulfur hexafluoride tracers have been identified as possible tracers for geothermal applications under two-phase or vapour conditions. Alcohol tracers could be used in two-phase conditions as they have significant solubility in both liquid and vapour phases.

Adams et al, 2000, have conducted experiments on the stability of these alcohol tracers. Data from their experiments showing the variation of reaction rate with temperature is presented in Figure 5. They also report that calculations indicate that these compounds partition with steam to liquid concentrations of one to three in typical geothermal conditions.

The equation for transport and reaction of single-phase tracers given in (2) was modified to account for the solubility of the tracer into the different phases. It becomes:

$$\varphi \sum_{p} \frac{\partial S_{p} \rho_{p} c_{p}}{\partial t} = \nabla \cdot \sum_{p} \left( C_{p} \rho_{p} \boldsymbol{u}_{p} - k(T) C_{p} \right)$$
(3)

$$C_p = \alpha_p(T)C \tag{4}$$

Where p is liquid or vapour phase, and  $C_p$  is the concentration of the tracer in liquid or vapour phase and  $\alpha_p$  is the relative solubility of the tracer in each phase.

### 3.1. Testing Alcohol Tracers

To test this approach for modelling two-phase alcohol tracers a synthetic horizontal 1-D model was constructed. The model was 2.1 km in length as shown in Figure 6. A production well and a reinjection well were placed at the ends of the model separated by 2 km. Temperatures throughout the domain were set to 270 °C with different vapour saturation conditions being applied in a series of tests. A flow rate of 20 kg/s was applied to the production and reinjection wells with a reinjection temperature of 220 °C.

First was a basic test to check the handling of two-phase conditions, two cases were run using an initial vapour saturation of 0.1. Here the reservoir state is close to liquid conditions and initially only the liquid phase can flow, so the results should be similar to a liquid only tracer. For the first case, the tracer was assumed to only be soluble in the liquid phase; for the second case, the tracer was partitioned into both phases using a ratio of vapour to liquid of one to three. For both cases it was assumed that the tracer was stable and did not breakdown. The results of these two cases are shown in Figure 7(a) and show that the two-phase and liquid-only tracers produce near identical results as expected.

The second test also included two cases and used an initial vapour saturation of 0.35, under these conditions both liquid and vapour can flow. The first case assumed a non-reactive tracer, whereas the second case simulated the tracer breakdown of n-propanol at a pH of 6.6. From the data in Figure 5, Arrhenius coefficients of A = 163 (1/day) and Ea = 42 kJ/mol were calculated. A comparison between these cases is shown in Figure 7(b) where the propanol tracer is observed at the production well but has peak returns of about half of the non-reactive tracer. This is due to the smaller reaction rates of propanol compared to 1,5 NDS with propanol having a half-live of approximates 46 days at 270 °C.

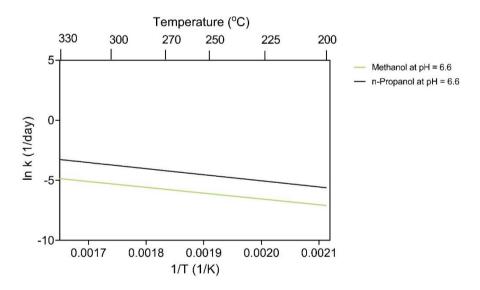


Figure 5: Reaction rates of two alcohol tracers for different temperatures, from Adams et al, 2000.

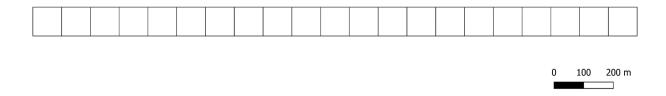


Figure 6: Grid used for the synthetic reservoir model for testing two-phase tracer modelling.

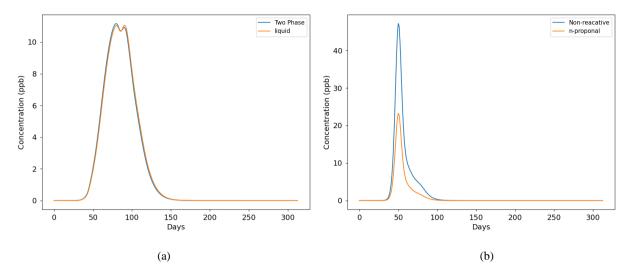


Figure 7: Calculated tracer returns at the production well for two synthetic examples. For (a) the vapour saturation was set to 0.1 and two-phase and liquid tracers were injected. For (b) the vapour saturation was set to 0.35 and two-phase tracers were injected with one being non-reactive and the other decaying at the same rate as methanol in Figure 5.

#### 4. CONCLUSION

This paper presents an approach to modelling tracer transport in a geothermal reservoir by coupling an advection equation to simulations performed by the TOUGH2 reservoir simulator. The software for solving the advection equation also simulates tracer reactions that result in breakdown that has been observed in laboratory experiments. A model of a Rotokawa-like reservoir model was developed and a tracer test similar to one undertaken in 2011 was simulated. Using a non-reactive tracer provided return times similar to an Iodine-125 tracer test done at Rotokawa in 2013. Incorporating measured tracer reactions rates showed similar results to the 2011 tracer test — namely no tracer returns were detected.

The result of modelling this test provides further evidence that the observations that no NDS tracers were observed at the production wells was due to the thermal breakdown of the NDS tracer. The reason being that the model incorporates estimates of the reservoir temperatures along the pathways between the reinjection well and production well. The previous analysis based on the laboratory experiments were based on temperature measurements from the pre-production state of the reservoir.

This paper also demonstrates that the same approach can be applied to model alcohol tracers that partition into the liquid and vapour phases.

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