

## Coupled Iodine-125 and 2NSA Reservoir Tracer Testing at the Rotokawa Geothermal Field, New Zealand

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### ABSTRACT

In 2011 a reservoir tracer test was conducted at the Rotokawa geothermal field to better understand the reservoir response to increased production following commissioning of the newly constructed 138 MWe Nga Awa Purua power station. The test used four types of naphthalene disulfonate tracer (1,5-, 1,6-, 2,6- and 2,7NDS) to trace the injection fluid movements. After more than one year of monitoring, no returns of injected NDS tracers were detected in any production wells. Following an extensive laboratory testing program in 2012, it was determined that these NDS tracers are not conservative at Rotokawa injection reservoir temperatures. Based on tracer stability experiments, a series of naphthalene based breakdown products and reaction pathways were hypothesized which led to the conclusion that 2-naphthalene sulfonic acid (2NSA) is a likely byproduct of NDS thermal breakdown, and is potentially the most stable of the available naphthalene tracers. Tracer samples from the 2011 test were re-analyzed and small quantities of 2NSA were confirmed in a number of key production wells. Based on these results, a new reservoir tracer test was planned and executed in 2013 which coupled radioactive iodine-125 ( $^{125}\text{I}$ ) and 2NSA in an effort to benchmark the performance of 2NSA against a known, conservative, and thermally stable tracer. Results from this test have demonstrated detectable returns of both  $^{125}\text{I}$  and 2NSA, though the response times and magnitudes are significantly different. These data have identified key limitations in the use of naphthalene tracers in high-temperature geothermal environments. When integrated with other resource monitoring information, the test results have helped identify important reservoir processes responsible for observed field changes.

### 1. INTRODUCTION

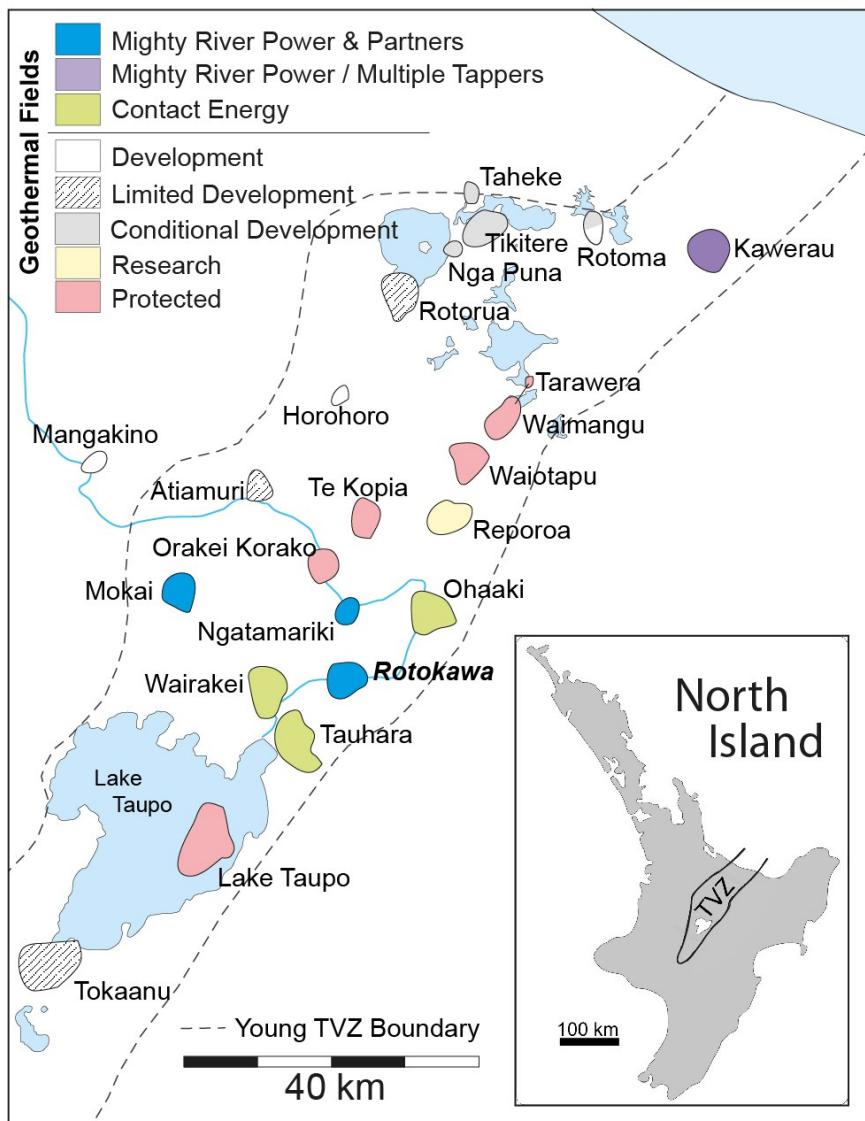
Reservoir tracer tests are commonly performed in the geothermal industry and they comprise a key component of Mighty River Power's integrated resource monitoring and management strategy. These tests are generally conducted at Rotokawa following a major change in mass extraction rates or in the operational configuration of the field. The tracer tests enhance our understanding of reservoir hydrology, and in particular, changes in fluid movements in response to production and injection activities.

Since commissioning the 138 MWe Nga Awa Purua (NAP) power station in early 2010, two reservoir tracer tests have been conducted at Rotokawa which used naphthalene based tracers. The more recent of those tests coupled 2-naphthalene sulfonic acid (2NSA) with iodine-125 ( $^{125}\text{I}$ ). In tandem with these field-based tests, experimental investigations were made into the thermal stability of naphthalene tracers under high temperature geothermal conditions, like those within the Rotokawa reservoir (Mountain and Winick, 2012). These integrated efforts have resulted in important field-based observations of naphthalene tracer behavior at Rotokawa, as well as new insights into the reservoir hydrology. This paper provides an overview of these collaborative efforts; including a review of the earlier 2011 naphthalene disulfonate (NDS) test results which provided the catalyst for experimental investigations into naphthalene tracer thermal stability and formed the basis upon which a coupled 2NSA and  $^{125}\text{I}$  tracer test was planned and executed in 2013.

### 2. BACKGROUND

The Rotokawa Geothermal Field is located within the Taupo Volcanic Zone on the North Island of New Zealand. To its southwest is the Wairakei-Tauhara geothermal field and to its north is the Ngatamariki geothermal field (Figure 1). The productive Rotokawa reservoir is a high temperature ( $>320^\circ\text{C}$ ), permeable geothermal resource which generally lies at depths below about 1000 m. Various elements of the conceptual model describing natural state reservoir hydrology, temperature, pressure, and chemistry at Rotokawa can be found in Hedenquist et al., (1988); Bowyer and Holt (2010); Winick et al., (2011); and Sewell et al., (2012).

The deep Rotokawa reservoir has supported commercial electricity generation since 1997. Power generation began with the installation of the of 24 MWe binary Rotokawa A plant (RGEN). Production was initially from wells RK5 and RK9 with shallow injection at about 500 to 1000 m depth into RK1, RK11, and RK12. In 2000, Mighty River Power and Tauhara North No. 2 Trust formed the Rotokawa Joint Venture (RJV) and generation was subsequently expanded to 34 MWe. In 2007, resource consents were obtained for a further development at Rotokawa, supported by conceptual and numerical modeling of the field based on RGEN production history and well results up to RK18 (Bowyer & Holt, 2010). The Nga Awa Purua (NAP) development began in 2008 with the drilling of 12 additional wells and construction of a 138 MWe, triple-flash plant which was commissioned in early 2010. Since this time, two make-up production wells have been drilled.



**Figure 1: Map showing the location of the Rotokawa Geothermal Field within the Taupo Volcanic Zone (TVZ) of New Zealand's North Island. The TVZ outline is shown as the dashed line after Wilson et al. (1995). The locations of other known geothermal fields are shown and these are located on the basis of resistivity anomalies after Bibby et al. (1995).**

Injection of flashed brines and condensate from both RGEN and NAP is currently through deep injectors drilled into the southern area of the reservoir. This injection reservoir is hot with measured natural-state well temperatures between 320-340°C (Sewell et al., 2012). Production of steam supplying both RGEN and NAP is from wells drilled along a SW-NE axis south of the Waikato River. The central field fault (CFF) is a major structure inferred to offset the injection and production reservoirs on the basis of well data (Nairn, 1984), and microseismicity evidence suggests this fault may act as a barrier to injection flow across its strike (Sewell et al., 2013; Sewell et al., 2015).

Following NAP startup, ongoing reservoir monitoring efforts have shown evidence of transient changes in the reservoir in response to the increased production. RJV's integrated monitoring strategy includes regular flowing and shut PTS, bi-monthly tracer flow testing and production fluid and gas chemistry sampling from operating wells, and reservoir tracer testing. The reservoir pressure response to NAP operations has been detailed elsewhere (Quiniao et al., 2013). In summary, relative to natural state pressures, pressure drawdown has been observed in some reservoir areas, while in other areas where significant mass is extracted, pressure drawdown is minor and recharge appears to play a key role (e.g., ~4 bar drawdown in well PW1, despite ~600t/h continuous production since NAP startup). The production enthalpy and chemistry changes tell a story of reservoir compartmentalization that is consistent with pressure responses, with areas variably showing evidence of boiling, marginal recharge, and in some cases chemical breakthrough from injection. Repeat temperature surveys have demonstrated that production well cooling due to injection is negligible, and therefore while these processes continue to be monitored closely, the current injection configuration appears to support sustainable generation.

### 3. NAPHTHALENE DISULFONATE TRACER TESTING (2011)

In April 2011, after one year of NAP operations, a reservoir tracer test was performed at Rotokawa in an effort to better understand the reservoir hydrogeology and fluid movements in response to the combined NAP and RGEN production and injection activities. 300 kg each of 1,5-, 1,6-, 2,6-, and 2,7NDS were injected as instantaneous, concentrated tracer slugs into four separate injection wells (IW1, IW2, IW3, and IW4). The selection of these tracers was based on their successful application at other geothermal fields managed by Mighty River Power as well as a number of geothermal reservoirs around the world including Ohaaki (New Zealand), Awibengkok (Indonesia), and Dixie Valley (USA) (Rose et al., 2000). Many of the naphthalene tracers had been tested to temperatures as high as 330°C in the presence of distilled water and were found to be stable.

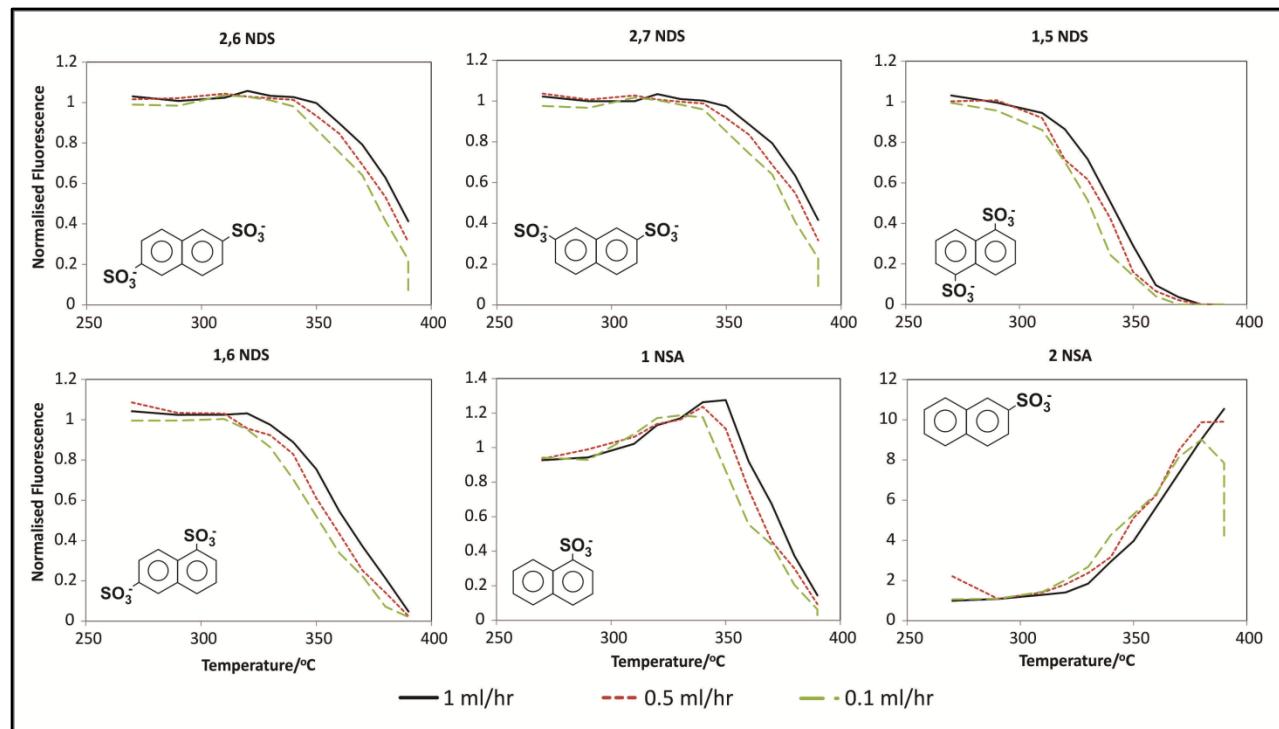
Production wells were monitored for the presence and concentration of injected NDS tracer for more than one year. After extensive analysis of the samples, none of the original NDS tracer compounds were detected. These findings were surprising given other geochemical indications of chemical breakthrough from injection. For example, on the basis of a chloride mass balance, production from well PW1 receives contributions of ~5.8% NAP brine injection fluid. This is consistent with other geochemical indicators, such as declining concentrations of non-condensable gas. However, with temperatures that exceed 337°C in the injection reservoir, Rotokawa is exceptional in that it is one of the hottest geothermal reservoirs currently in commercial operation (Sewell et al., 2012). Considering these factors, concerns arose as to the stability of injected NDS compounds under Rotokawa reservoir conditions.

#### 3.1 Tracer Stability Experiments (Mountain and Winick, 2012)

RJV commissioned a laboratory study with GNS Science in order to investigate NDS tracer stability at Rotokawa reservoir temperatures, pressures, and chemistry conditions. The experimental investigation used a one-pass, continuous flow, fluid-rock interaction simulator. These results are detailed in Mountain and Winick (2012) and have confirmed that at higher reservoir temperatures, the tracer compounds either break down completely or to more refractory naphthalene compounds that had not previously been recognized or analysed as part of the 2011 reservoir tracer test.

Figure 2 shows a graphical summary of Mountain and Winick's (2012) autoclave stability results for the six naphthalene disulfonic and sulfonic acids (NDS and NSA) which were tested. The results indicate the following:

1. 2,6- and 2,7NDS (injected at wells IW3 and IW4) appear to be thermally stable until ~340°C.
2. 1,5NDS (injected at IW1) begins to degrade at temperatures as low as 280°C with nearly complete loss by ~350°C.
3. 1,6NDS (injected at IW2) begins to degrade at 320°C.
4. 1NSA increases markedly at 310°C, peaks between 330-350°C, and then declines.
5. 2NSA increases continually until 370°C then it begins to decline.



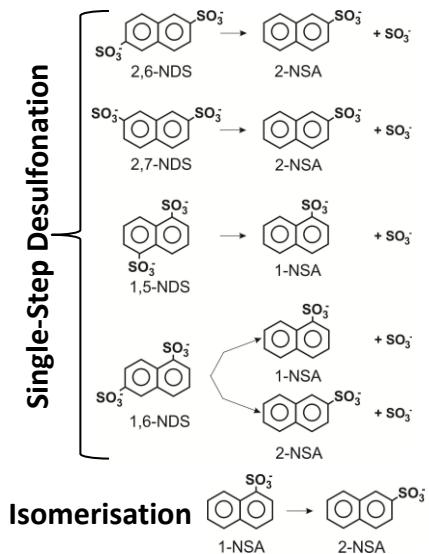
**Figure 2: Normalized fluorescence of six naphthalene sulfonic acids versus temperature at three different experimental autoclave flow-thru rates (after Mountain and Winick, 2012).**

The experimental autoclave water:rock ratios (~2:1) were more water-dominated than typical reservoir conditions. Additionally, the fluid residence times in the experiment were significantly less than actual residence times in a typical geothermal reservoir (hours to days in the experiment vs. weeks to months in a reservoir). Considering these factors and the large influence that varying

flow rate and residence time have on tracer stability, we can expect tracer breakdown behaviour to be more strongly expressed within a geothermal reservoir.

Some complex reactions appear to be responsible for the tracer decomposition, and these are explored in greater detail in Mountain and Winick (2012). As summarized below and shown in Figure 3, three possible reactions or processes are hypothesized to explain the experimental behaviour:

1. Desulfonation - the loss of one or more sulfonate groups;
2. Isomerisation - the switching of the sulfonate group position; and
3. Naphthalene pyrolysis - the breakdown of the naphthalene backbone and a complete loss of fluorescence (i.e., tracer detectability).



**Figure 3: Desulfonation and isomerization processes for selected naphthalene sulfonate tracers (after Mountain and Winick, 2012).** While isomerization may also occur, it is expected to be a second order process as kinetically, desulfonation is the favored breakdown pathway. Due to the mirror-plane symmetry of 2,6- and 2,7NDS, both will desulfonate to 2NSA. 1,5NDS will desulfonate to 1NSA and because of its lack of symmetry, 1,6NDS can desulfonate to either 1NSA or 2NSA.

Although 2NSA appears to be the most stable of the tracers and the other NDS and NSA isomers appear to be variably breaking down to 2NSA, a comparison of total fluorescence showed clear degradation of the naphthalene moiety begins above about 340°C. While complete pyrolysis of the 2NSA probably occurs above 370°C, some of this naphthalene pyrolysis likely begins at temperatures around 340°C. Complicating tracer behaviour further, comparative experiments using greywacke drill cuttings and crushed quartz have demonstrated that rock substrate likely influences naphthalene sorption, and this may play an important role in reservoir retention and breakdown of the tracer.

### 3.2 Experimental Implications

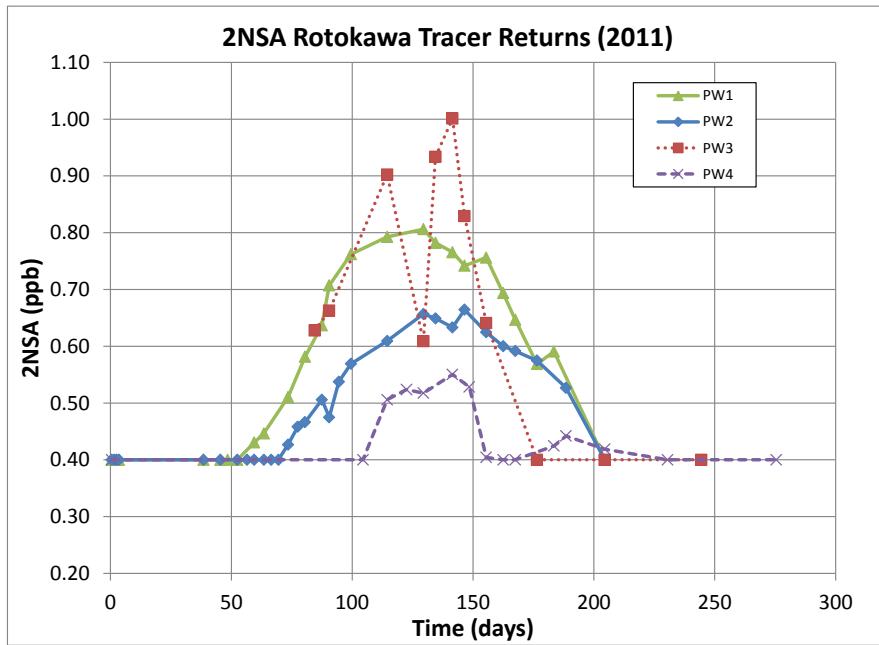
Based on the experimental work, it was hypothesized that for a reservoir dosed with either 2,6- or 2,7NDS, tracer returns should show no change in isomer below about 330°C. Above this temperature, 2NSA would be the only isomer expected. Injection of 1,5NDS in reservoirs hotter than 270°C would be expected to show returns of both 1,5NDS and 1NSA, with increasing breakdown to 1NSA at higher temperatures between 270–330°C, and no 1,5NDS returns above 330°C. Dosing a reservoir with 1,6NDS is predicted to result in a mixture of 1NSA and 2NSA up to temperatures of about 340°C. At higher temperatures, only 2NSA would be expected, though this too may continue to breakdown as the naphthalene moiety is pyrolyzed with both increasing residence time and temperature.

Given that the initial-state injection reservoir temperatures at Rotokawa exceeded 337°C and that temperatures in the main production reservoir are between 300–330°C, the experimental findings suggest that the isomers of NDS injected in 2011 would probably not have lasted in the reservoir as NDS for a significant period of time. This provides an important explanation for why none of the injected NDS from the 2011 tracer test was detectable, despite more than one year of monitoring and other independent geochemical evidence of injection chemical breakthrough. These findings prompted a re-analysis of the 2011 sample suite specifically targeted at 1NSA and 2NSA.

### 3.3 NSA Re-analysis and Results

Re-analysis of the 2011 tracer sample suite for 1NSA and 2NSA resulted in the positive detection of 2NSA in production wells PW1, PW2, PW3, and PW4. Of equal importance, no 1NSA was detected in any of the re-analysed samples. It is noteworthy that by this point in time, neither 2NSA nor 1NSA had ever been used as a tracer at Rotokawa. Therefore the presence of 2NSA in the reservoir could only come from the breakdown of the injected NDS tracers, or as naturally occurring trace organic constituents. We consider the latter to be very unlikely as measurements of 2NSA (and 1NSA) background samples are always below detection limits. Figure 4 shows the actual 2NSA returns observed at Rotokawa. The first arrivals of these tracer returns occur between

about 59 days and 3.5 months following injection of the tracer at Time=0 days. Tracer behavior for PW3 and PW4 is more complex with multiple peaks, suggestive of discrete flow paths between injection and these two particular wells. The total mass of 2NSA recovered from all wells is very small (<2.6 kg), and PW1 comprises more than 55% of this amount.



**Figure 4: 2NSA tracer returns detected in Rotokawa wells following a re-analysis program targeting NDS breakdown products. Analytical detection limits for 2NSA at this point in time were 0.4 ppb, which have been improved by an order of magnitude in later tracer tests.**

When considered within the context of the experimental findings summarized above, these results allow for the formulation of the following hypotheses with important implications to Rotokawa reservoir hydrogeology:

1. The 1,5NDS injected in IW1 most likely desulfonated to 1NSA. The natural state temperatures in the vicinity of IW1 were unlikely to have been much higher than 300°C and therefore secondary isomerization from 1NSA to 2NSA probably did not occur. Both IW4 and IW3 are closer to production and have a combined injection mass flow more than five times the amount of IW1. It is unlikely that significant 1NSA (or isomerized 2NSA) from IW1 would be present as fluid recharge to the production area.
2. Because of its lack of symmetry (Figure 3), the 1,6NDS injected in IW2 has the most complex desulfonation pathway and can breakdown to either 1NSA or 2NSA. Both would be expected to persist in the reservoir until temperatures of ~340°C. Injection in IW2 is within an intermediate aquifer overlying the clay cap to the deep production reservoir. The lack of 1NSA returns provides confirmation that shallow injected fluids were not descending into the deep reservoir at the time of the test.
3. The two-fold rotation symmetry in 2,6NDS and the mirror plane symmetry in 2,7NDS (Figure 3) results in a desulfonation reaction to 2NSA, and in both cases this occurs at temperatures above 330°C (Figure 2). The 2,6NDS and 2,7NDS were injected into IW3 and IW4 respectively, and initial-state well data demonstrate temperatures >325°C, with nearby reservoir reaching at least 337°C. Under these conditions, all 2,6 and 2,7NDS could break down to 2NSA and the tracer origins would not be distinguishable between wells IW3 or IW4.
4. Regardless of whether the recovered 2NSA originated as IW3, IW4, or some combination of the two wells, assuming a one-to-one breakdown by mass of NDS to 2NSA, the total recovered tracer from all production wells is very small. The system may be relatively open with a net loss of injection fluid between the points of injection and production (Shook, 2005), and/or the 2NSA may also be pyrolyzing.

Based on these results and hypotheses, a basic conceptual hydrologic model was developed whereby some limited injection recharge is provided to production wells along the south-eastern margin of the main production axis. Microseismicity data suggests that the CFF acts as a barrier to injection flow across its strike and could focus the cooler, dense injection fluids to significant depths aiding in their reheating prior to being drawn toward the production zone along pressure gradients (Sewell et al., 2013; Sewell et al., 2015). Injection fluid which does reach the production wells appears to be extracting significant heat from the hot injection reservoir, such that all of the injected 2,6- and/or 2,7NDS has broken down to 2NSA. The broad peaks and relatively normalized distribution patterns, particularly from wells PW1 and PW2, are suggestive that the bulk reservoir between the injection and production sectors consists of a relatively homogeneous distributed fracture network as opposed to discrete fracture paths between injection and production. This would be expected to aid in the efficiency of heat extraction. Considering fluid residence times and experimental tracer behavior, fluids are likely being re-heated to at least 330°C.

The observations from the 2011 tracer test, when combined with the experimental characterization of naphthalene tracer temperature stability and re-analysis of 2011 samples targeted at detecting breakdown products, provided important understandings of tracer behaviour in the Rotokawa reservoir. They confirmed that NDS isomers are not stable at Rotokawa reservoir temperatures

and that they generally break down to 2NSA given sufficient residence time. However, the experimental work also showed that 2NSA is potentially an intermediate step on a path to complete naphthalene pyrolysis at temperatures above 340°C. Additionally, the reservoir substrate is inferred to play a role in tracer sorption and retention. Therefore, leaving temperature stability issues aside, naphthalene tracers in general may not behave as conservatively at Rotokawa as, for example, other naturally occurring ionic species such as chloride or iodide.

#### 4. COUPLED 2NSA AND RADIOACTIVE $^{125}\text{I}$ TRACER TEST (2013)

A new field-based tracer test program was planned and executed in 2013 in order to provide additional clarity on 2NSA behaviour and to achieve the fundamental, yet elusive, goal of fingerprinting injection fluid at Rotokawa. Because of the newly recognized thermal instability of the naphthalene tracers at Rotokawa (including 2NSA), and the limitations in alternative available tracers, an attempt to trace more than one injection well in this test was deemed impractical. Rather, a decision was made to focus the test on well IW4, which accepts the bulk of total Rotokawa field injection fluid, roughly 850t/h of NAP brine. The philosophy underpinning this test was to benchmark the performance of 2NSA against a known, thermally stable and conservative tracer. A radioactive isotope of iodine,  $^{125}\text{I}$ , was selected for this task.  $^{125}\text{I}$  has a known decay half-life of 59.4 days and is generally suitable for reservoir tracer tests up to about one year in duration (McCabe et al., 1983). Reservoir tracer tests using radioactive iodine isotopes (both  $^{125}\text{I}$  and  $^{131}\text{I}$ ) have been carried out more than 70 times across various New Zealand geothermal fields, including at Wairakei, Ohaaki, Kawerau, and Ngawha (Barry et al., 1979; Barry et al., 1982; Hunt et al., 1990; McCabe et al., 1995; Bixley et al., 1995).

##### 4.1 2013 Tracer Test Preparation, Injection, and Sampling

###### 4.1.1 Assessment of Tracer Background

In preparation for the injection tracer test, two separate sets of samples were collected in June from all production wells in order to determine background concentrations and activities of 2NSA and  $^{125}\text{I}$ . In the case of 2NSA, all background samples were below the 0.05 ppb detection limit. Similarly, the radioactivity for both  $^{125}\text{I}$  background sample sets were below detection levels.

###### 4.1.2 2NSA Injection

Prior to 2NSA procurement, tracer purity testing was performed on aliquots from the chemical supplier and the tracer was determined to have a bulk purity of 90% 2NSA. Only trace impurities of 2,6- and 2,7-NDS (<0.5%) were found with the remaining 9.5% of the bulk tracer presumably as un-sulfonated naphthalene. Solubility testing was also conducted on the bulk 2NSA to determine the ease of mixing with river water and to assess the injectivity of the resulting slurry. Relative to the other NDS tracers with which we have some familiarity, 2NSA was found to be of low solubility (only ~70% dilution could be achieved for mixtures of ~50 g per litre of river water). Modifications were made to the tracer injection setup to ensure rapid pumping of a 2NSA slurry. In July, 500 kg of bulk 2NSA were mixed with about 5000 litres of river water and the concentrated slurry was pumped into IW4. This was immediately followed by a further 5000 litres of clean river water to flush any residual tracer through the system and clean the injection equipment. Considering estimated tracer losses of ~50 kg while mixing, an effective dose of 405 kg pure 2NSA was administered to IW4.

###### 4.1.3 $^{125}\text{I}$ Injection

One week after the 2NSA injection, 16.5 GBq (~0.44 Ci) of radioactive  $^{125}\text{I}$  was injected in IW4. Injection of the  $^{125}\text{I}$  was performed by GNS Science following similar methodology to that outlined in McCabe et al. (1983), with some modifications to improve safety of the injection procedure and ensure complete injection of the isotope. These modifications included the use of a vacuum chamber to draw the 2.5 ml radioactive iodine tracer solution into the injector. This was followed immediately by a 60 ml KI solution and then by high volume pumping of 1000 litres of river water. This modification is significantly safer and more effective than previous methods which relied on physically crushing the vial containing the radioactive tracer solution within the injection apparatus.

###### 4.1.4 Sampling and Analysis

Sampling for both  $^{125}\text{I}$  and 2NSA was conducted at all Rotokawa production wells, subject to their operational availability. Sampling events followed an expanded tracer sampling schedule, whereby high frequency sampling was conducted immediately following the tracer injection to ensure capture of any rapid returns. Tracer returns are expected to demonstrate broader peaks with increasing time after injection due to the effects of tracer dispersion within the reservoir. These broader peaks may be adequately characterized with more infrequent sampling (Axelsson et al., 2005). Because the original  $^{125}\text{I}$  activity continuously decays with time, analyses of the  $^{125}\text{I}$  are time sensitive, and there is minimal opportunity to skip analyses and retroactively define the tracer recovery curves by selecting earlier samples to “fill in gaps.” Therefore, all available  $^{125}\text{I}$  samples were analyzed as part of this test. However, the  $^{125}\text{I}$  peak response was used to guide the frequency of analyses of 2NSA samples to help minimize analytical costs.

Sampling involved condensing two-phase production fluids through simple cooling coils attached to the production well branch lines. The cooling coils were fully purged and flushed before each sampling event to minimize the potential for sample contamination and erroneous results. Measurements of pH, temperature, and conductivity were collected in the field and tracer samples were collected only after these parameters were stable, providing additional assurance that the brine coils were conditioned with fresh sample. In addition to laboratory analyses for the 2NSA and  $^{125}\text{I}$  tracers, the samples were also analyzed for sodium which enabled a comparison against routine two-phase production well chemistry and enthalpy monitoring. This information was used to make the necessary steam dilution corrections to the tracer data. The 2013 tracer returns presented herein encompass more than nine months of monitoring data. Monitoring for additional tracer returns is on-going and is planned to continue until at least July, 2014 (one year following the start of the test).

#### 4.2 Results

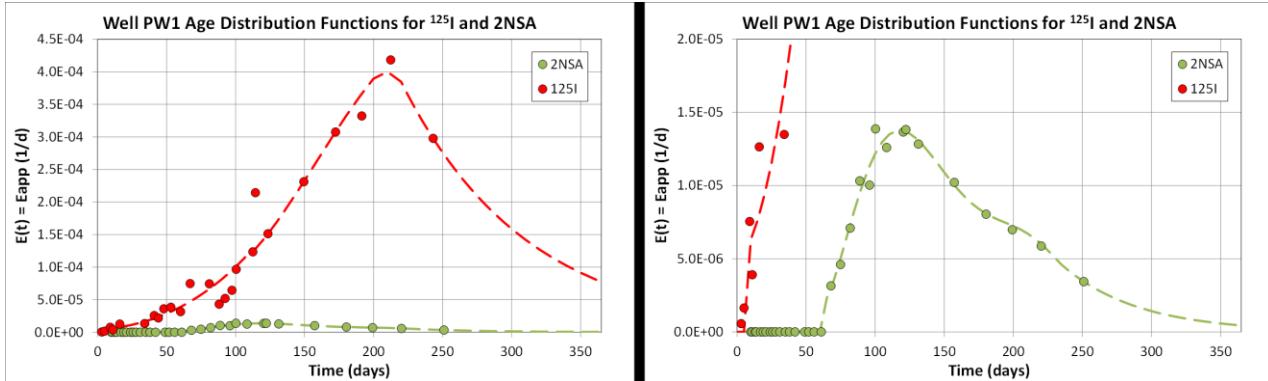
Similar to the 2011 tracer test, minor 2NSA was detected in wells PW1, PW2, and PW3.  $^{125}\text{I}$  was also detected in these wells in larger quantities. The largest and most significant 2NSA and  $^{125}\text{I}$  recoveries were observed in well PW1. Total recovered  $^{125}\text{I}$  from

all wells is estimated to be less than 10% of the total injected activity. This again suggests a relatively open system with net discharge from the reservoir between injection and production under the existing flow conditions. The results and discussion herein are focused on the well PW1 tracer response as this is the most prolific well in the field with the largest and fastest tracer responses, and based on routine pressure and chemistry monitoring the well appears to receive some pressure support and chemical breakthrough from injection of NAP brine at IW4.

#### 4.2.1 Tracer Recoveries

The tracer data are corrected for the effects of steam dilution and are presented as apparent age distribution functions,  $E_{app}(t)$  following the methodology of Shook and Forsmann (2005). This not only allows for direct comparison of the  $^{125}\text{I}$  and 2NSA response curves by normalizing the data against injection well mass flow rates and total injected tracer mass or activity, but it is required as input to temporal moment analysis.

With the exception of a few short operational interruptions, e.g. NAP station outages, production and injection flows were generally maintained at a constant rate through the duration of the test. The tracer data were corrected for these operational outages by subtracting these periods from the time series data in order to obtain uninterrupted tracer response curves. Production and injection activities for the wells of interest effectively cease during this time. While some limited production associated with RGEN did continue during these periods, the interruptions are believed to have minor effect on the overall tracer results. The 2NSA and  $^{125}\text{I}$  corrected age distribution profiles for PW1 are shown in Figure 5.



**Figure 5: Normalized tracer returns for 2NSA and  $^{125}\text{I}$  expressed as age distribution functions following the methodology of Shook and Forsmann (2005). Figure 5B is an expanded scale of Figure 5A, to provide resolution on the 2NSA response curve. First arrival and peak arrival times, as well as peak magnitude are significantly different for the two tracer response curves.**

The characteristics of the 2NSA and  $^{125}\text{I}$  tracer recovery profiles are quite different in several respects. Most notably is the order of magnitude larger response curve for  $^{125}\text{I}$  as compared to 2NSA (Figure 5). At their respective peaks,  $^{125}\text{I}$  returns are 28 times larger than the 2NSA returns. In addition to the large difference in normalized signal, the first arrivals of the two tracers also differ by as much as 55 days, with  $^{125}\text{I}$  first arrivals at around 10 days post-tracer injection and 2NSA first arrivals at about 65 days.

Recovery of the 2NSA and  $^{125}\text{I}$  tracers in production well PW1 are calculated as percentages of the total mass or activity injected to IW4. This is achieved by integrating the area under the PW1 tracer recovery curves with production well mass flow rates and known fluid densities. The resultant tracer recoveries in PW1 are more than an order of magnitude larger for the  $^{125}\text{I}$  (3.4%) as compared to the 2NSA (0.1%). Simple multiplication of these recoveries by the integrated ratio of injection to production mass flows enables an estimate of the quantities of traced injection fluid which contribute to PW1 production. On the basis of the  $^{125}\text{I}$ , production well PW1 is estimated to receive a 5.6% injection fluid contribution from injection well IW4. This is very consistent with independent estimates of 5.8%, made on the basis of chloride mass balance. The same calculation made on the basis of the 2NSA response curve suggests <0.2% IW4 injection contribution to PW1. The evidence indicates that 2NSA grossly underestimates the contribution of IW4 injection fluid to PW1.

Some of the diminished 2NSA response may very well result from unavoidable differences in instantaneous tracer dose concentrations. It takes longer (minutes) to pump a 5000 L slurry of naphthalene tracer as compared to the 2.5 ml of radioactive iodine. Therefore, the iodine tracer can be effectively dosed instantaneously to the reservoir. However, the calculated instantaneous dose rates achieved for this 2NSA test compare favorably to other naphthalene injection tests we have conducted. In those cases, naphthalene tracer returns were commonly of the order of tens of ppb, as compared to maximum 2NSA concentrations of 0.4 ppb in this test. It is worth noting that 2NSA responses from the 2011 test registered peak concentrations of 0.8 ppb for PW1 and yet similar instantaneous dose concentrations were achieved for this earlier test. It is not entirely clear why twice the amount of 2NSA was detected in the 2011 test as compared to the 2013 test, though it may relate to differences in injection well flow rates or bulk quantities of tracer injected. Regardless, if instantaneous dose concentration were the only cause of the difference between 2NSA and  $^{125}\text{I}$  response, we would still expect very similar tracer first arrival and peak arrival times. In fact, both the 2NSA and  $^{125}\text{I}$  first- and peak arrival times, as well as the overall response curve shapes are quite different. Considering the experimental evidence that 2NSA tracers potentially pyrolyze above 340°C, and that reservoir formation appears to influence tracer retention, we hypothesize that thermal decay and some minor component of sorption of 2NSA are responsible for the differential tracer behavior of 2NSA and  $^{125}\text{I}$ .

#### 4.2.2 Temporal Moment Analysis

Following the methodology of Shook and Forsmann (2005), a temporal moment analysis was performed on both 2NSA and  $^{125}\text{I}$  recovery curves. This was done in order to estimate inter-well flow volumes, mean tracer residence times, and to give semi-quantitative description of the fracture geometry (an F-C plot of flow capacity vs. storage capacity).

The first step in performing moment analysis of geothermal tracer data is to correct for thermal decay. As the principals of radioactivity are governed by nuclear forces and quantum theory, isotope decay rates are independent of temperature. Therefore  $^{125}\text{I}$  is not subject to thermal decay in the reservoir and does not require any corrections to the data. For the reasons elaborated above, 2NSA is believed to be susceptible to thermal decay, though the decay kinetics are not currently constrained. It was therefore not possible to correct the 2NSA data. Rather, the difference in the temporal moment analysis for  $^{125}\text{I}$  and 2NSA highlights the influence that thermal decay can have on 2NSA in underestimating reservoir properties.

Table 1 summarizes some of the key tracer recovery characteristics described above and the results of the temporal moment analyses. Mean residence times and pore volumes swept by the tracer are unrealistically low for the 2NSA as compared to  $^{125}\text{I}$ . Mean tracer velocities are estimated to be between about 4.5 and 6.1 m/day.

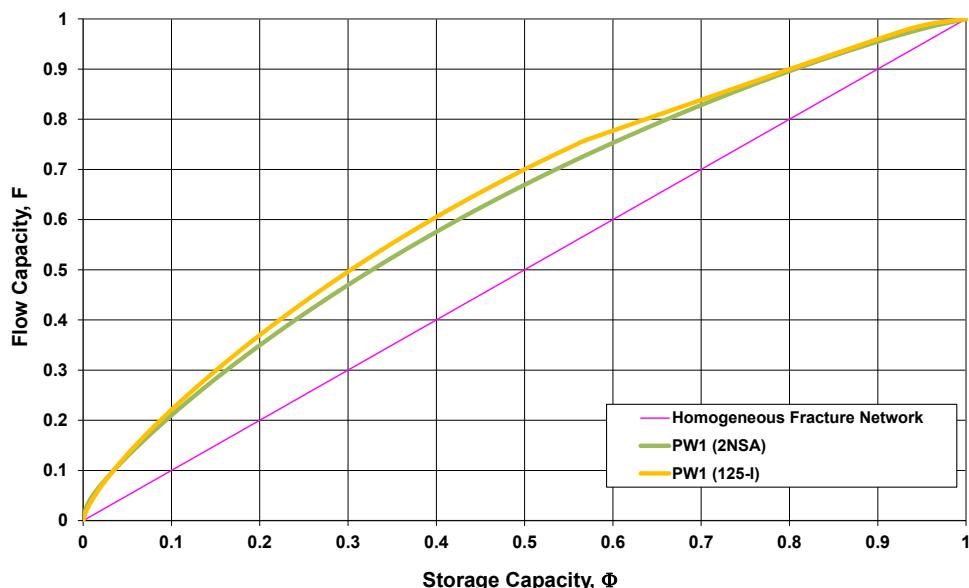
**Table 1. Summary of well IW4 tracer test results for well PW1**

Tracer Test	Injected Tracer in IW4	Injected Tracer Mass (Activity)	Recovered Tracer	First Arrival in PW1	Peak Arrival in PW1	% Tracer Recovered in PW1	% IW4 in PW1	Mean Tracer Residence Time	Swept Pore Volume	Mean Tracer Velocity
		kg (GBq)		Days	Days	%	%	days	m3	m/day
2011	2,7NDS	300 kg	2NSA*	59	129					Unknown*
2013	2NSA	405 kg	2NSA	65	105	0.11%	0.17%	158	6,857	6.1
2013	$^{125}\text{I}$	16.5 GBq	$^{125}\text{I}$	10	212	3.80%	5.60%	228	339,058	4.2

\*While 2NSA was recovered in the 2011 test, because it could have originated via multiple breakdown pathways from the NDS which was injected in multiple wells, it is not possible to trace the injection well(s) origins of the 2NSA. Therefore, without making significant and unconstrained assumptions, it was not possible to calculate percentages of tracer recovery, injection flow in PW1, mean tracer residence time, swept pore volumes, or mean tracer velocities.

The F-C plot for  $^{125}\text{I}$  and 2NSA is shown in Figure 6. On the basis of both tracer response curves, the fracture geometry of the reservoir between wells PW1 and IW4 is estimated to be a relatively homogeneously distributed set of fractures. As the moment analysis “sees” the bulk reservoir properties, the long mean residence time and broad recovery peak of  $^{125}\text{I}$  does not preclude the possibility that a low permeability feature, such as the CFF, could play a key role in focusing injection fluid to significant depths where it is reheated prior to breakthrough at production (Sewell et al., 2015). Its presence would suggest that the surrounding reservoir would be characterized by a relatively homogeneously distributed set of fractures. This is revealing given the currently known reservoir characteristics of Rotokawa that demonstrates some level of compartmentalization over similar areal extents. It suggests that wells PW1 and IW4 may share a large reservoir compartment and could help explain why this area of reservoir is so prolific both in terms of production and injection.

**Well IW4-Well PW1 F- $\Phi$  Diagram**



**Figure 6: F-C plot from temporal moment analysis of 2NSA and  $^{125}\text{I}$  tracer response curves (after Shook and Forsmann, 2005).**

#### 4. CONCLUSIONS

In addition to important new insights on Rotokawa field-specific reservoir properties, some important conclusions are developed regarding the behavior of naphthalene tracers within high-temperature geothermal reservoirs. From this work, 2NSA was found to be thermally unstable within the Rotokawa geothermal reservoir as determined from the experimental data of Mountain and Winick (2012) and as confirmed from the field-based behavior of 2NSA in actual reservoir tracer tests performed at Rotokawa. None of the naphthalene tracers we have investigated will behave conservatively within the Rotokawa reservoir, and these would be expected to present similar issues within other very hot geothermal systems around the world. At present, the only known liquid phase tracers which will exhibit true conservative behavior and allow for targeted fingerprinting of individual injection wells in the Rotokawa reservoir are those using radiogenic isotopes (e.g. iodine and tritium).

The  $^{125}\text{I}$  tracer behaves conservatively and the calculated tracer returns and contributions of injection fluid in production based on  $^{125}\text{I}$  closely match that of the routinely monitored chloride response in production well PW1. The injection returns from the NAP brine injection well IW4 has been estimated to be at 5-6% of produced fluid in PW1. The monitored chemistry and pressure responses combined with repeat temperature surveys acquired over the last four years of production from PW1 demonstrate that this well is receiving sufficient pressure support through injection without any degradation in reservoir temperature or performance. On the basis of expected vs. actual tracer returns, as well as experimental data, injection fluids are likely reheating significantly prior to their arrival at production. This helps confirm the positive impact of IW4 injection in sustaining production from PW1, and suggests an optimum operational injection configuration that can be maintained for the Rotokawa field. The results also provide valuable constraints on numerical simulations of pressure support and the speed of thermal front advancement within the reservoir. These forecasts are crucial to ensuring an optimal injection and production strategy, and they form a central part of our reservoir management strategy.

Not only does 2NSA not reflect real fluid movements through the reservoir in the way that  $^{125}\text{I}$  does, but the temporal moment analysis highlights the extent to which 2NSA grossly underestimates a number of important reservoir characteristics and properties; in particular reservoir volumes swept by the tracer and mean tracer residence times.

Finally, additional work is required to understand the kinetic breakdown rates of 2NSA. Once this is known, it should be possible to semi-quantitatively assess reservoir temperatures along the flow paths between IW4 and production wells by comparison and correction of the 2NSA tracer data to a thermally stable tracer like  $^{125}\text{I}$  (Adams and Davis, 1991; Axelsson et al., 2005). Mighty River Power continues to support research and development efforts into naphthalene tracer stability and thermal decay kinetics through collaborative efforts with GNS Science and the University of Victoria Wellington (Dashkevich et al., 2015). It is hoped that this will allow for a retroactive correction of the 2NSA data and will open options for multi-well reservoir tracer testing at Rotokawa where we are currently constrained by the availability of a limited suite of known, thermally stable tracers.

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