

# GEOCHEMICAL MODELLING OF PLANT AND RESERVOIR PROCESSES AT THE NGATAMARIKI GEOTHERMAL FIELD

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## ABSTRACT

This paper discusses two examples of geochemical modelling applied to the plant and reservoir processes at the Ngatamariki geothermal field. The first case simulates the cooling of the geothermal fluid as it flows through a series of heat-exchangers in the Ngatamariki binary plant and aims at characterizing the deposition of sulfide minerals on the heat-exchange surfaces. Modelling results provide indications of the most likely locations for these minerals to deposit as well as their typology and the amount of minerals deposited. The results are relevant in designing suitable maintenance activities for the heat-exchangers and in improving the operational process through increased understanding of deposition types, rates and locations.

In the second case a reactive transport model is used to assess the impact of injection fluid in the Ngatamariki geothermal reservoir. Modelling results provide semi-quantitative information to interpret and validate the fluid chemistry composition observed in the production wells, in particular the increase in sulfate concentration.

Both examples highlight the value of geochemical modelling in enhancing the understanding of geochemical processes at the plant or in refining the reservoir management strategy. As modelling results rely heavily on thermodynamic data that can be very different across the literature, this paper also looks into the challenges and limitations of using geochemical modelling in an operational perspective and suggests areas for improvements.

## 1. INTRODUCTION

In an undeveloped state, a geothermal reservoir is the seat of continuous mineral-fluid reactions naturally occurring. Additional chemical processes are taking place in a producing geothermal field (Figure 1):

- As the fluid is withdrawn from the reservoir through a production well, it boils and may deposit calcite on the wellbore walls;
- During heat extraction at the surface, either through conductive cooling via a heat-exchanger or further boiling through a separator, the cooler or more concentrated fluid has the potential to deposit minerals;
- Reinjecting a fluid out of equilibrium with the natural reservoir condition lead almost inevitably to deposition of minerals in the reservoir;
- Reservoir processes induced by production and/or reinjection such as boiling, injection returns or cold

marginal recharge may result in changes in fluid chemistry and in most cases enhance potential for minerals precipitation. Condensation of steam in the subsurface can produce low-pH fluids that can affect the geothermal well casing integrity due to corrosion.

These processes have a number of detrimental effects in a commercial development: scaling in production/injection wells reduce the fluid flow and can lead to reduced power generation, pipes at the surface get clogged, scaling in the heat-exchangers reduce their efficiency, and scaling in the reservoir can impact the reservoir permeability.

Several of these processes can be encountered in geothermal fields and because of the significant resources allocated to deal with them, there are a number of strong commercial incentives to:

- Enhance the value of the chemical information to better understand these chemical processes, and rationalize the monitoring and field surveillance;
- Optimize the production/injection strategy and the station design in order to prevent or mitigate scaling in the reservoir or in the surface facilities (pipeline, separator, heat exchangers, etc.)
- Better understand the chemical processes to minimize risks to geothermal power generation.

In this context, geochemical modeling could prove immensely useful. However, geochemical processes taking place during the commercial operation of a geothermal field are complex. Modeling these processes is even more challenging, usually restricted to the realm of academic research at present. There is also a widely held belief that geochemical modelling does not produce practically useful results (Zhu and Anderson, 2002).

This paper presents two examples of geochemical modelling applied to the plant and reservoir processes at the Ngatamariki geothermal field, and discusses the challenges and opportunities of implementing geochemical modelling in an operational perspective.

The Ngatamariki geothermal field is located in the central part of the Taupo Volcanic Zone (TVZ), 17 km north of Taupo, New Zealand. A 83 MWe binary plant was commissioned in October 2013, making use of the field with a geothermal fluid consented take of up to 60,000 t/d from four production wells. About 98% of the produced fluid is reinjected back to the reservoir.

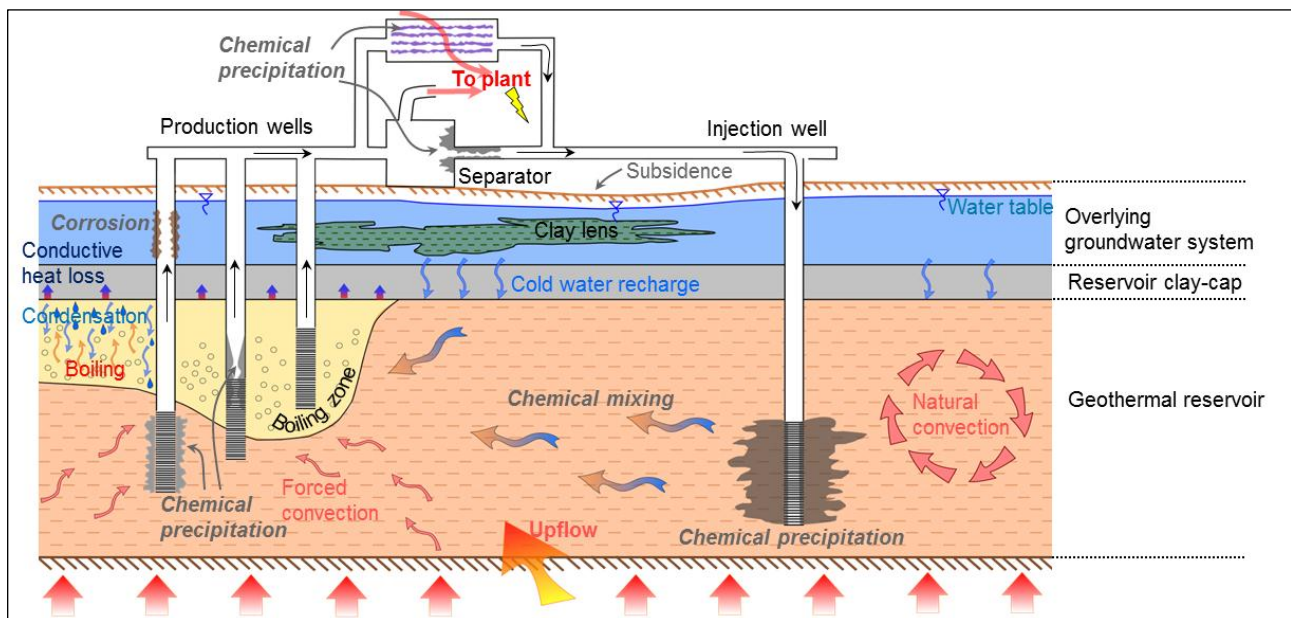


Figure 1: Schematic of geothermal reservoir processes (adapted from Bodvarsson and Witherspoon, 1989)

## 2. GEOCHEMICAL MODELLING OF As/Sb SULFIDES IN BINARY PLANT

### 2.1. Heat-exchange process and scaling occurrences

The Ngatamariki power station is made up of 4 independent OEC units (Ormat Energy Converter), which use n-pentane as the motive fluid. Produced geothermal fluid (steam and brine) is used to heat, vaporize and superheat the n-pentane through a series of heat-exchangers (pre-heaters, vaporizer and super-heater). In particular, the pre-heating unit uses the mixed steam-condensate and brine to heat up the pentane. This process conductively cools down the geothermal fluid from about 175°C to 90°C (Figure 2). Under these conditions and because of the geothermal fluid composition (Table 1), antimony (Sb) and arsenic (As) sulfides can precipitate in the heat-exchangers, causing a loss of heat transfer and potentially blocking the heat exchangers.

These precipitates were characterized during the Ngatamariki development plant trials (Addison and Brown, 2012; Brown et al., 2014) and more generally in geothermal binary plants in New-Zealand (Wilson et al., 2007, Brown, 2011). It was initially estimated that about 275kg of Sb-sulfides and 70 kg of As-sulfides would deposit within 6 months in one such pre-heating unit under the expected flow conditions. This scaling process is also extremely sensitive to pH and redox variations.

Table 1: Chemical composition of the geothermal fluid at the plant

Fluid	pH (22°C)	As (mg/kg)	Sb (mg/kg)	SO <sub>4</sub> <sup>2-</sup> (mg/kg)	H <sub>2</sub> S <sub>aq</sub> (mg/kg)
Brine	7.4	2.5	0.14	4.6	7
Condensate	4.9	-	-	-	102
Reinjection	5.5	2.0	0.03	2.9	26

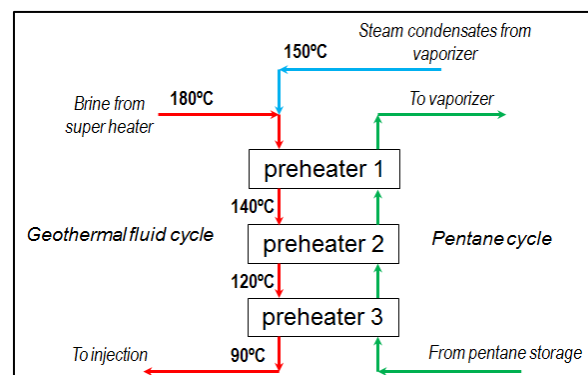


Figure 2: Schematic of the Ngatamariki pre-heating process

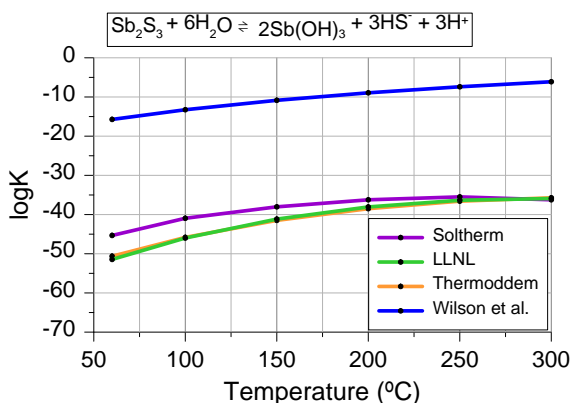
### 2.2 Geochemical modelling setup

Geochemical modelling is used to characterize and assess the amount of Sb and As-scales depositing in the pre-heating unit, in order to provide information for mitigation options and maintenance scheduling.

The reaction path is relatively simple and assumes that only conductive cooling process is happening, with no phase changes or interactions with minerals (scales) in the heat-exchanger tubes. Modelling is achieved using the Geochemist's Workbench (Bethke, 2011) and Solveq/Chim-xpt (Reed, 1982).

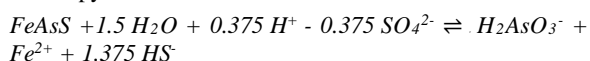
Three databases are considered: Soltherm (Reed, 1982), LLNL (Wolery et al. 1992) and Thermoddem (Blanc et al., 2012), as well as additional experimental data from Wilson et al. (2007) and Brown (2011). In these databases, Sb- and As-minerals are principally defined as Stibnite (Sb<sub>2</sub>S<sub>3</sub>), Berthierite (FeSb<sub>2</sub>S<sub>4</sub>) and Arsenopyrite (FeAsS), Orpiment (As<sub>2</sub>S<sub>3</sub>) or Realgar (AsS) respectively. Sb-minerals are described mainly in Soltherm and Thermoddem. The quality of the thermodynamic data is a subject of endless debate, exemplified here by the stibnite solubility shown in Figure 3. While the available databases are in a relative

agreement, the solubility data from Wilson et al. are significantly different, yet deemed to be more consistent with observed stibnite deposition at Ngawha and Rotokawa (Wilson et al., 2007).

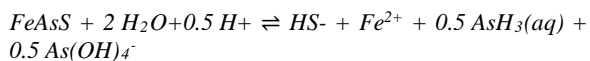


**Figure 3: Solubility of stibnite (for the reaction as written in the title) in various thermodynamic databases**

Another difficulty arises from the reaction describing the mineral solubility. For example, Soltherm and Brown et al. (2011) uses the reduced As(III) form to describe Arsenopyrite:



On the other hand, in the LLNL database, arsenopyrite dissociation is described using a “hydroxide” As(III) species but also aqueous arsine  $\text{AsH}_3(\text{aq})$  (-III). This form of arsenic is not expected under geothermal condition, but no alternative definition is offered in this database. It is defined as follow:



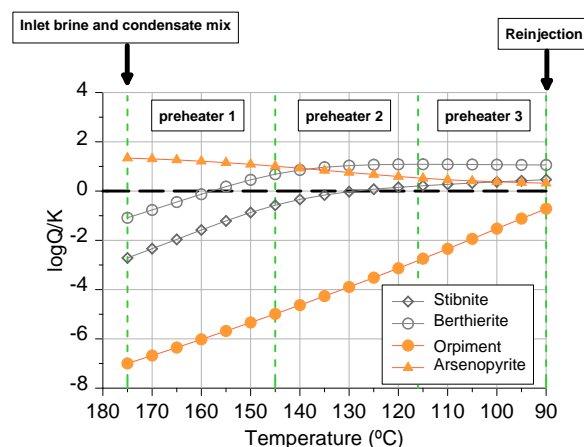
Such differences in the basis render comparisons between database and results more difficult. It also points out that the adequate species must be chosen to describe the system properly.

Kinetic rates of dissolution/precipitation for these minerals are not available and the reaction path is simulated using thermodynamic equilibrium only. It is first run without precipitation to assess the thermodynamic stability of the As/Sb minerals and in a second simulation it is run removing precipitates (“flow-through” option in GWB or “solid fractionation” in Chim-xpt). Redox is a key parameter controlling Sb and As-minerals precipitation and is described using the  $\text{H}_2\text{S}(\text{aq})/\text{SO}_4^{2-}$  redox couple.

### 2.3 Results

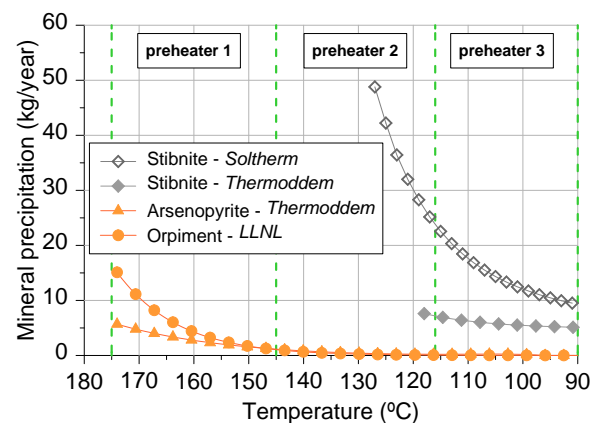
Modelling results (Figure 4, from Soltherm) show that arsenopyrite can precipitate in all the pre-heaters while berthierite and stibnite are mostly supersaturated in preheaters 2 and 3. These results only indicate which minerals can conceivably precipitate. Similar results are obtained using the Thermoddem database. In contrast, no Sb-minerals appear to be saturated over this range of temperature using the LLNL database, even using the stibnite solubility mentioned in Wilson et al. (2007); while orpiment and realgar are oversaturated and could potentially precipitate. Overall results suggest that preheaters 2 and 3 are more at risk with respect to scaling as

more minerals are supersaturated in these temperature ranges.



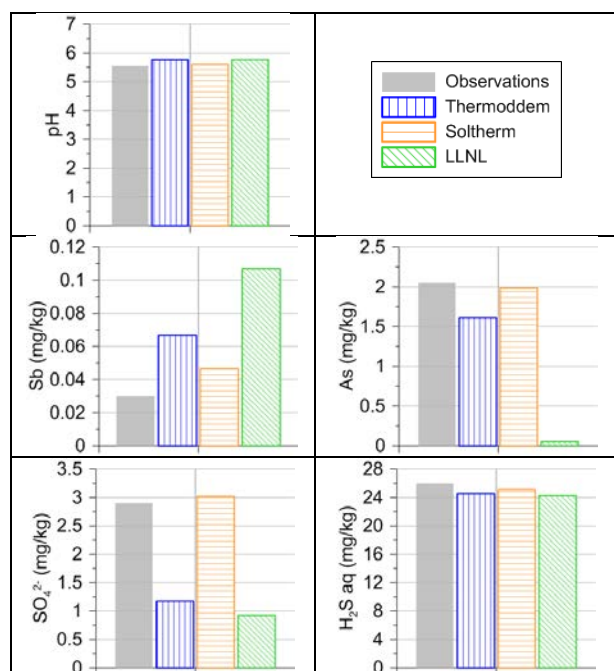
**Figure 4: Saturation indices for As/Sb minerals from Soltherm**

The reaction path is run again this time allowing the minerals to precipitate (Figure 5). Stibnite is precipitating below 130°C in both Thermoddem and Soltherm databases and total modelled amount of stibnite deposited in the preheaters unit ranges from 210 kg/year to 420 kg/year respectively under the current operating conditions (fluid flow of ~460 t/h, the total amount is obtained by calculating the area under the modelled deposition curve). The bulk of the deposition takes place in the preheaters 2 and 3. Results also suggest that orpiment and arsenopyrite are precipitating mostly within preheater 1 (total of 125 kg/yr. and 200 kg/yr. respectively).



**Figure 5: Modelled deposition of As/Sb scales in the preheaters for various databases**

The modelled fluid composition at the end of the cooling process is presented in Figure 6 below (for selected elements): calculations with Soltherm appear to be the closest to the observations, suggesting that a relevant amount of minerals is deposited.



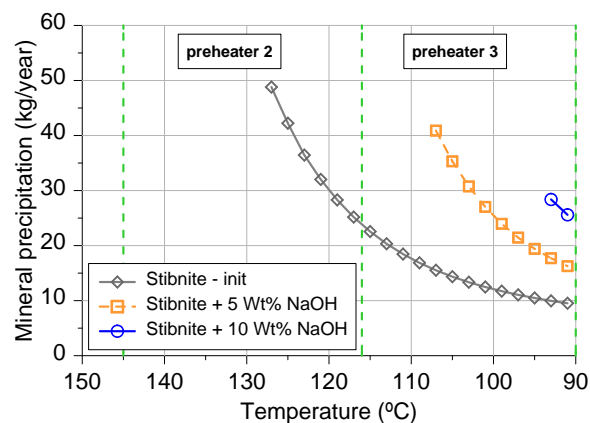
**Figure 6: Observed and modelled chemistry of the reinjection fluid**

After about 2.5 years of service since the commissioning of the plant in 2013, a decrease in the heat-exchangers performance was observed and the preheaters unit from OEC2 underwent a chemical cleaning in early 2016. Concentrations of antimony and arsenic were measured in the resulting effluent and it was calculated that approximately 800 kg of Sb-materials and 80 kg of As-materials were removed from all 3 preheaters. The recovered amount is consistent with the modelled expectations over the running period (about 2.5 years). The decrease in heat-exchangers performance was most noticeable in the last preheater. As modelling results show that most of the scales are expected to drop out in preheater 3, the model is also in agreement with this observation.

## 2.5 Modelling on-line sodium hydroxide dosing

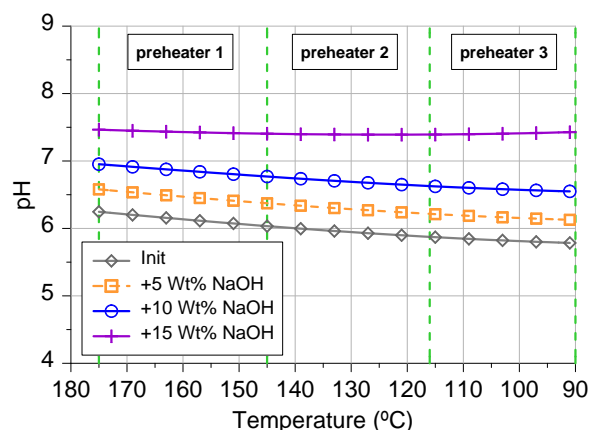
As the low-pH environment favors the deposition of Sb-sulfides, dosing the geothermal fluid with sodium-hydroxide to raise the pH before the heat-exchangers is an option to mitigate the deposition.

The potential benefits of on-line sodium hydroxide (NaOH) dosing are assessed through the model: various concentrations of NaOH(aq) are added at a 1‰ ratio (i.e. about 0.5 t/h for 500 t/h of geothermal fluid) prior to cooling. Addition of NaOH progressively pushes stibnite deposition further down the temperature range (Figure 7), minimizing the scaling effect on the last preheater. Beyond 10 Wt.% NaOH addition, stibnite is not thermodynamically stable anymore and deposition is entirely mitigated (using the Soltherm database).



**Figure 7: Modelling addition of caustic in the geothermal fluid (Soltherm)**

Fluid pH rises up to 7.5 due to NaOH addition (Figure 8) and may adversely promote silica polymerization in the preheaters.



**Figure 8: Modelled pH with addition of caustic (Soltherm)**

This modelling indicates that the costs of treating the fluid with sodium hydroxide to prevent deposition in the heat exchangers are significantly higher than the costs of periodically cleaning the heat exchangers.

## 2.4 Implications for plant operations

In this particular example, geochemical modelling provides a first-order estimate of the amount of minerals deposited, which can be used to design and implement a remediation option. In the case of a one-off chemical cleaning, it gives a basis for the amount of chemicals required to remove the desired amount of the scales. In the case of an online dosing system, it provides the amount of chemicals required to prevent the deposition of Sb-scales.

It also indicates which section of the pre-heaters unit is likely to be the most affected by deposition (i.e. preheater 3) and as such identifies the best candidate for a targeted cleaning option, if plant outage time and budget are constrained.

From a practical perspective, several thermodynamic databases had to be used to model the full spectrum of Sb and As-scales observed in the heat exchangers. While Soltherm provides satisfying approximations for Sb-minerals, it does not forecast As-minerals. On the other hand, Thermodem simulates the presence of As-minerals



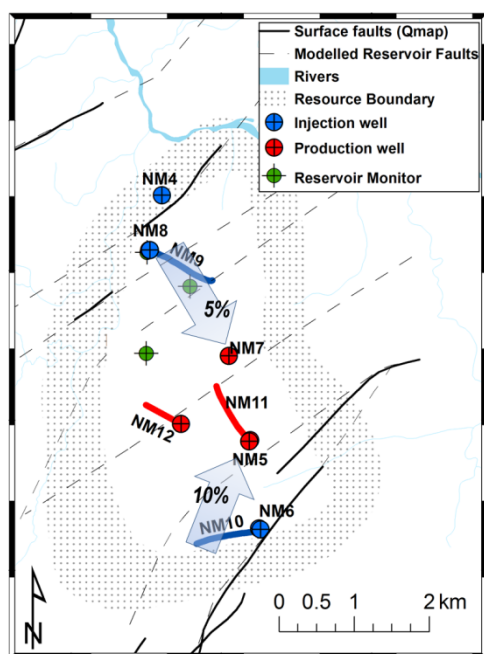
in reasonable amount but fails to model Sb-minerals deposition. As a result, it is not possible to rely on a single database to assess scaling in this case.

### 3. REACTIVE TRANSPORT MODELLING OF INJECTION RETURNS

In this second case study, geochemical modelling is applied to provide a semi-quantitative understanding of the production fluid chemistry.

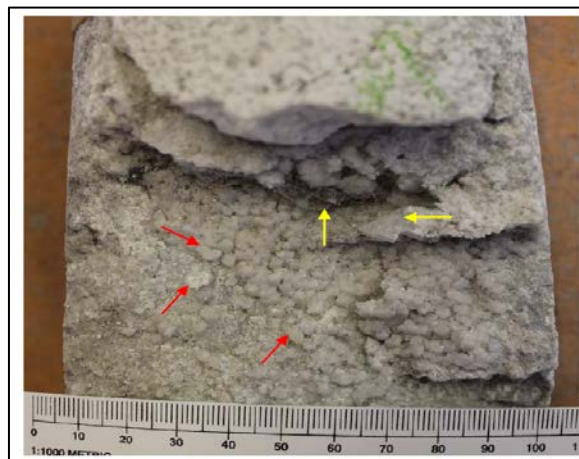
#### 3.1 Injection returns at Ngatamariki

Since the Ngatamariki power station is a binary plant, the reinjection fluid is almost identical to the produced fluid, being only degassed (A portion of non-condensable gases (NCG) are vented off to the atmosphere during the heat-exchange process) and much cooler. As such, there are no immediate chemical indicators for injection returns in the production fluid and the composition of the production fluid has thus remained largely unchanged since commissioning. The only noticeable trends overall have been a decrease in total gases content and a steady increase in sulfate in both NM5 and NM7. On the other hand, a reservoir tracer test conducted in 2014-2015 showed that about 10% of tracers were recovered in NM5 from the southern injector NM10 and 5% in NM7 from the northern injector NM9 (Buscarlet et al., 2015, Figure 9). The reduced gas content observed in the production fluid at NM5 and NM7 suggests initially the presence of injection returns.



**Figure 9: Ngatamariki Geothermal Field layout. Blue shaded arrows represent the percentage of tracers recovered during the 2014-2015 tracer test.**

In addition, anhydrite ( $\text{CaSO}_4$ ) has been observed in rock cores in both the northern and southern injection wells, for instance in open fracture in NM9 (Figure 10). Owing to its retrograde solubility it has the potential to be dissolved by the cooler injection fluid. The low pH of the injectates is also likely to favor the dissolution process. Anhydrite dissolution through injection and injection returns provides a plausible explanation for the increase in sulfate at the production wells.



**Figure 10: Oblique view of a remnant open fracture in NM9 core sample (3,204 mRF), showing anhydrite crystals (yellow arrows). (picture: GNS Science – scale in mm)**

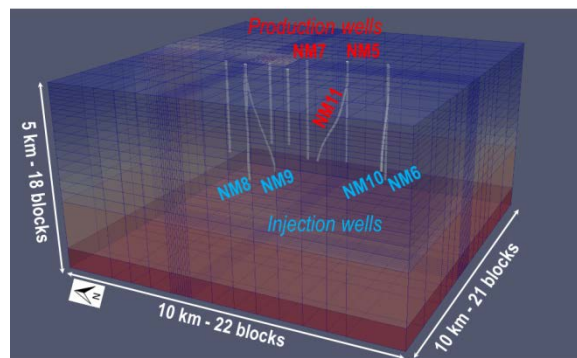
#### 3.2 Process model setup

This hypothesis is tested using a reactive transport process model with TOUGHREACT v2.0 (Xu et al., 2010). A process model is a simplified numerical model used to refine reservoir processes and understanding through testing various hypotheses.

##### Initial Tough2 process model

In this approach, a reduced version of the Ngatamariki full field model (Clearwater et al., 2012) is built up with 8,316 blocks (Figure 11). Similar to the full-field model, it is a dual porosity model and has the same overall rock properties and boundary conditions (deep upflow, marginal recharge and rainfall infiltration). The modelled reservoir is entirely liquid and its initial temperature is about 285°C. The model is run for 10 years, using the measured produced/injected flow rates for the first 3 years and maintained at this average take for the rest of the simulation (Total take of ~1720 t/h, entirely reinjected with 60% in the northern injectors and 40% in the southern injectors).

Although simplified, the process model provides an acceptable match with the reservoir pressure data monitored in the reservoir monitoring wells. This modelled reservoir flow pattern is deemed reasonable enough to add the reactive transport component upon it.



**Figure 11: Process model structure (well tracks in grey)**

### Fluid chemistry

The production wells fluid chemistry (brine and gas) is monitored on a quarterly basis as part of the reservoir management strategy. Calculated back to reservoir conditions with WATCH 2.4 (ISOR, 2013) using the quartz geothermometer, the reservoir fluid is dilute, near neutral pH and low in gas (Table 2). It contains initially low concentrations in calcium and sulfate. The injection fluid is similarly analysed quarterly and reveals the same composition as the produced fluid, minus the NCG (Table 2). These concentrations are used as inputs in TOUGHREACT.

**Table 2: Selected composition of the reservoir fluid and the reinjection fluid**

Fluid	Temperature (°C)	pH	SiO <sub>2</sub> (mg/kg)	Cl (mg/kg)
Natural state reservoir (NM7)	290 (Quartz geothermometer)	6.5 (at 290°C)	640	920
Reinjection	90	5.5 (at 22°C)	640	920

Fluid	Ca <sup>2+</sup> (mg/kg)	SO <sub>4</sub> <sup>2-</sup> (mg/kg)	Total CO <sub>2</sub> (mg/kg)
Natural state reservoir (NM7)	2.2	2.4	2780
Reinjection	2.0	2.9	285

### Reservoir mineralogy

Types and abundance of primary and alteration minerals are obtained from the geological logs of each well. The productive horizons of the reservoir are mostly ignimbrites and andesite lava units. Deep alteration products (below the clay-cap) reflect a propylitic mineral assemblage (Chambefort et al., 2016), including calcite and anhydrite as mentioned above. For the modelling purpose, a simplified mineral composition is chosen, which only retained the most reactive minerals that are likely to influence the fluid composition over the simulated timespan (Table 3). To assess the potential impact of anhydrite, various amounts of anhydrite are considered, from none, up to 10% of the rock volume in the injection areas. The remaining percentage of the rock volume is assumed to be non-reactive.

**Table 3: Modelled reservoir rock composition**

Mineral	Volume fraction (%)
K-feldspar	25
Quartz	15
Albite	15
Calcite	6
Anhydrite	Variable (0-10)

These minerals are set to react under kinetic constraints, using corresponding rates of dissolution/precipitation described in Palandri and Kharaka (2004). Thermodynamic data are defined using the Soltherm database (Reed, 1982).

### 3.3 Model results

Model results are shown in Figure 13 for selected components in the production block representing NM7. The results suggest that the main chemical trends observed in the production fluid are controlled by injection returns. The modelled decrease in total CO<sub>2</sub> in the fluid is consistent with the observed concentration in NM7, as well as the increase in calcium. Even in the absence of anhydrite, this increase in calcium is expected because of the presence of

calcite in the reservoir, which also has a retrograde solubility and has a similar behavior as anhydrite under injection (Figure 14, left).

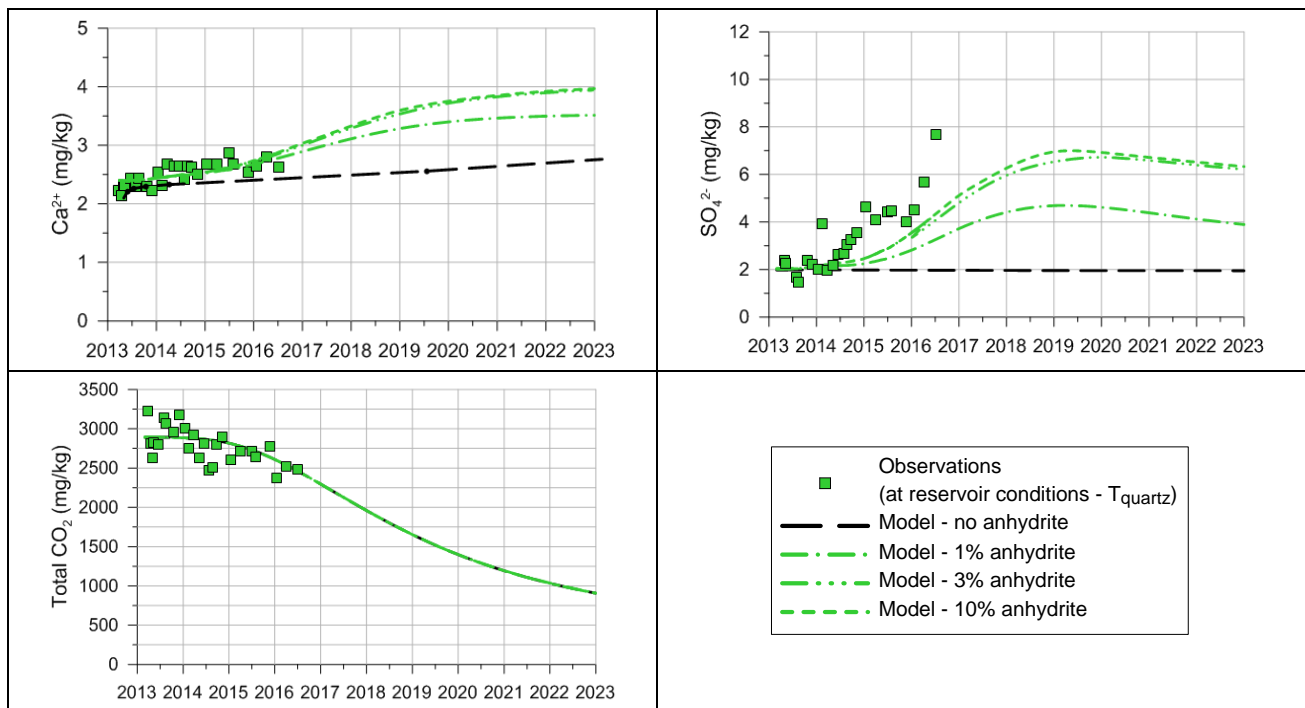
If no anhydrite is considered in the model, the sulfate concentration at the production well remains the same as the natural state. When various amount of anhydrite are introduced in the injection blocks, sulfate concentration is increasing in the production well as a result of dissolution by cooler injection fluid and subsequent transport. The modelled increase in sulfate becomes similar to what has been observed to date when amount of anhydrite gets higher than ~3%.

Model results also suggest that anhydrite is re-depositing along the flow pathway between injection and production, as the fluid heats up. There are only small differences in the sulfate concentration feedback in NM7 between the 3% or 10% of anhydrite, indicating that sulfate in solution is buffered by precipitation of anhydrite. In the model, anhydrite deposition is indeed taking place along the way to production, as shown by the modelled precipitation of anhydrite in selected blocks located 200 m and 500 m away from NM9 toward NM7 (Figure 14, right).

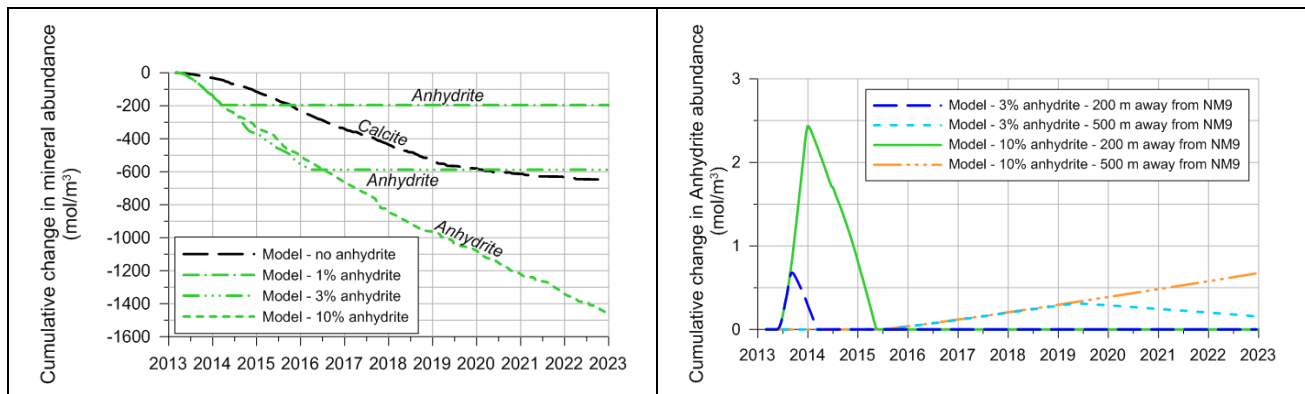
In 2016, a routine check on the permanent downhole pressure gauge installed in the reservoir monitoring well revealed the presence of anhydrite scales deposited on the pressure chamber (Figure 12). The downhole pressure gauge was last inspected in late 2014. The scales were analyzed using qualitative XRD. The presence of anhydrite in this monitoring well, located halfway along the pathway between injection and production, provides additional evidence supporting the hypothesis of anhydrite mobilization and re-deposition.



**Figure 12: Anhydrite scales on the monitoring well pressure chamber (set depth: 1650 m measured depth)**



**Figure 13: Modelled reservoir fluid produced from NM7 versus measured well chemistry (corrected to reservoir conditions using the quartz geothermometers)**



**Figure 14: Modelled calcite/anhydrite dissolution in the NM9 injection block (left) and anhydrite precipitation in selected blocks located halfway between NM9 and NM7 (right)**

### 3.4 Reservoir management implications

Increases in sulfate in the production fluid usually indicate cooling and potential marginal recharge. In this case, the model results suggest that this trend is associated with injection returns, in accordance with the reservoir tracer test results. The model results also support the hypothesis that the increasing sulfate observed in NM7 (and NM5) is a signature of injection returns rather than marginal recharge at this stage of the field development. Depending on the volume fraction of anhydrite that may be present in the injection areas, assumptions can be made on the expected sulfate trends in NM5 and NM7, and can in turn be compared against the actual sulfate concentrations from ongoing monitoring data. Until now, no decrease in downhole reservoir temperature has been measured in the production wells and the geothermometers (Quartz, NaK, and NaKCa) have remained stable.

Because the injection fluid only remobilizes calcite and anhydrite already present in the reservoir, it is not deemed to

be detrimental to the overall reservoir permeability. On the other hand, the model results suggest that as production and reinjection within the field progresses, the anhydrite deposition front is expected to migrate closer towards production.

The modelled increase in calcium and decrease in total CO<sub>2</sub> content at the production well should affect the potential for calcite scaling upon boiling. At this stage, boiling calculations on the expected fluid composition to be produced at NM7 using Watch 2.4 show little variation on the calcite saturation index. It also indicates that the modeled decrease in total CO<sub>2</sub> is offset by the modeled increase in calcium with respect to the calcite deposition potential in the production fluid. Modelling results suggest that injection returns would not diminish the risk of calcite scaling in the production wells within at least the next 5 to 10 years.

Throughout this case study, the model provides useful information that enables adaptive reservoir management of the Ngatamariki geothermal field.

#### 4. CONCLUSIONS

These two case studies demonstrate that despite the complexities and the uncertainties involved in geochemical modelling, it is a valuable tool in understanding current chemistry-related challenges in producing geothermal fields.

While geochemical modelling does not provide “direct” answers, it is extremely useful to interpret and predict processes that may take place in the geothermal reservoir and the surface facilities, which are not directly measurable or observable. From a reservoir management viewpoint, geochemical modelling can be applied to optimize remediation efforts, identify parameters of importance in geothermal systems and help design effective techniques to better manage chemistry-related issues.

Although geochemical modelling is by no means a substitute to field experiment, it allows a narrowing down of the range of possibilities by assessing potential reactions and the amount of minerals precipitating or dissolving. Mitigations options such as chemicals addition or dosing can be evaluated; eventually providing incentives for optimum operating options.

Thermodynamic data are major source of uncertainty in geochemical modelling and application of laboratory data to field situations is a perilous exercise. In that regard, geothermal power plants can be considered as field-scale, live experiments. Therefore, any field observations and monitoring data gathered are of immense value to improve thermodynamic databases, assess kinetic rates and improve the understandings of geochemical processes. This would in turn reduce uncertainties in geochemical modelling and provide improved tools for the geothermal energy sector.

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