

# Thermodynamic modelling of water chemistry in geothermal systems

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## ABSTRACT

Thermodynamic modelling of a geothermal system in the Netherlands exhibited conditions for precipitation in the production well where BaSO<sub>4</sub>, SrSO<sub>4</sub>, and FeCO<sub>3</sub> precipitated. Precipitation in the topside facilities were identified as CaCO<sub>3</sub> and BaSO<sub>4</sub>. No precipitation was found in the injection well or in the mixing between injected brine and the original brine found in the reservoir.

## **1. INTRODUCTION**

Geothermal energy was proven technically viable as a heat source in Denmark in 1984, with the first geothermal plant being established in Thisted (Mahler et al. 2013). However, since then, other geothermal projects followed and the doublet system, which is used in Thisted, with a production well and an injection well has shown to be troublesome due to increasing challenges with injectivity over time (Schreiber et al. 2016).

The focus of this paper is the change in water chemistry and the effect it may have on the system over time. This effect is examined by studying the thermodynamic equilibrium of the brine for the conditions in the given system.

# 2. ANALYSED SYSTEM

The system that was analysed was a geothermal doublet in the Netherlands. The cycle of the geothermal doublet system includes the production of the brine, cooling and degassing at the topside, injection of the cooled brine, and mixing of the altered, re-injected brine with the original brine in the reservoir. These four stages are indicated in Figure 1.



# Figure 1: Analysed sections in a simplified geothermal doublet system.

# **3. METHODOLOGY**

The modelling was done with the thermodynamic model: extended UNIQUAC model. This is a model that is capable of predicting the solid-liquid equilibrium in a complex aqueous mixture, which consists of electrolytes and non-electrolytes. It is a model that uses the original UNIQUAC with an added Debye-Hückel term (Thomsen 2005). The inputs in the model included the following:

- Temperature
- Pressure
- Gas content
- Ion composition

The output included a composition of the aqueous phase as well as a composition of the solid phase determined by more than 150 potential salts.

The model uses an excel implementation, and the interface in excel is seen in Figure 2.



# Figure 2: Excel implementation of the extended UNIQUAC model.

The assumptions used in the modelling are as follows:

- Equilibrium at reservoir conditions.
- Thermodynamic equilibrium is achieved for each section of the well.
- A linear change in temperature.
- A linear change in pressure.
- The partial pressure of CO<sub>2</sub> remains a constant percentage of the total pressure throughout the well.
- Electroneutrality is achieved for the brine.

### 4. RESULTS

The results for the geothermal doublet include scale profiles from the production and injection well, expected precipitation of the topside, and an analysis of the mixing of cycled brine and original brine. The resulting scale profile for the production well is shown in Figure 3.



Figure 3: Scale profile for the production well.

Figure 3 shows that  $BaSO_4$  will potentially precipitate at the bottom of the well, and that  $SrSO_4$  will potentially precipitate at the top of the well. These precipitations can mainly be contributed to the change in temperature. The precipitation of FeCO<sub>3</sub> at the very top is due to a decrease in dissolved CO<sub>2</sub>.

The topside analysis showed that there was a risk of both  $CaCO_3$  and  $BaSO_4$  precipitation. The  $CaCO_3$  precipitation is caused by the degassing procedure, while the  $SrSO_4$  precipitation is caused by the cooling of the brine. The results are shown in Table 1.

#### Table 1: Expected precipitation at topside.

Salt	Precipitation [g/ kg water]
CaCO <sub>3</sub>	0.030
$BaSO_4$	0.0018

The next step in the modelling process was the injection well. The scale profile for the injection well is shown in Figure 4.



#### Figure 4: Scale profile for the injection well.

Figure 4 shows that no precipitation is expected in the injection well, however, this profile is a result of the modelling and assumptions. These assumptions resulted in precipitation in the production well and the topsides. The precipitation is a removal of salts, and thus the salinity of the brine dropped which limits the

risk of scaling at a later point in the system such as the injection well.

The last part of the system that was modelled was the mixing of the injected brine and the original brine found in the reservoir.

The modelling did not result in any precipitation due to the previous precipitation as discussed earlier. Instead the saturation index for each case is plotted in Figure 5.



Figure 5: The maximum saturation index in the mixing of the reservoir brine and the injected brine.

The mixing of the two brines was done with a linear change in temperature, pressure, and composition, thus the 0% injection fluid in Figure 5 is the original brine in the reservoir, and 100% injection fluid in Figure 5 is the injection fluid when it exits the injection well. The extended UNIQUAC model determines the saturation index (SI) for each of the salts in the model, and the salt with the highest SI is the salt closest to precipitation. It is the highest saturation index that is plotted in Figure 5. For this case BaSO<sub>4</sub> is the salt that is most saturated for all cases. If the SI exceeds 1 then the salt precipitates, thus, Figure 5 shows that the original brine is saturated in the reservoir and that the brine that is injected is under saturated.

The analysis of the geothermal doublet system showed that all precipitation occurred in the production well and topside, with no precipitation in the injection well or in the mixing between the original brine and reinjected brine. The reality is, however, that scaling is present in the injection well, and possibly in the reservoir close to the injection well. One explanation for this is that thermodynamic equilibrium is not reached, and that the salts might precipitate at a later point. Another explanation could be that the salt precipitates but does not attach to the surface of the well and will instead be led to another part of the system and settle there. These suggestions are purely speculative, and the data and analysis required to prove these theories are beyond the scope of this paper.

#### 5. CONCLUSIONS

In conclusion, the analysis showed that precipitation is thermodynamically viable in different sections of the production well. More specifically  $BaSO_4$ ,  $SrSO_4$ , and  $FeCO_3$  can potentially precipitate, where the  $BaSO_4$  and  $SrSO_4$  precipitation is due to the change in temperature and the  $FeCO_3$  precipitation occurs when the  $CO_2$ content has decreased at the top of the well.

Precipitation in the topside facilities have also been proven thermodynamically viable. Here the precipitation was CaCO<sub>3</sub> and BaSO<sub>4</sub>.

Due to previous scale in the system the modelling did not show any precipitation in the injection well, nor in the mixing between injected brine and the original brine in the reservoir. This is due to the assumption that equilibrium would always be reached, and that precipitation would be instant. Thus, all precipitation occurred in the first parts of the system.

Further work will be carried out to analyse any possible precipitation in injection wells and reservoirs as a possible explanation to the well-known challenges with injectivity over time.

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