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Thermodynamic Modelling of Water Chemistry in Geothermal Systems

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ABSTRACT

Thermodynamic modelling of a geothermal system in Denmark exhibited conditions for precipitation in the production well where $BaSO_4$, $SrSO_4$, $CaCO_3$ and $FeCO_3$ precipitated. Precipitation in the topside facilities were identified as $CaCO_3$ and $BaSO_4$. No precipitation was found in the injection well or in the mixing between injected brine and the original brine found in the reservoir. The lack of precipitation in these sections of the system are due to the assumption that the kinetics of the reactions are not accounted for.

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 the increasing challenges with injectivity over time, Schreiber et al. (2016).

The focus of this paper is to examine the change in water chemistry due to changes in temperature, pressure and gas, and what effect this has on a geothermal system over time.

2. METHODOLOGY

The modelling was done with the thermodynamic model: the extended UNIQUAC. This is a model that is capable of predicting the solid-liquid equilibrium in a complex aqueous mixture consisting 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 include the following:

- Temperature
- Pressure
- Gas content
- Ion composition

The output includes a composition of the aqueous phase and the solid phase which is determined by more than 150 potential salts. The output of the model also includes a saturation index for each of these salts both before and after equilibrium.

The model uses an Excel implementation as an interface. This interface is shown in Figure 1 along with an overall overview of the main sections of the inputs and outputs.

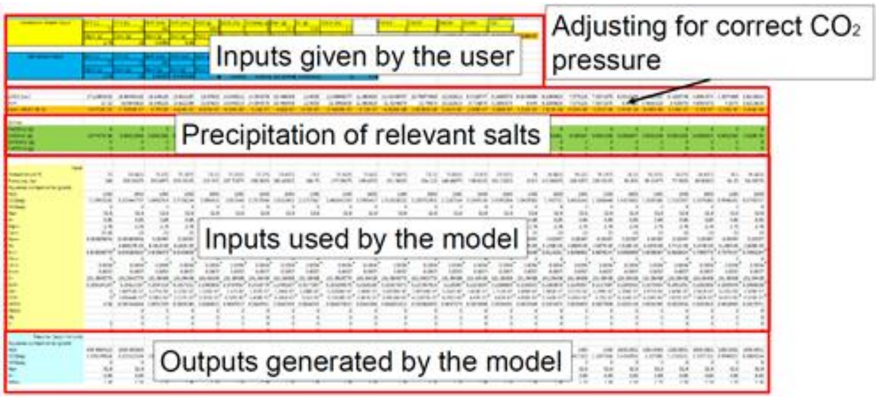

Figure 1: Excel implementation of the extended UNIQUAC model.

The model requires a number of assumptions in order to give a viable output. These assumptions include the following:

- Equilibrium at reservoir conditions.
- The well is separated into sections, and thermodynamic equilibrium is achieved for each of these sections.
- Each of the sections in the well maintain any solids that precipitate. Only the aqueous phase is used in the following section.
- A linear change in temperature.
- A linear change in pressure.
- The partial pressure of CO_2 and CH_4 remains a constant percentage of the total pressure throughout the well.
- No O_2 is present in the system.
- Electroneutrality is achieved for the brine.

Our assumptions towards the modelling are quite simple and straight forward. In our calculation we have a very accurate thermodynamic approach. The effect of brine composition on gas solubility is taken into account and the gas phase fugacities are treated correctly using an SRK equation of state, Thomsen (2005).

3. ANALYSED SYSTEM

The system that was analysed is a geothermal doublet in Denmark. The brine and gas composition that was used for the modelling is shown in Table 1.

Table 1: The composition of the brine and the gas used in the modelling. This composition is found at bottom hole conditions.

Gas composition		Brine composition	
Component	mol%	Component	mg/l
N_2	84	Na^+	52900
CO_2	7	K^+	650
CH_4	7	Mg^{2+}	2760
O_2	N/A	Ca^{2+}	23000
		Sr^{2+}	860
		Mn^{2+}	15.1
		Fe^{2+}	9.4
		NH_4^+	20.5
		Ba^{2+}	8.3
		Cl^-	132000
		Br^-	790
		SO_4^{2-}	272
		HCO_3^-	60

This composition is found at the bottom of the production well.

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 include temperature and pressure and the different stages are indicated in Figure 2.

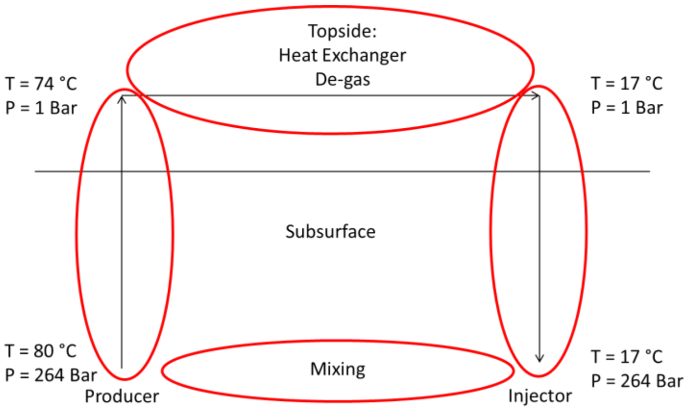

Figure 2: Analysed sections in a simplified geothermal system. The four sections of the system that were analysed are marked by a red circle. These areas are the production well, topside, the injection well and mixing between re-injected brine and the original brine.

4. RESULTS AND DISCUSSION

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. The profile is based on one water sample, and thus the analysis should not be extrapolated on without further investigation and data collection. The scaling profiles are given in g (precipitation)/kg water.

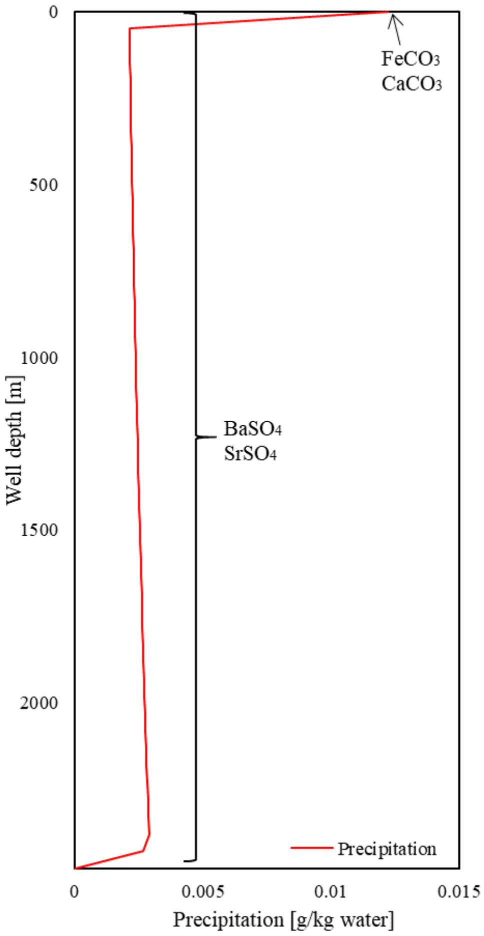

Figure 3: Scale profile for the production well. $SrSO_4$ and $BaSO_4$ are present throughout the well while $CaCO_3$ and $FeCO_3$ are only present in the top of the well due to drop in the CO_2 content.

Figure 3 shows that both $SrSO_4$ and $BaSO_4$ can precipitate throughout the well. The precipitation of the $SrSO_4$ and $BaSO_4$ is mainly due to the change in temperature in the production well. At the very top of the well both $CaCO_3$ and $FeCO_3$ precipitate. The precipitation of the carbonates is linked to the CO_2 content in the well, and the CO_2 content is linked to the total pressure, as assumed previously. As the total pressure decreases so does the CO_2 partial pressure. A decrease in the partial pressure of CO_2 results in less CO_2 dissolved in the brine. At the very top of the well the dissolved CO_2 is at its lowest and low enough so that the carbonates $FeCO_3$ and $CaCO_3$ both exceed a saturation index of 1 and thus $FeCO_3$ and $CaCO_3$ precipitate.

As mentioned in Section 3. Analysed System, the modelling is done by separating the well into 50 equally spaced sections, which results in each section being 50 m tall for this well. The section at the bottom is assumed to be in equilibrium with the reservoir, and thus no precipitation will be observed in this section. In the following section the temperature and pressure are changed, and thus salts will precipitate which is observed in Figure 3. The sharp increase of both the $BaSO_4$ and $SrSO_4$ at the bottom of the well and the $FeCO_3$ and $CaCO_3$ at the top of the well are caused by these 50 m sections, as it is the accumulated values for each of these 50 m sections that are plotted in Figure 3.

The assumption that the mol% of both CO_2 and CH_4 remains constant throughout resulted in a change in the dissolved CO_2 and CH_4. The mass of dissolved CO_2 changed from 3.08 g/kg water at the bottom to 0.013 g/kg water at the top of the well, which equals a 7 mol% of CO_2 at both the top and the bottom of the well.

The topside analysis included both a degasser and a heat exchanger, and thus both the total pressure and the temperature decreases topside. The calculations of the partial pressure of CO_2 are done by a VLS flash calculation, Thomsen (2005). It is assumed that all CO_2 that is dissolved in the aqueous phase before the flash calculation will be removed, and a new equilibrium will form. The result of this examination is shown in Table 2.

Table 2: Expected precipitation at topside.

Salt	Precipitation [g/ kg water]
$CaCO_3$	0.010
$BaSO_4$	0.0032

The results show that both $CaCO_3$ and $BaSO_4$ precipitate. The precipitation of the $CaCO_3$ is due to the degasser that removes CO_2. The precipitation of the $BaSO_4$ is caused by the heat exchanger, and thus a drop in temperature.

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

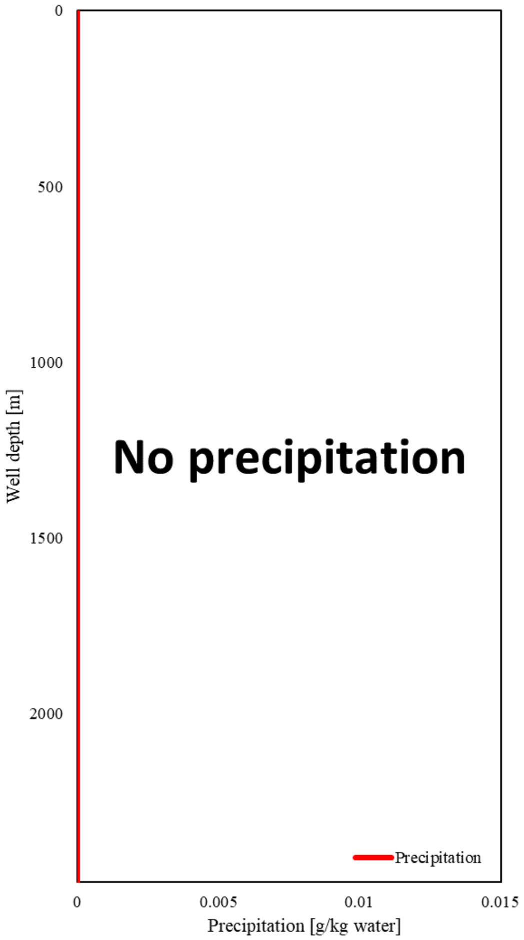

Figure 4: Scale profile for the injection well. No precipitation is observed in the injection well.

Figure 4 shows that no precipitation is expected in the injection well, however, this profile is a result of the modelling and the assumptions. One of the assumptions to assume equilibrium in each section results in the kinetics being disregarded in the model. These assumptions resulted in precipitation in the production well and the topside, as these sections where the first in the system to have conditions favourable for salt precipitation. 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. As the conditions in the injection well were within what had already been observed previously, no additional salts precipitated.

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 a mixing of the two brines are plotted in Figure 5.

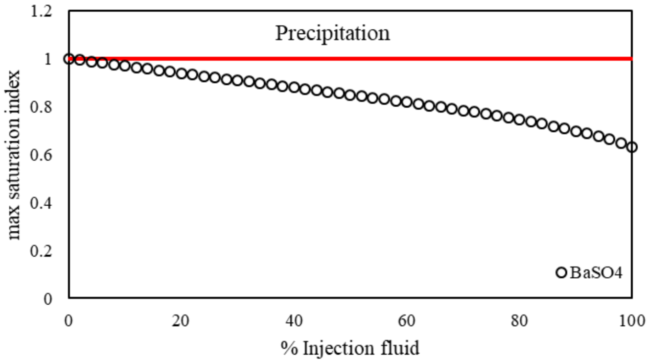

Figure 5: The maximum saturation index for the solid salts when mixing re-injected brine and original brine. The original brine is represented at 0% injection fluid while the re-injected brine is seen as 100% injection fluid.

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 $BaSO_4$ 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 undersaturated, and thus no precipitation is expected in the mixing phase.

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. COMMERCIAL USE

It is the theory that precipitated particles will flow with the brine and end up in the injection well, either in the filters/screens or in the reservoir around the wellbore. In either case, they will build up and over time form a blockage that will require an increased injection pressure. With the capability to map the precipitation and increased insight in the water chemistry, it is the expectation that recommendations can be given in terms of how to hinder the particle build-up and thereby give an improved injectivity over time. In addition, it will be possible to perform a well cleanup or workover using the correct methodology rather than a trial and error approach.

6. CONCLUSION

In conclusion, the analysis showed that precipitation is thermodynamically viable in different sections of the production well. More specifically $BaSO_4$, $SrSO_4$, $CaCO_3$ and $FeCO_3$ can potentially precipitate, where the $BaSO_4$ and $SrSO_4$ precipitation is due to the change in temperature and the $CaCO_3$ and $FeCO_3$ 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 $CaCO_3$ and $BaSO_4$.

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.

The precipitation of the carbonates $CaCO_3$ and $FeCO_3$ can be avoided by maintaining or injecting CO_2 into the system. The sulphates, $BaSO_4$ and $SrSO_4$, precipitation is due to the change in temperature, and thus the re-injection temperature could be altered if possible, or inhibitors could be added to avoid the precipitation.

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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