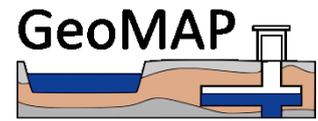




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# Preventing calcite precipitation in deep geothermal energy plants

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## 1. Introduction

When groundwater, which is in equilibrium with calcite and carbon dioxide, is pumped from 2 to 4 km depth to the surface, the pressure decreases and the water becomes supersaturated with respect to calcite (Eq. 1). Depending on the flow rate and casing diameter, a certain amount of calcite will precipitate according to the kinetics of the calcite precipitation which can be up to two orders of magnitude slower than calcite dissolution (Dreybrodt et al. (1991)). This can lead to precipitation of scales on the well pipe walls leading to clogging of wells, reducing injectivity, and damaging the pumping system. Besides, experience from existing plants in the region show that in addition to precipitation on pipe walls and heat exchanger surfaces, a suspension of carbonate crystals is formed. These crystals can precipitate inside the fractures and disturb the continuous production as well as causing technical damage. A small reduction in porosity due to precipitation can cause significant permeability reduction (Bacci et al. 2011). If there is not sufficient permeability or the permeability is reduced due to precipitation, heat cannot be exploited from the geothermal reservoir (Tester et al. 2007).



One method of countering calcite precipitation could be adding of CO<sub>2</sub> to the geothermal water to increase the CO<sub>2</sub> partial pressure and under-saturate the water with respect to calcite. Carbon dioxide addition will boost the negative saturation index (SI) which may also dissolve calcite in the aquifer in the near field of the injection well on the other side. This innovative idea of adding CO<sub>2</sub> to geothermal water was investigated in the BMUB funded research project, LERWTG (Langfristige Verbesserung und Erhaltung von Reservoir-Wegsamkeiten in der Tiefen Geothermie) (Arab et al. (2017)).

Scale inhibitors that are used in geothermal energy production can be inorganic or organic substances. Organics have the advantage to decompose over time. In the ideal case, decomposition starts after reinjection of the geothermal water into the aquifer and ends up as inorganic compounds after a short time. However, the formation of biofilms in particular in the geothermal plant (constructing materials) and the aquifer has to be considered as well. In the ongoing BMWi (Federal Ministry for Economic Affairs and Energy) funded joint research project, EvA-M (Einsatz von Ausfällungsinhibitoren im Molassebecken), thermodynamic and kinetic modeling of the processes in a geothermal plant utilizing NC47-1B as inhibitor is done which includes kinetic modeling of calcite precipitation, complexation of calcium and/or slowing calcite precipitation by NC47-1B (Niederrhein Chemie) as well as microbial degradation of the inhibitor over time.

## 2. Methodology

### 2.1. LERWTG

#### 2.1.1. Sample Material Description

The sample materials used in the batch experiments consisted of rock cuttings from the injection well (GT1) and production well (GT2a), analog representative rocks and a drill core, steel well

casing, and well concrete. In the bypass system (pilot plant), analog samples were used because the amount of drilling material would have been insufficient for filling the columns. The representative rock materials were taken from Ziegenfelder (Frankendolomite, Malm Delta), a quarry located in the same geological formation as the geothermal wells in Kirchweidach. XRD data based on qualitative and semi-quantitative analysis with the Rietveld method was performed on all the rock samples to obtain mineral compositions. The steel casing sample was analyzed by EDX.

### 2.1.2. Batch experiments

Two different types of autoclaves (shown in figures 1 and 2) at a pressure of 40Mpa (400 bar) and a temperature of 105 °C were used to perform both batch kinetic and endpoint experiments. The kinetic experiments were done using GT1 and GT2 rock samples to investigate the effect of CO<sub>2</sub> on the reservoir rock and obtain the change of concentrations over time. The endpoint experiments were done to also determine the effect of CO<sub>2</sub> and water on the sample material (analog rock, drill core, steel casing and well concrete) after a predefined period, which was assumed to be sufficient to reach quasi equilibrium. Upon completion of all the experiments, the sampled solutions were tested for their chemical composition by means of ICP-MS and IC. The amount of CO<sub>2</sub> dissolved in the water was also measured in some experiments.



Fig. 1: Autoclave at TU Bergakademie Freiberg which was used for batch experiments

### 2.1.3. Bypass system

During the operation of the bypass system, thermal water was diverted from the pipeline of the geothermal plant and enriched with CO<sub>2</sub> before entering five cylinders (reaction columns) that were filled with analogue A2 rock samples. The water gradually heated up while going through the reaction columns and the test path. The actual scheme of the plant and bypass system are

shown in Figure 3a while figure 3b shows one of the reaction columns before completion and the details of each of the columns are given in table 2. The bypass system was technically tested and optimized during a period of 3 months, and the actual experimental ran for 6 months.

The water flow in the plant was approximately 10 ml/s and the CO<sub>2</sub> inflow was adjusted to approximately 1.5 Nl/min<sup>1</sup>. This amount of CO<sub>2</sub> corresponds to a gas content of 2500 Nml/l water and as a result, a pH value of 4.8 to 5.5 is achieved. The pore volume in the total system is 403 liters. Therefore, the thermal water had a residence time of 11.2 h in the reaction columns. The pressure in the bypass system was set to a range of 5 to 6 bar.



Fig. 2: (a) Bypass system in Kirschweidach and (b) Reaction columns while being set up

## 2.2. EvA-M

The log<sub>k</sub> values were determined from laboratory experiments with different inhibitor concentrations at different temperatures by measuring electrical conductivity, pH, free Ca<sup>2+</sup> ions by means of nano-membrane separation, and LC-OCD. LC-OCD is a liquid chromatography method that includes, in addition to UV/Vis (UV), fluorescence (FL) and conductivity (LF), a carbon-selective detector and in part also an OND (organic nitrogen detector). This type of liquid chromatography is based on size-exclusion chromatography (SEC) and ultimately provides a distribution of molecular masses over time. The combination of the detectors enables a distinction between Natural Organic Matter (NOM) and Specific Organic Matter (SOM).

A 1D reactive transport model using PHREEQC and a modified Plummer-Wigley-Parkhurst (PWP) equation (Plummer et al. (1978)) was built. A modification to the PWP equation is necessary because the situation in a geothermal power plant is not easily comparable to an aquifer. For example, at the beginning of commissioning, there is carbonate precipitation in the production well, in the heat exchanger, or the injection well. Therefore, there are no crystallization seeds available at which crystal growth can begin. Thus, an empirical factor (F) based on the work of Dreybrot et al. (1996) was implemented into the model which becomes effective only in the case of supersaturation. This made it possible to simulate the extraction of groundwater with a realistic precipitation of calcite scales in the production well and in the heat exchanger.

## 3. Results

### 3.1. LERWTG

Laboratory experiments showed that rock material underwent a preferred dissolution of major rock forming minerals caused by increased pCO<sub>2</sub>. Casing material showed a weight loss of 1.7 %

<sup>1</sup> Normal liter per minute is unit of volumetric flow rate of gas corrected to “normalized” conditions of temperature and pressure.

during the test period of 28 days and no indications of passivation on the casing surface were found. As for the concrete samples, results demonstrated that there is a weight gain of 5-10 wt. %, which is associated with carbonation of the cement.

During the 6 months operational period, redox potential, EC, pH, flow and temperature in the inlet and outlet of the columns were monitored. Water was sampled continuously and analyzed for main cations, DOC, and acid / base capacity. The pilot plant system which was used in this research allowed for flexible simulations of boundary conditions and tracking of the corresponding reactions during the reinjection of geothermal thermal water back into the aquifer.

### 3.2. EvA-M

The results of the 1D model extracting groundwater with a realistic precipitation of calcite scales in the production well and in the heat exchanger are shown in Fig 3. The effects of the ratio of surface to water (P1) and F on the model outcome are depicted in different scenarios (a-d). The green curve indicates the SI of calcite while the red curve shows calcite precipitation. As the hot water moves up to the surface, the pressure decreases and  $SI_{\text{calcite}}$  increases which indicates calcite precipitation. In the heat exchanger, the water is cooled to 60 °C and this changes the  $SI_{\text{calcite}}$  from supersaturation to undersaturation. For the final calibration, the estimation of carbonate precipitation in the production well and in the heat exchanger should be used.

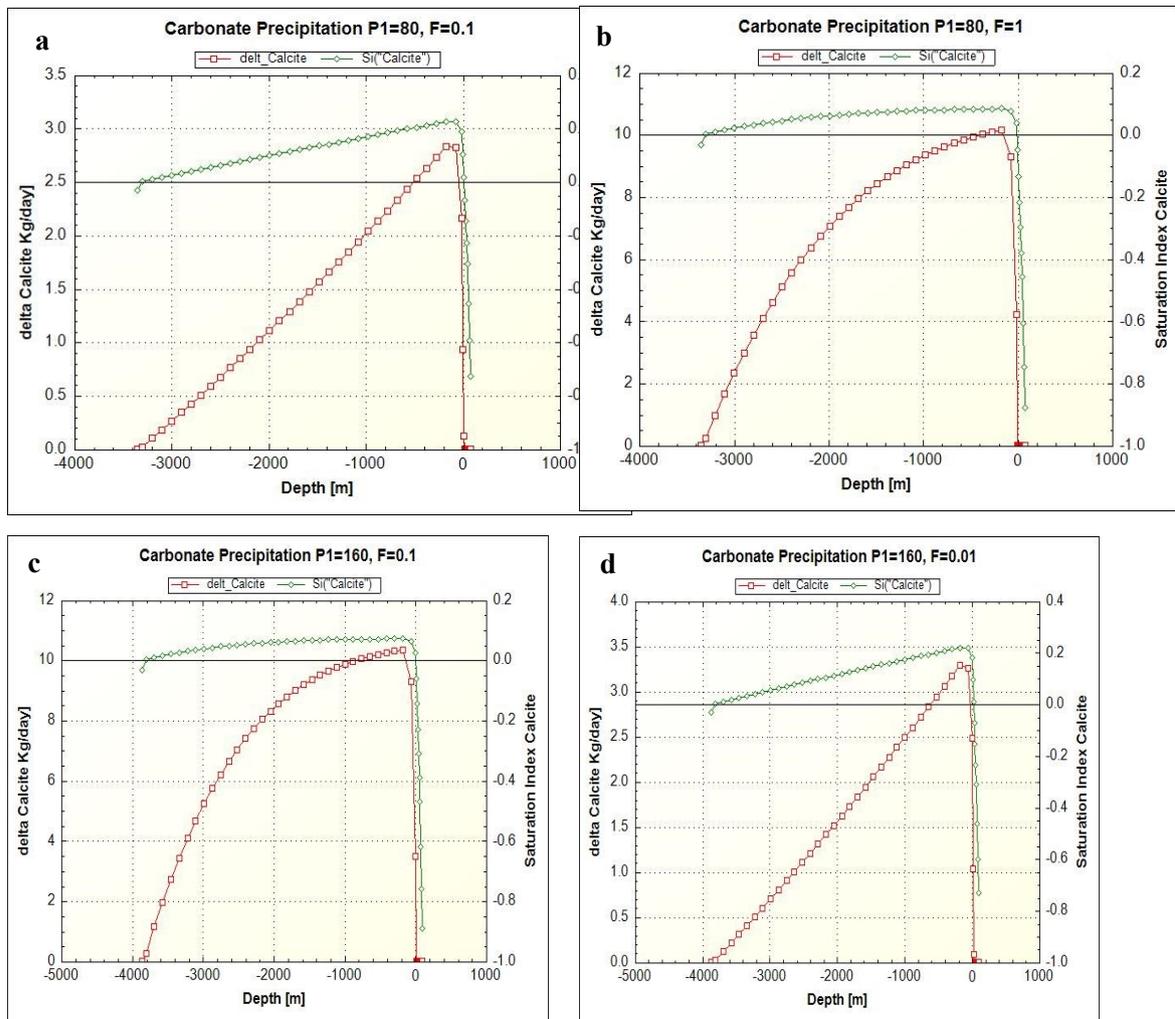


Fig. 3: Results of modeling with different parameters (P1 and F). P1 is the ratio of surface to water and F is the scaling factor. The effects of the P1 ratio and F on the outcome of the model are depicted in different scenarios (a-d).

## 4. Conclusions

Overall results showed that by adding CO<sub>2</sub>, precipitation of carbonate minerals and the formation of scales which deteriorate the transmissivity of reservoir pathways can be prevented due to under-saturation with respect to carbonates. Furthermore, this suggested approach could eventually become a safer and resource-conserving alternative to current techniques especially due to the fact that above ground energy production is not interrupted while CO<sub>2</sub> is being added. This and the positive CO<sub>2</sub> storage as by-effect (Carbon Capture, Utilization and Storage) can be important factors for policymakers.

Carbonate precipitation can be described by a reactive mass transfer model that takes into account both thermodynamic and kinetically controlled chemical reactions. It is also possible to integrate the influence of biodegradable inhibitors into the model. Thus, by such a reactive mass transport model, the optimal inhibitor concentrations can be determined when the thermodynamic and kinetic constants of the inhibitor are known. All results available to date suggest that the biodegradable polycarboxylates inhibitor is effective as a complexing agent as well as by means of sorption on calcite crystals. Reliable numerical models can be built using data from batch and by-pass experiments to determine optimal inhibitor concentrations and predict outcomes.

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