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Investigating and Modeling a Biodegradable Inhibitor to Prevent Calcite Scales in Deep Geothermal Wells and Plants in Southern Germany

Alireza Arab and Broder Merkel

Technische Universität Bergakademie Freiberg, Gustav-Zeuner-Str. 12, 09599, Freiberg, Germany

araba@geo.tu-freiberg.de, merkel@geo.tu-freiberg.de

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ABSTRACT

Inhibitors are used in many geothermal production systems around the world to prevent scale formation, such as in various geothermal plants in the Upper Rhine Graben (ORG), Iceland (Krafla), the Netherlands, Austria, and Turkey. So far, no inhibitors have been used in the geothermal plants of the southern German Molasse Basin. However, some plants in this region are prone to scaling which mainly consist of calcium carbonates and iron sulfides and undesirably occur almost everywhere including the submersible pump, riser pipe, above ground pipes, filters, and heat exchanger. The occurrence of these scales makes the operation of geothermal energy production difficult and by using precipitation inhibitors these problems can be solved. Since these inhibitors are sent together with the cooled groundwater back into the geothermal reservoir, the inhibitors would need to be harmless and biodegradable in all respects according to the German and European water law.

Investigating the use of NC47.1B (Niederrhein Chemie) as a biodegradable inhibitor in geothermal plants in the Bavarian Molasse basin is the major aim of the BMWi (Federal Ministry for Economic Affairs and Energy) funded joint research project EvA-M. As part of the project, pilot plants were used onsite to perform static and dynamic investigation of the stability of the inhibitor and its interactions with the reservoir. Changes to the aquifer rock, the chemical and isotopic composition of the geothermal water and the inhibitor were also examined. Thermodynamic and kinetic modeling of calcite precipitation, complexation of calcium/ or slowing calcite precipitation by means of NC47.1B as well as degradation of the inhibitor over time was done by means of PHREEQC and TOUGHREACT.

By using data from batch and bypass experiments, reliable numerical models can be used to determine optimal inhibitor concentrations and predict outcomes. The results of this research allow for the use of biodegradable inhibitors in southern German Molasse Basin and similar carbonate aquifers, which will lower production costs due to minimizing plant downtimes and breakdowns as well as damages to system components such as pumps, valves and measuring instruments.

1. INTRODUCTION

Calcite scales are a major problem in carbonate dominated aquifers such as the Malm aquifer in the Bavarian Molasse Basin. These scales become an even greater concern in wells deeper than 3,000 meters and temperatures above 120 °C where they can cause the pumps and heat exchangers to fail, clog pipes and wells, and noticeably reduce reinjection capacity. Furthermore, these scales could cause a buildup of hazardous elements (Radium, Uranium). Formation of calcite is dependent on the concentration of water constituents and in particular calcium and inorganic carbon ($CO_{2\,(g)}$, HCO_3^-), temperature and pressure as well as the pH and the redox potential (Eh). When a complete water analysis is available together with the pressure and temperature values, the saturation index (SI) of each relevant mineral can be calculated by thermodynamic modeling.

$$SI = \log(\frac{IAP}{K}) \tag{1}$$

Where IAP is the ion activity product and K is the solubility product of the particular mineral. For the thermodynamic calculation of the activities of all species present in the water, however, the Peng-Robinson equation of state or a corresponding derivative must be used to take into account the non-linear gas solubility (here CO_2) as a function of the total pressure.

A SI from -0.1 to +0.1, taking into account the analytical errors (including pH measurement) and impurities in the crystal lattice, should be interpreted as the value that a water is in equilibrium with the mineral. If the SI for e.g. calcite is < -0.1 the water is undersaturated with respect to calcite and can dissolve carbonate. On the other hand, if the $SI_{Calcite}$ is > 0.1, the water is supersaturated with respect to calcite and there is a tendency for calcite mineral to precipitate. But thermodynamic modeling does not tell us at what speed this reaction takes place. For this, kinetic modeling is required. The kinetics of calcite solution and precipitation is very well studied. A very often used approach is the Plummer-Wigley-Parkhurst (PWP) equation (Plummer et al., 1978). It applies to a temperature range of 0 to 100 °C and thermodynamic states close to the lime-carbonic acid equilibrium (Shiraki and Brantley, 1995):

$$R = k_1 aH^+ + k_2 aH_2CO_3 + k_3 aH_2O - k_4 aCa^{2+} + aHCO_3^- \tag{2}$$

Where R is the reaction rate and k_i are kinetic coefficients that are a function of temperature and CO_2 partial pressure; a denotes the respective activity (not concentration) of the ions involved. Dreybrodt et al. (1991) found that the precipitation of calcite depends on the geometric structure of the crystals. The model of Buhmann and Dreybrodt (1985 a, b) suggests that at small V/A ratios, where V is the volume of the solution and A the area of the mineral surface, the rates are controlled by the slow reaction of

$$H^+ + HCO_3^- = CO_2 + H_2O \tag{3}$$

When V/A < 0.1 cm for stagnant, laminar, and turbulent flow conditions, mineral precipitation rates can be dramatically lower than the PWP model. Therefore, the slow conversion of HCO_3 into CO_2 in a modified PWP model (Dreybrodt et al., 1997) was considered in the form that k_4 in Eq. 2 is multiplied by an empirical factor f <1 and thus simulates a natural inhibition in the precipitation. It has also been found that the precipitation rate in groundwater can be up to 2 orders of magnitude lower than the dissolution rates.

Inhibitors are inorganic or organic substances that prevent or slow crystal growth in various ways. One possibility in the case of calcite is that the inhibitor forms a complex with Ca^{2+} ions in the water and thus the ionic activity product in Eq. 1 and accordingly also the $SI_{Calcite}$ is affected. Another process may be the sorption of the inhibitor on the growing crystals, thereby preventing or slowing further growth of calcite. Our ongoing research project uses an organic, biodegradable inhibitor labeled NC47.1B. Chim et al. (2017) investigated the effect of polycarboxylates in water and the sorption on calcite crystals and the blocking of crystal growth. The larger the number of carboxyl groups, the more effectively the crystal growth is suppressed. This coincides with the results of Lei et al. (2012). Moreover, carboxyl groups also bind cations (e.g. Ca^{2+} and Mg^{2+}) by complex formation.

In a reactive transport model, this can be modeled by surface complexing or complex formation within the aqueous phase. For the modeling of thermodynamic reactions, such as the binding of the inhibitor to calcite crystals by surface complexation or to Ca^{2+} ions, equilibrium constants (log_k values) from laboratory experiments must be determined. The main problem is that the inhibitor which is used in this project is not a specific substance but an unknown mixture of different polycarboxylates. In addition to the influence of the inhibitor on carbonate precipitation from calcite-supersaturated water, the reactive transport model must also consider and simulate biodegradation of the inhibitor under anaerobic conditions at different temperatures. The biodegradation of inhibitors under aerobic conditions has been well studied (Harris, 2011), but this is not the case for anaerobic conditions. A priori can be assumed that biodegradation at low and high temperatures is less than in the range of 40°C to 60°C, because in this area microorganisms have better living conditions than at low and high temperatures. Also, a thermal decomposition would be conceivable at temperatures of 120°C to 130°C. In the BMWi project Thermoinhibitor (Zotzmann and Rehenspurg, 2014), a similar inhibitor (1:1 diluted with water) behaved relatively stable over a period of 4 weeks at a pressure of 10 bar and 150°C. However, the individual components of the inhibitor behaved quite differently on closer inspection. In a sub-project (Project ID: 0325424B) the inhibitor was tested in various concentrations between 38°C and 62°C and in the presence of bacteria. Based on the formation of CO_2, CH_4 and H_2, microbiological degradation was detected, which was completed after 215 days.

2. METHODS AND RESULTS

2.1 Numerical Modelling

2.1.1 One-dimensional Thermodynamic Simulation of a Geothermal Doublet

In the aquifer model, temperatures of approx. 123°C prevail at a pressure of approximately 340 bar (3,400 m depth). Modeling the water chemistry analysis (Table 1) with PHREEQC using the phreeqc.dat database and considering the pressure and temperature conditions, the calcite ($CaCO_3$) saturation index $SI_{calcite}$ is -0.03. Taking into account the analysis error, this means that the groundwater is in equilibrium with calcite. This is to be expected due to the high residence times in the aquifer. With regard to dolomite ($MgCO_3$), the groundwater in the aquifer is significantly undersaturated ($SI_{dolimite}$= -1.01).

The 1D reactive transport model in PHREEQC is based on the finite difference method. A cell size of 117 m was chosen and the sensitivity analysis showed that refinement of the grid does not have a significant impact on the result. The water analysis at the well head was used as an initial condition and as a boundary condition for the aquifer which is given in Table 2. The average diameter was 224.5 mm for the pumping well, 400 seconds were set as a time step. The pumping and injection rates were 150 L/s under quasi-stationary conditions. Fig. 1 shows the calculated saturation index $SI_{calcite}$ for the four phases (production well, heat exchanger, injection well, spread in the aquifer) of the 1D reactive mass transport model.

Table 1: Major constituents of the geothermal water from the production well and the power plant output

	Production well	*After heat exchanger*
Component	Concentration (mol/L)	Concentration (mol/L)
Na	6.964×10^{-3}	6.964×10^{-3}
K	6.475×10^{-4}	6.398×10^{-4}
Ca	8.464×10^{-4}	7.865×10^{-4}
Mg	2.058×10^{-4}	1.893×10^{-4}
HCO_3	4.626×10^{-3}	4.763×10^{-3}
Cl	4.516×10^{-3}	4.516×10^{-3}
SO_4	2.969×10^{-4}	3.021×10^{-4}
NO_3	8.069×10^{-6}	8.069×10^{-6}
pH (25°C)	6.5	6.4
Redox potential (eH)	-118 (mV)	-120 (mV)
Analysis error %	+0.08	-1.74

In the production well, the pressure decreases linearly while according to the Robinson-Peng equation of state the CO_2 partial pressure (pCO_2) does not change linearly. This alteration also changes the solubility product for calcite. As a consequence, the saturation index rises to a value of about 0.23 in the area of the submerged pump and about 0.28 at the wellhead which means that the water is supersaturated in terms of carbonate (Fig. 1, Phase 1). In the heat exchanger, the water is cooled to 60°C. This changes the $SI_{calcite}$ from supersaturation to undersaturation ($SI_{calcite}$= -0.7, Fig. 1, Phase 2). In the injection phase, the temperature remains almost unchanged, but the pressure increases. As a result, the $SI_{calcite}$ reaches its lowest value of about -0.95 (Fig. 1, phase 3) and is extremely undersaturated in terms of calcite. Only after warming in the aquifer the water regains its original SI of ± 0.05 (Fig. 1, Phase 4).

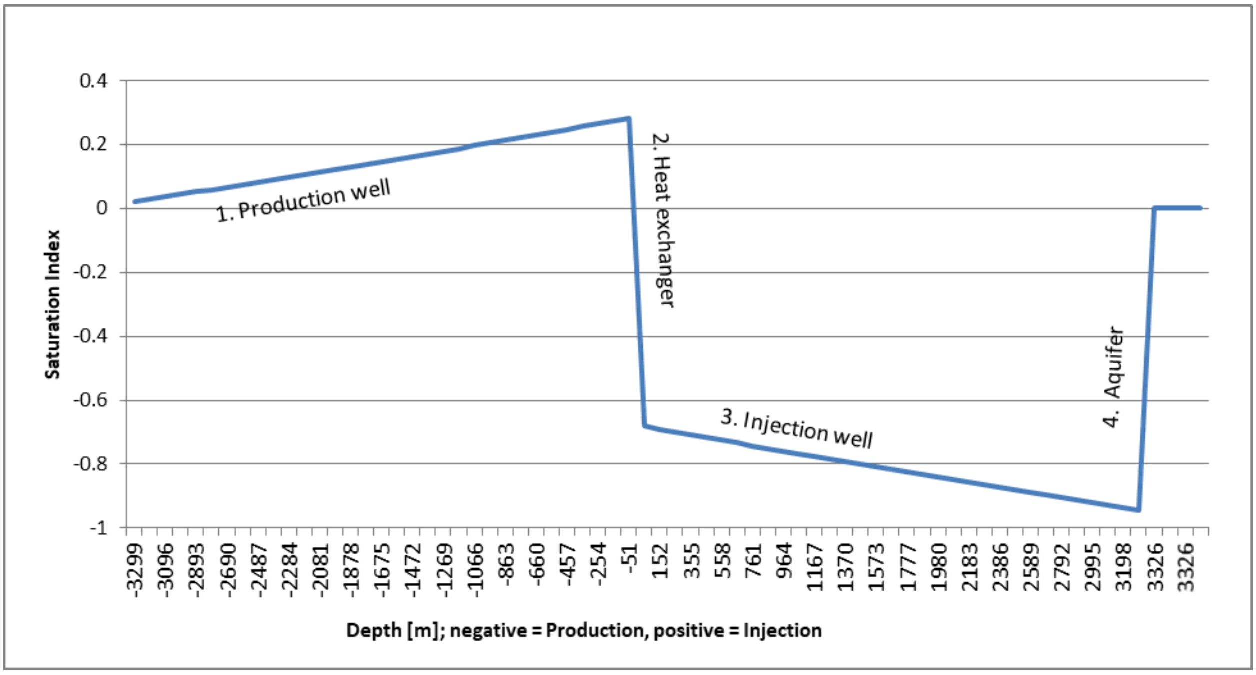

Figure 1: Calcite saturation index in the 1D PHREEQC model. Phase 1: pressure of 335 bar at the bottom, 10 bar at the well head, temperature 123 °C. Phase 2: pressure of 10 bar, temperature decreases from 123 °C to 60 °C. Phase 3: increase of the pressure from 10 bar at the well head to 335 bar at the well foot. Phase 4: pressure of 335 bar and increase in temperature from 60 °C to 135 °C in the aquifer.

When the groundwater in the production well is pumped to the surface, the water first releases heat to the annulus around the well. However, this effect decreases rapidly with a quasi-constant flow, because the thermal conductivity of rocks is relatively low. This means that after a short time the groundwater at the top of the well has almost the temperature of the aquifer. Without assuming a calcite precipitation, the water at the well head (120°C and 10 bar) reaches a $SI_{calcite}$ of 0.33 and the water is thus clearly oversaturated and has a tendency to precipitate calcite and this is observed in reality in the actual power plant. However, the deposition of calcite is kinetically controlled, because if this were not the case, 0.29 mmol calcite per liter would precipitate. That would be equal to 350 kg calcite per day assuming a delivery rate of e.g. 140 L/s.

2.1.2 Modeling the Kinetics of Calcite Precipitation

As demonstrated in the previous section, precipitation in a reactive model should not be thermodynamic and must be modeled as a kinetically controlled reaction. Here, this is done as a 1D PHREEQC model using a modified PWP equation. The modification is necessary because the situation in a geothermal power plant is not easily comparable to an aquifer. At least at the beginning of commissioning, there is no precipitated carbonate in the production well, in the heat exchanger, or the injection well. Thus, there are no crystallization seeds available at which crystal growth can begin. Therefore, the PWP equation in the model was extended by an empirical factor (F) based on the work of Dreybrot et al. (1991), 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 riser of the well and in the heat exchanger. The effects of the ratio of surface to water (P1) and F on the outcome of the model are shown in Fig. 2.

2.1.3 3D Reactive Transport Model of the Spread of the Re-injected Geothermal Water inside the Aquifer

To simulate the spread of the reinjected geothermal water inside the aquifer, Petrasim, an interactive pre-processor and post-processor for the TOUGH family of codes was employed. TOUGHREACT is a non-isothermal reactive geochemical transport model, developed by Xu and Pruess (1998) and was established by introducing reactive geochemistry into the multi-phase fluid and heat flow code TOUGH2. The 3D model constructed consists of 50 layers and a total of 7,500 cells. The size of the model is 500 m in the x-direction (from the injection well) and 600 m for the thickness of the aquifer. The hydrogeological parameters were adopted from an existing verified FEFLOW model. The model was initially run for 100 years to achieve realistic hydrostatic pressure conditions between 280 and 345 bar in the aquifer. The aquifer temperature in the 3D TOUGHREACT model based on measured aquifer temperatures. Figure 3 shows the grid and pressure distribution in the model. Two types of rocks were assigned in the 3D model: calcite with 25% and dolomite with 75%. For the chemical boundary conditions, analyzes of the water from the production and injection wells were used (Table 1). Based on the results of the laboratory tests and the pilot-plant, the complexation of Ca^{2+} and the surface complexation with NC47.1B will be implemented into the model and published in a future report.

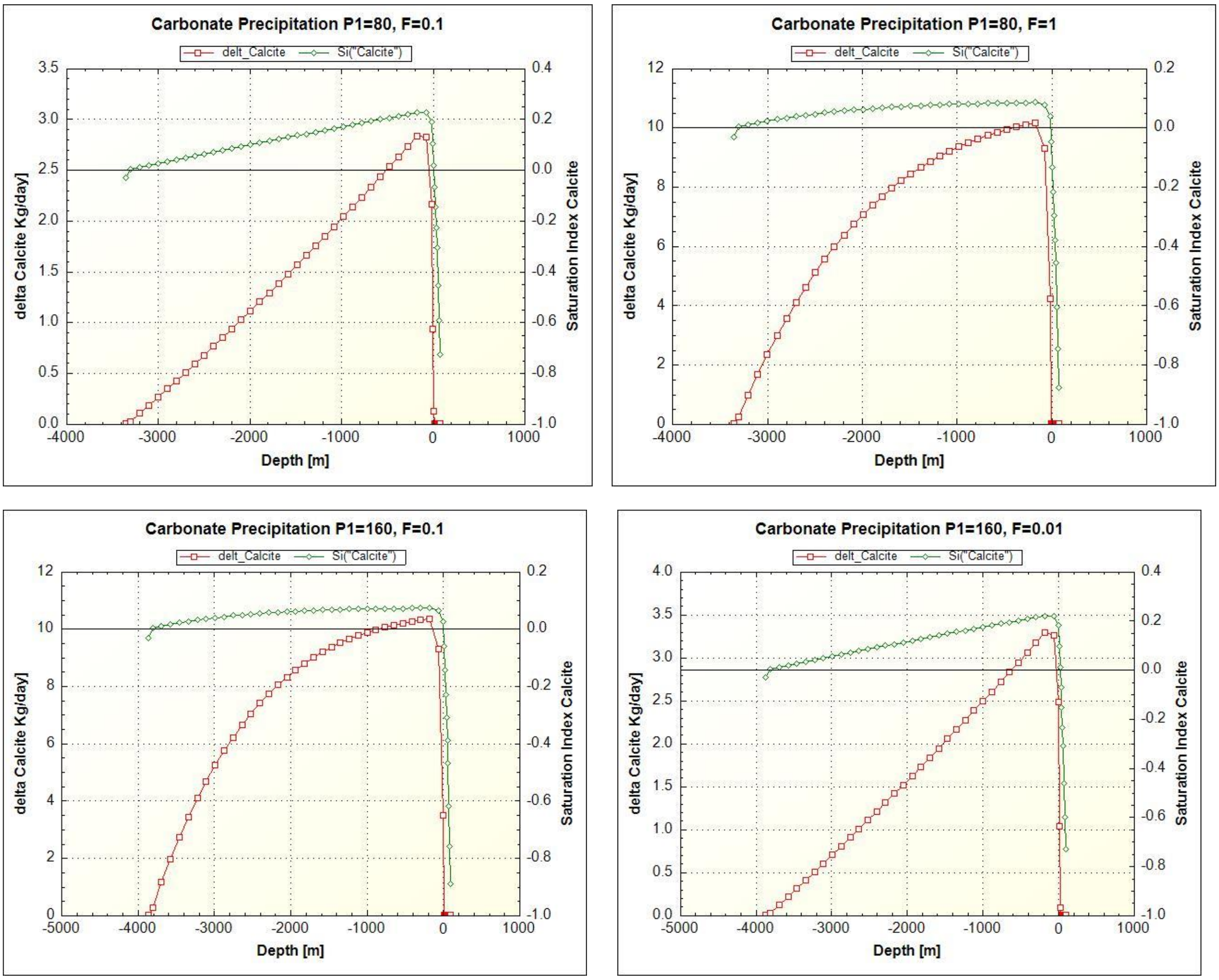

Figure 2: Results of modeling with different parameters (P1 and F). P1 is the ratio of surface to water and F is the scaling factor. For the final calibration, the estimation of carbonate precipitation in the production well and in the heat exchanger should be used.

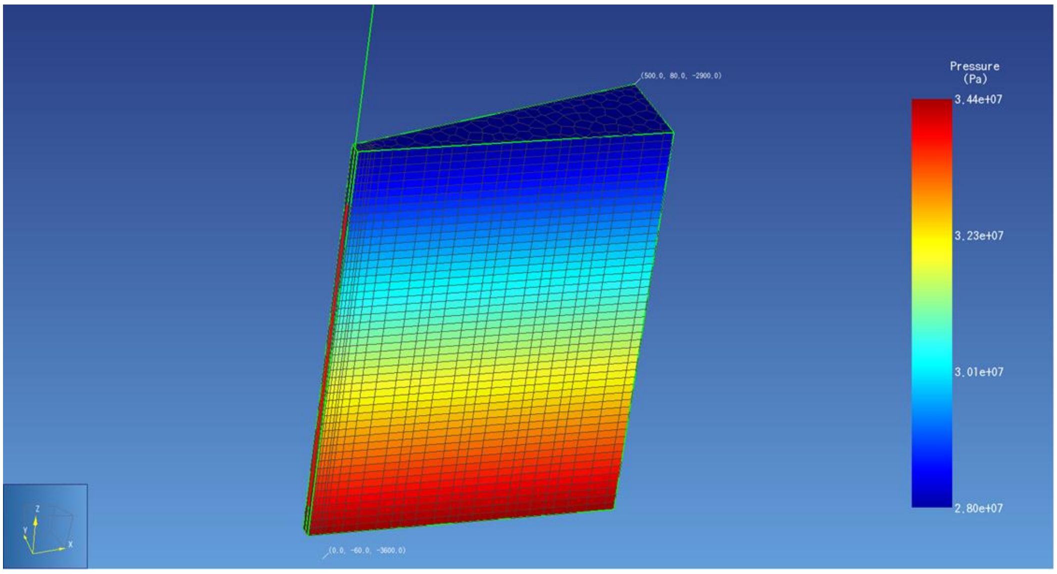

Figure 3: Grid and pressure distribution in the TOUGHREACT 3D model. Based on the results of the laboratory tests and the pilot-plant, complexation of Ca^{2+} and the surface complexation with NC47.1B will be implemented into the model.

2.2 Pilot Plant

A pilot plant was designed and commissioned onsite for performing static and dynamic investigation of the stability of the inhibitor and its interactions with the geothermal reservoir (shown in Fig. 4). The plant will continue running until the end of 2020. It consists of 4 steel cylinders which are filled with reservoir rocks into which the geothermal water is circulated at different temperatures. Onsite parameters (e.g. temperature, pressure, pH, Eh, O_2, electrical conductivity) are recorded online under pressure conditions. Daily and weekly sampling runs are performed to determine:

- Gases: CO_2, CH_4, H_2S, N_2, O_2, H_2
- Major and minor ions: S, Si, Fe, Cu, Sr, Ba, Al, Pb, As, Sb, Mo, W, U, Th (analytical method: ICP-MS), NH_4, sulfide, TIC and DOC, acid-base titration (K_B and K_S)
- Concentration of the inhibitor
- Isotopes: C-13, H-2, O-18
- S species: sulphate, sulphite, thiosulphate, S(0), sulphide, As and Sb species.
- Investigation of rock surfaces with SEM (scanning electron microscope)

Figure 4: Onsite pilot plant for performing static and dynamic investigation of the stability of the inhibitor and its interactions with the rocks of the geothermal reservoir.

2.3. Laboratory Determination of Inhibitor Characteristics

2.3.1 Nano-membrane Separation

Inhibitors or detergents have the property of complexing cations or anions (so long as they have the hydrophilic group) while amphoteric (zwitterionic) detergents can bind both cations and anions. In addition, detergents sorb on solids. In addition, detergents sorb solids such as calcite and can thus prevent further crystal growth causing the water to remain supersaturated e.g. with respect to calcite. This sorption can be described deterministically by surface complexing models. Nonionic surfactants also sorb on solids, and in this case too, modeling can be done via a surface complexation model because hydrogen bonding causes sorption of the nonionic surfactant (Jian et al., 2016). In order to be able to calculate complex formation constants, the concentrations of the complexed ions must be determined for different boundary conditions (temperature, pH, ionic strength). Since the usual analysis methods, such as ion chromatography and inductively coupled plasma mass spectrometry (ICP-MS), cannot distinguish between uncomplexed (in this case Ca^{2+}) and complexed ions, other methods were considered. A method which detects only free Ca^{2+} ions is using ion-sensitive electrodes. However, research showed that there are no commercial Ca-selective electrodes suitable for temperatures above 50 °C. Consequently, measurements in the range of 100 or 120 °C would be impossible. Even voltammetry and polarography, i.e. methods that are in principle able to determine free ions analytically, were ultimately not applied, because the effort seemed too large and the chances of success seemed too small. Nano-membrane filtration is a method which was suitable for carrying out the desired analysis at temperatures up to 120 °C.

According to (Chhim et al., 2017), Lei et al. (2012)) and Zotzmann and Rehenspurg (2014), the molar mass of similar inhibitors were estimated to be between 2000 and 20000 g/mol. Therefore, experiments were carried out with a polyamide Nano-membrane with a cut-off value of 1000 Daltons (about 1 nm pore diameter) and 200 Daltons. Fig. 5 shows schematic and actual pictures of the pressure cell setup used in the experiments. Macromolecules larger than 1nm (10 Å) and 0.2 nm cannot pass through these membranes. When these macromolecules complex cations with Ca^{2+} occur, a decrease in Ca and DOC concentrations are observed. In the experiment using the 1,000 Daltons Nano filter, 34.7 ppm/L of the NC47.1B inhibitor were added to an 8 mmolar $CaCl_2$ solution and was membrane-filtered by means of a pressure of 20 bar. The temperature, electrical conductivity and pH of the $CaCl_2$ solution, the $CaCl_2$ solution + inhibitor and the retentate and permeate after nano-filtration were also determined. In addition, the DOC, anions, and cations were analyzed by ion chromatography (IC) and about 40 elements by ICP-MS. DOC results and electrical conductivity measurements of permeate and retentate showed that approximately 20% of the DOC was accumulated in the retentate and indicated as a first approximation that about 20% of the inhibitor has a molecular weight of >1,000 Daltons. IC and ICP-MS analysis results showed that about 4% of the Ca^{2+} and about 12% of the Cl^- were complexed by the inhibitor.

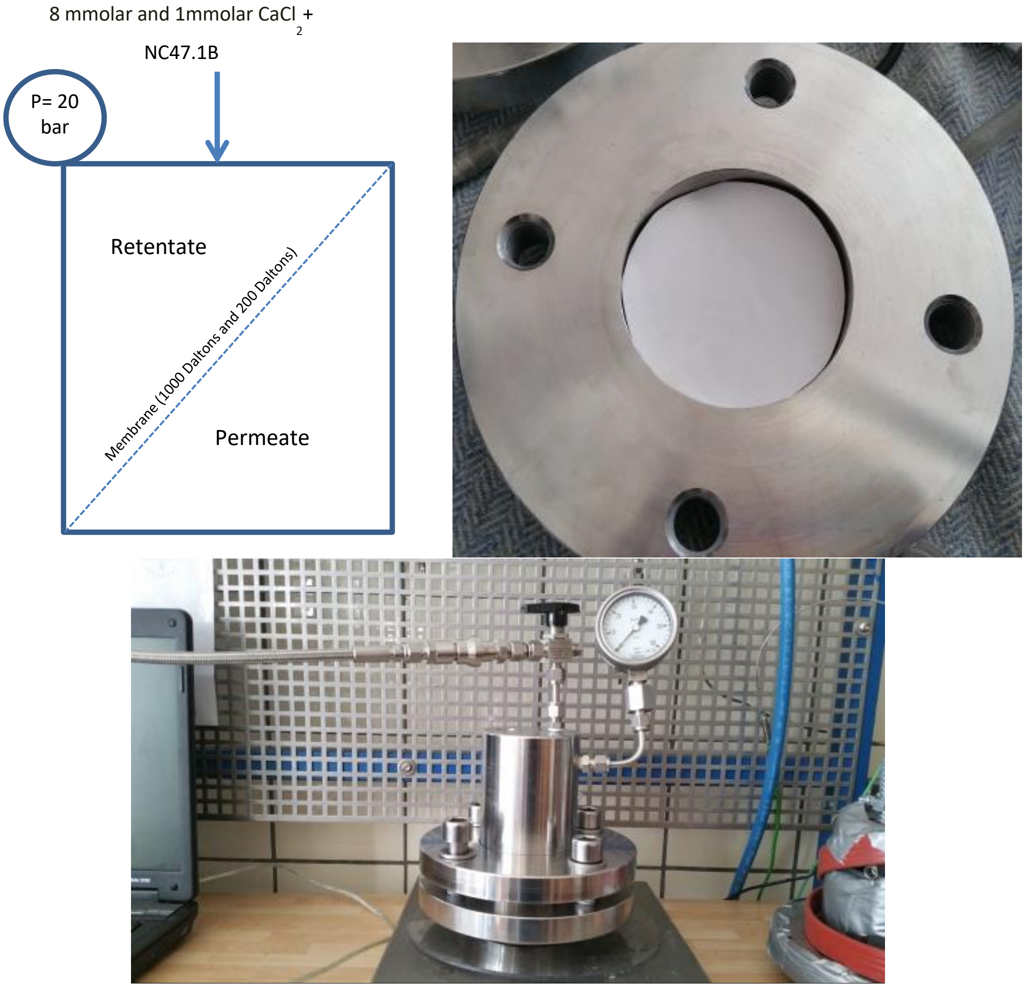

Figure 5: Nano-membrane filtration pressure cell

2.3.2 Liquid Chromatography-Organic Carbon Detection (LC-OCD)

LC-OCD is a liquid chromatography system 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). The NC47.1B Inhibitor was analyzed with LC-OCD. The chromatogram of the inhibitor shown in Figure 6 suggested that 2.3% of the organic constituents have a molecular weight between 10,000 and 100,000 Daltons and are thus biopolymers. 34.8% have molecular weights between 500 and 10,000 Da ("building blocks") and 48.2% have molecular weights <500 Da ("low molecular weight neutrals"). These may be alcohols, aldehydes, ketones or amino acids.

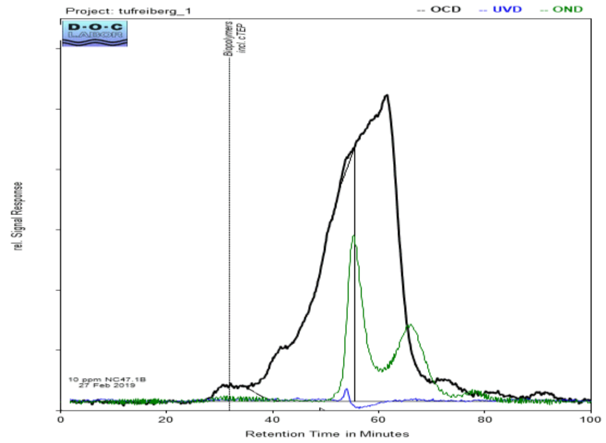

Figure 6: LC-OCD chromatogram of the NC47.1B organic inhibitor

2.3.3 Molar Conductivity

To characterize the contribution of the inhibitor to the electrical conductivity and the dissociation of the inhibitor or its functional groups, the quotient EC/[NC47.1B] is plotted in Figure 7 (left) and shows that the dissociation of the inhibitor decreases extremely with increasing of concentration. In this research project, a maximum range up to 200 mg/L is of interest. The relationship between inhibitor concentration in this range and the quotient can be well fitted by a polynomial function ($R^2 = 0.9949$). Correspondingly, the quotient of the concentration can also be calculated for modeling.

2.3.4 Acid-Base Titration

To determine pKa values for the inhibitor, an acid-base titration was performed with a calcium hydrogen carbonate solution in equilibrium with the atmosphere. In order to ensure equilibrium with the pCO_2 of the atmosphere, ambient air (400 vol. ppm) was continuously bubbled through a solution made with distilled water and fine marble powder ($CaCO_3$) which was continuously stirred. After 1 day, the solution was stripped of excess marble powder by using a 200 nm filter. The filtered solution was divided into two aliquots and 10 mg/L of NC47.1B was added to one of them. With the aid of a Metrohm auto-titrator, both solutions (with and without inhibitor) were titrated with 0.1 normal HCl or NaOH and the change in the pH was quasi continuously recorded. Figure 7 (right) shows the effect of the inhibitor on the buffering capacity and the pKa value.

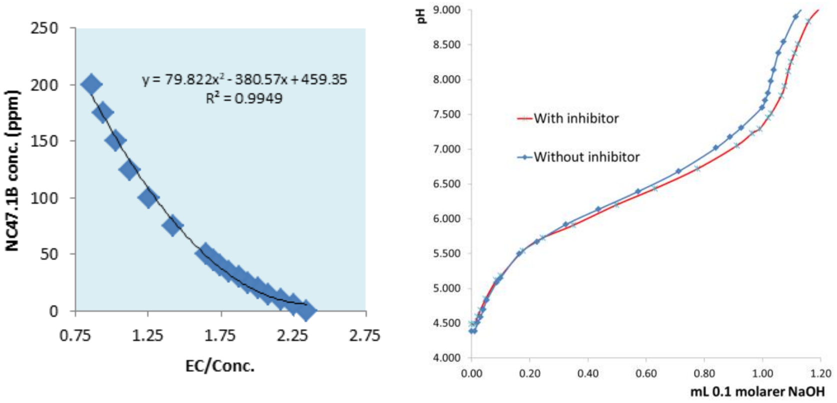

Figure 7: (Left) Relationship between inhibitor concentration in a calcium chloride solution and the quotient EC/concentration. (Right) Titration curves in the range of the pH 4.5 up to the range of calcium carbonate solution.

3. CONCLUSIONS AND FUTURE WORK

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. The log_k values are determined from laboratory experiments with different inhibitor concentrations at different temperatures by measuring electrical conductivity, pH, free Ca^{2+} ions by means of nano-membrane separation, and LC-OCD.

Experiments will be performed to determine how the inhibitor behaves in the aquifer over time at high temperatures. By using the results obtained from batch and pilot plant experiments an empirical equation will be compiled, which describes the microbiological anaerobic degradation of the inhibitor at reservoir conditions over time. The 3D TOUGHREACT reactive transport model will be updated to simulate the spread of the inhibitor-containing reinjection water inside the aquifer using the obtained results. Still open is the question to what extent the formation of metabolites including the final products CO_2, methane and hydrogen can be reliably modeled.

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