Reactive Reservoir Systems – Crystal Nucleation and Filter Processes in Geothermal Systems

Philipp Zuber, Sascha Frank, Jürgen Schreuer and Stefan Wohlnich
Ruhr-University Bochum, Universitätsstraße 150, D-44801 Bochum, Germany
philipp.zuber@rub.de

Keywords: barite, scaling, crystal nucleation, morphology, filter processes

ABSTRACT
During geothermal energy generation, the change of temperature and pressure conditions can lead to supersaturation in the extracted fluids and therefore to the precipitation of crystalline phases. Well-documented crystalline deposits on the inner walls of pipes are the consequences. In addition, turbulence-induced inhomogeneities and mechanical disturbances also lead to the spontaneous formation of free-floating crystal nuclei. A significant part of them are carried along and reinjected into the reservoir. There, the crystal nuclei are possible centers for crystallization and cementations processes or can accumulate by filter effects. Both processes contribute to scaling effects which limit the permeability of the geothermal reservoir and therefore the profitability of a geothermal power plant. So far, such effects have been barely considered in previous studies.

Our investigations focus on a better understanding of the formation and growth of crystal nuclei in saturated geothermal solutions during thermal and pressure relaxation, and their role in decreasing permeability of fractured geothermal reservoirs. For this purpose, a high-pressure-high-temperature apparatus is built and used which is based on the working principle of a geothermal cycle. Circulating flow-through experiments with fractured reservoir rocks, i.e., two sandstones, and barite-supersaturated fluids are conducted under geothermal conditions with the option to simulate heat extraction and injection of colder crystal-contaminated fluids. Furthermore, the size and morphology of precipitated barite crystals are studied as important factors influencing the potential filter processes in fractures. First results show substantial change in barite morphology with different sodium chloride concentrations in solution. To minimize the scaling effects, the goal is to develop approaches to control crystal nucleation.

1. INTRODUCTION
The profitability of a geothermal power plant is very dependent on high flow rates and therefore high permeability of the reservoir rock. Permeability in geothermal systems is supported by fracture zones and not by porous matrix as fracture permeability exceeds matrix permeability (Vidal and Center, 2018). During a geothermal energy production cycle, a fluid is produced, the heat is extracted, and the cooled fluid is reinjected through injection wells into the reservoir where it can be heated again and circulate back to the production wells through fractures. However, examples show that the decrease of permeability in fractured reservoirs is a serious threat to the long-term use of geothermal resources and requires cost-intensive measures, e. g. hydraulic or chemical stimulation (Blöcher et al., 2016).

The change of temperature and pressure conditions during heat extraction leads to a change of the chemical equilibrium and can therefore lead to a supersaturation and precipitation of crystalline phases (scales). The fluid composition and the degree of temperature and pressure reduction determine the phases precipitating. The main phases are carbonates (CaCO$_3$), sulfates (CaSO$_4$, BaSO$_4$, SrSO$_4$), silica (SiO$_2$), and sulfides (FeS, PbS, CuS) (Stober and Bucher, 2014). As a result, these phases are primarily deposited on the inner walls of heat exchangers, pipes and even the inner casing of injection wells, reducing the efficiency of the power plant (Bott, 1995; Scheiber et al., 2013). These scaling processes are already well-documented for many geothermal systems (Wolfframm et al., 2011).

In addition to the deposits on inner walls, turbulence-induced inhomogeneities and mechanical disturbances lead to homogeneous nucleation of free-floating crystallites. A significant part of them are carried along and reinjected into the reservoir. There, the crystal nuclei are possible centers for crystallization and cementations processes or can accumulate by filter effects. These effects change considerably with different crystal morphologies as the clogging behavior increases from isometric to lamellar and acicular crystal habits.

A high-pressure-high-temperature apparatus was developed and built to simulate a geothermal cycle and its scaling processes. An artificial fluid is circulated under geothermal conditions through a water reservoir autoclave, a heat exchanger and a sample autoclave which holds a fractured cylindrical rock sample. The fluid is preconditioned regarding to the used sample to minimize mineral dissolution during flow-through. Furthermore, the used fluid is saturated with a mineral phase to force precipitation during cooling in the heat exchanger. The fluid and precipitated crystallites are then led into the sample autoclave in front of the fractured core. Additionally, it’s possible to inject suspensions into the system containing specific crystal seeds with different morphologies through a high-pressure pump to study the filter effects of different crystal habits.

This study focuses on barite precipitation and two different rock samples, i.e. Flechtinger and Remlinger sandstone. The Flechtinger sandstone is an analogous rock for the reservoir at Groß-Schmeinebeck (Germany) while the Remlinger sandstone is an outcropping equivalent of one reservoir rock in the Upper Rhine Valley (Germany). Both locations are known for barite scalings in the surface installations (Scheiber et al., 2014; Regensburg et al., 2015). Complementary laboratory experiments are conducted to study the size and morphology of barite crystals precipitated from artificial geothermal fluids.
2. METHODS

2.1 Flow-through Experiments

2.1.1 High-Pressure-High-Temperature Apparatus

The high-pressure-high-temperature apparatus shown in fig. 1 consists of three main components: a water reservoir autoclave, a heat exchanger system and a sample autoclave. The fluid is pumped in a closed circuit under geothermal conditions. The flow rate can be adjusted between 0.5 to 4.5 g/s by a piston-membrane pump. This is monitored by a Coriolis flow meter. The apparatus is designed for temperatures up to 200 °C (our current setup allows up to 100 °C) and pore pressures up to 300 bar.

The sample autoclave is made of austenitic stainless steel 1.4571, has a usable height of 300 mm and an internal diameter of 100 mm. There are different insets to fixate the rock sample inside of it. The water reservoir autoclave is upstream, has a volume of 5 L and is made of austenitic stainless steel 1.4301. In between is a heat exchanger to simulate the heat extraction during geothermal power production, i.e., the hot fluid from the reservoir is cooled down, injected into the fractured rock sample located in the sample autoclave and pumped back into the reservoir. To study the influence of specific crystal habits, it’s possible to inject a crystal-contaminated suspension through a high-pressure pump after the heat exchanger in front of the sample.

Further components are digital pressure transducer, an analog manometer, a sampling point, an electrical conductivity meter, three temperature sensors, a gas cylinder to pressurize the system and multiple ball valves allow different pathways to in- or exclude some components, e.g. for maintenance.

The temperature is mainly regulated by two thermostats, one each for the water reservoir and sample autoclave. In addition, there are two electric heating elements for each smaller autoclave and an electric heating wire along the pipes.

During the experiments all system data (temperatures, pressure, flow rate, pH, electric conductivity) are recorded and displayed on a computer with a LabVIEW-system (National Instruments).

![Diagram of the high-pressure-high-temperature apparatus](image)

Figure 1: Schematic flow diagram of the high-pressure-high-temperature apparatus. The fluid flow direction is clockwise.

2.1.2 Fluid Composition

The artificial fluids are made to be in equilibrium with the rock samples to minimize dissolution effects in the flow-through experiments. Pure water (type II) is mixed with crushed rock material in 5 L borosilicate glass flasks on a shaking table at 90 °C for 120 h. In future experiments NaCl is added to gain desired concentrations of 0.1 mol/L and 0.5 mol/L.

2.1.3 Laboratory Glassware

Complimentary flow-through experiments in glassware are conducted in the laboratory (fig. 2). A double-walled borosilicate glass vessel (1.2 L) is used as a fluid reservoir and the sample core is clamped between two flow-through attachments. Everything is
connected through silicone tubes and a peristaltic pump circulates the fluid. It is possible to inject crystallites into the reservoir vessel or add a heat exchanger in between. Temperatures up to 90 °C can be applied to the double-walled vessel while no pressurization is possible. Although this setup is lacking some big advantages of the high-pressure-high-temperature apparatus, its simplicity allows short feedback loops. The ability to observe the experiment in situ makes fast results and adjustments possible. Furthermore, there is no risk of corrosion as no steel parts are exposed to the fluid. This allows experiments with high salinities at elevated temperatures.

Figure 2: Simple flow-through setup with glassware and a peristaltic pump. The rock sample is fractured and jacketed with a shrinkable PVC-sleeve, then clamped between the two flow-through attachments. The middle magnetic stirrer is just used as a stand while the left one is to stir the suspension in the reservoir vessel. The heating thermostat for this double-walled vessel and isolation material is not pictured.

2.2 Rock Samples

To study possible permeability changes in geothermal system it’s obvious to choose fractured rock samples for flow-through experiments because fracture permeability is the most important parameter. Two different sandstones, i.e., Flechtinger and Remlinger sandstone, were chosen as outcropping equivalents of the Groß Schönebeck (North German Basin) and the Upper Rhine Valley geothermal reservoir (e.g. Bruchsal or Soltz-sous-Forêts). The samples were collected as blocks from quarries in Bebertal northwest of Magdeburg (Flechtinger sandstone) and Remlingen west of Würzburg. From these blocks’ cores were drilled in the dimensions of 150 mm length and 99.5 mm diameter by TU Darmstadt. The fractures were induced with a hydraulic press at the Ruhr-University Bochum. The samples were then jacketed with a shrinkable PTFE-sleeve (PVC-sleeve for preliminary tests) and saturated with artificial fluid before fitted into the sample autoclave.

Both sandstones are red, well-sorted, fine-grained and consist mainly of quartz with some potassium feldspar and lesser hematite, rutile, baryte and apatite. The grain density is 2.67 g/cm³. They are both mainly cemented by phyllosilicates. The Flechtinger Bausandstein is a Lower Permian (Rotliegend) sedimentary rock and cross-bedded, sometimes laminated. The mean grain size is 0.5 mm. The phyllosilicate is mainly illite. The porosity and permeability (not fractured) is 10 ± 1 % respectively 0.04 ± 0.02 mD (Heiland and Raab, 2001; Hassanzadegan et al., 2012). The Remlinger Plattensandstein belongs to the Lower Triassic (Upper Buntsandstein). It’s clearly more homogenous. The mean grain size is 0.3 mm. The phyllosilicates are mainly muscovite and biotite. Its porosity and permeability (not fractured) is 13 ± 1 % respectively 0.1 ± 0.1 mD (Schuster, 2017).

2.3 Precipitation Experiments

2.3.1 Mixing of Solutions

To be able to produce crystallites with specific habits it’s necessary to study the size and morphology of spontaneously nucleated crystallites as a function of temperature, time and concentrations of solutes (e. g. Na, K, Ca, Mg, Sr, Ba, Cl, SO₄). For this reason, precipitation experiments were conducted. One method to force precipitation is to produce a supersaturation by mixing of two solutions (fig. 3). In each case barium chloride dihydrate (Riedel-de Haën AG) and sodium sulfate decahydrate (VWR Chemicals) were solved in pure water (type II), stirred for 5 minutes and mixed together. The solids were separated from the resulting suspension by vacuum filtration with 0.45 and 0.10 µm cellulose nitrate filter membranes (Sartorius AG), rinsed with pure water and dried.

Different concentrations of Ba and SO₄ were used (0.04 to 2 mmol/L) to determine the amount of solids needed for further investigations (X-ray powder diffraction, scanning electron microscope and energy-dispersive X-ray spectroscopy) and the duration after mixing of the two solutions was varied (1 min to 144 h). Furthermore, precipitation experiments were conducted at elevated temperatures (60 and 90 °C). The main investigations were carried out to study the influence of sodium chloride in solution (0 to 5 mol/L) on the morphology of barite. However, since the solubility of barite strongly depends on the concentration of sodium chloride it’s not trivial to supersaturate different sodium chloride solutions to the same degree (He et al., 1995; Shi et al., 2012). To solve this problem different sodium chloride solutions were saturated with powdered barium sulfate (Alfa Aesar) at 30 °C and filtered (0.10 µm) before adding barium chloride and sodium sulfate. Calculations made with PHREEQC (Parkhurst and Appelo, 2013) and different databases (phreeqc.dat, pitzer.dat and llnl.dat) didn’t produce satisfactory results.
Zuber et al.

2.3.2 Temperature Difference Method

The supersaturation and precipitation of crystalline phases in geothermal systems happens mostly due to the cooling of the geothermal fluid. To be able to compare the results from the precipitation experiments through mixing of two solutions complimentary cooling experiments are conducted. A hot fluid (90 °C) is saturated with natural crushed barite and cooled down to 30 °C. Depending on the salinity of the fluid and due to the low solubility of barite the resulting amount of solids is very little (He et al., 1995; Shi et al., 2012). About one litre of fluid had to be used.

2.4.1 X-ray Powder Diffraction (XRD)

The produced solids were analyzed by X-ray powder diffraction to confirm the crystallinity and phase. A PANalytical Empyrean X-ray diffractometer was used. The tube (CuKα) was operated at 45 kV and 40 mA. Data were collected from 5 – 80 ° 2θ in step size of 0.026.

2.4.2 Scanning Electron Microscope (SEM) and Energy-dispersive X-ray Spectroscopy (EDX)

To study the chemistry, size and morphology of the precipitated phases a ZEISS - Gemini2 - Merlin HR-FESEM was used. It was operated at different voltage and amperage settings (8, 10, 20 kV and 170, 200, 300, 330, 500, 1000 pA). A representative piece with about 2 x 2 mm was cut from the membrane filter, glued on to a holder and carbon coated. Images were recorded at 500 x, 2000 x and 5000 x magnification. Energy-dispersive X-ray spectroscopy was used to determine the chemistry of the solids.

3. RESULTS AND DISCUSSION

3.1 Flow-through Experiments

Initial functionality of the high-pressure-high-temperature apparatus was tested. First flow-through experiments at elevated pressure and temperature conditions were conducted. The LABVIEW data acquisition system is working. The temperature of the water reservoir and sample autoclaves can be kept constant with a precision of 0.2 °C. The heat exchanger is easily able to cool down the fluid from 90 to 30 °C with tap water as a cooling fluid (14 °C). The piston-membrane pump circulates the water in the system although some pore pressure (5 bar) is necessary. Furthermore, pressure oscillations of about 2 – 4 bar depending on the flow rate are observed. Pore pressures of up to 150 bar were tested and the apparatus has remained tight. The preliminary experiments show that the build apparatus fulfils the design criteria and is functional for the proposed investigations. Geothermal conditions and processes during geothermal energy production can be simulated realistically.

Laboratory flow-through experiments with the glassware equipment show that barite particles are deposited on the fracture surface (fig. 5). About 5 h after injecting a suspension with 0.5 g of barite crystallites into the 1.2 L reservoir the fluid becomes clear again. Three subsequent injections show the same behavior. This shows clearly that there are filter processes happening in the fracture as expected. As no elevated temperatures and no temperate gradient were used the barite particles didn’t grow together or solidified, yet.
3.2 Precipitation Experiments

The precipitation experiments with pure water as a fluid show no dependency on crystallization duration. Seconds after mixing the barium chloride and sodium sulfate solutions crystallization takes begins and the produced solution gets cloudy. There also no change in size or morphology visible. The concentration of barium and sulfate doesn’t have a big influence on the size and morphology, too. Only above about 1.0 mmol/L a rounding of crystal faces is recognizable.

Rising concentrations of sodium and chloride in solution as a background electrolyte shows an inhibition or slowdown of the crystallization process as described in the literature (Canic, 2015; Goulding, 1987). The first turbidity is visible after 10 to 20 minutes depending on the concentration of NaCl. Furthermore, the morphology of barite changes significantly. Fig. 6 shows SEM images of precipitated barite crystals with 0, 0.1, 0.5 and 1.0 mol/L NaCl (top to down) in solution. It’s clear that the background electrolyte inhibits the growth of crystal faces. The model shows an inhibition in \{001\} and \{100\} – these faces are getting more surface. At 0.5 and 1.0 mmol/L new faces become visible. The crystallite sizes become smaller with the biggest change from 0 to 0.1 mmol/L. With this changes in morphology and crystal habit it’s important to pay attention to the fluid chemistry of further flow-through experiments.
Figure 6: SEM images (left) of the change in barite morphology with rising sodium chloride concentrations (top to down: 0, 0.1, 0.5 and 1.0 mol/L) in solution. Pictured model (right) is made with Vesta (Momma and Izumi, 2011).
4. CONCLUSION
The high-pressure-high-temperature apparatus is ready to use for experiments under geothermal relevant conditions. Well-known mineral precipitation can be simulated through cooling or injection of crystallites and filter effects in fractured sandstones can be studied. Complimentary flow-through experiments in the laboratory give the possibility of quick preliminary tests and short feedback-loops to react and adjust experimental parameters. The possibility to study potential scales through fast precipitation experiments further optimizes the workflow.

As the first experiments have shown it’s important to pay attention to the fluid chemistry as the mineral precipitation depends heavily on it. Natural geothermal fluids are far more complex than the artificial fluids used but it’s complicated to use natural fluids in flow-through experiments as there are practical challenges (e. g. getting a pressurized and hot geothermal fluid into an apparatus) and far too many changing parameters to pinpoint reason and effect. Further precipitation experiments can narrow down important factors for geothermal experiments.

In the next step experiments with high-pressure-high-temperature apparatus start and permeability changes in the fractured rock samples due to precipitation of barite and filter processes are expected.

5. ACKNOWLEDGEMENT
The authors gratefully acknowledge the financial support of the Federal Ministry for Economic Affairs and Energy (BMWi) managed by Forschungszentrum Jülich. Further we thank our project partners at TU Darmstadt, JGU Mainz, GFZ Potsdam and Geomecon GmbH.

REFERENCES