Procedure for the Determination of Rock-Fluid Interaction Reactions with Barium Sulfate Supersaturated Fluids

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ABSTRACT

In the German Upper Rhine Graben (URG), the main geothermal reservoirs that are exploited for heat and electricity production are the Middle Bunter sandstone in combination with Rotliegend sediments and the underlaying granitic basement.

The produced highly saline fluids are supersaturated in barium sulfate which leads to the precipitation of barite and barite-celestine solid solutions when the fluids are cooled down. In addition, metal sulfides like lead sulfide and even pure lead have been observed. Formation of sulfate scaling in geothermal plants could be prevented through the application of phosphonate-based inhibitors. The precipitation of the other phases could be reduced by simultaneously dosing a corrosion inhibitor.

Within the scope of this BMWK-backed R&D-project, inhibitor combinations were formulated and tested for their efficiency. The focus of the research was to evaluate if the corrosion inhibitors are compatible with the phosphonate-based inhibitors and if they have an effect on the reservoir rocks. The research was carried out using the HydRA rock flow through device (Hydrothermal Reaction Apparatus) that was developed at the KIT-ITES. The apparatus allows the flow of an original or synthetic, barium sulfate enriched geothermal brine through a rock sample at reservoir like p-T conditions (up to 420 bar and 250 °C). As a result of the experiments, which each lasted several days, it was possible to show that mineral precipitation in the rock samples could be prevented and that the severity of the formation of new phases depends on the inhibitor concentration. An inhibitor mix with an added corrosion inhibitor did not show any negative influence on the efficiency of the scale inhibitor. In addition to the pressure monitoring on the HydRA apparatus, geochemical analyses of the fluids and SEM-EDX analysis on thin section from rock samples were carried out. The result of the HydRA experiments can also provide information about the application concentration of the inhibitor on site.

1. INTRODUCTION

The geothermally utilized fluids of the URG with a maximum temperature of T = 170 °C, a salt content of up to 125 g/L and gas contents of up to 1.3 Nm³ per m³ of fluid represent a challenge for operational management (Scheiber et al., 2020). Binary power plants of the URG operate the geothermal loop as a closed system which means that non-condensable gases are kept pressurized in the brine and are re-injected into the reservoir. Surface pressures in the geothermal plants range from 19-25 bar (Hettkamp et al., 2020). Despite this operation, cooling of the fluid produces solids, first of all in the heat exchangers and then in all devices of the return line (cold side/injection side) and even in the injection well (Scheiber et al., 2012). Problems related to scaling are therefore not limited to the surface facilities, but can also affect the injectability and performance of the reservoir.

Scales in the URG contain significant amounts of barium-strontium sulfate solid solutions, heavy metals and metalloids (Pb, As, Sb) (Jähnichen et al., 2019). The best results for scale inhibition of both types, barium sulfate scales and heavy metal scales were obtained by combining scale and corrosion mitigation measures because more than 50 % of scale deposits consist of metalloids and metals like arsenic, antimony and lead in their elemental form As(0), Sb(0) and Pb(0). After careful pre-selection, corrosion inhibitors were applied in combination with the barium sulfate antiscalant (Schreiber et al., 2020).

In practice, both inhibitors are dosed separately into the fluid flow in front of the heat exchanger. In order to reduce operating costs, the aim is to use only one product consisting of scale and corrosion inhibitor. A combination of both kinds of inhibitor is challenging, as it must be ensured that the two compounds do not react with each other and that the product mixture is compatible with the formation fluid. A combination consisting of a phosphonate and a polyamine compound fulfilled these requirements. In this paper the fluid-rock-interactions obtained from the flow through experiments are discussed.

2. ROCK FLOW THROUGH FACILITY HYDRA

The rock flow through facility HydRA was developed and built at KIT-ITES to simulate the conditions that occur during the re-injection of thermal water. The principle of the HydRA facility is based on the fact that two separate mass flows, after pressure and temperature is applied, mix and then flow through a rock sample. In this way kinetic controlled precipitation reactions can be simulated, in case that

two differently composed undersaturated solutions are used which, after mixing, are supersaturated at the adjusted reaction conditions. The fluids can be natural or synthetically composed thermal water.

To store the two differently composed saline solutions, two corrosion- and pressure-resistant cylinders (hereinafter referred to as receiver tanks) are used, each of which has a piston inside dividing the cylinder into two zones. The corrosive thermal waters are filled into the zone above the pistons. In each cylinder, a membrane pump (by LEWA) conveys demineralized water to the zone below the piston, causing it to move and the thermal water to flow into the device. By this way, the membrane pumps are protected with respect to the corrosive thermal water. The thermal water runs through heatable feed lines to the heated mixing zone where the mixing tee is located. The resulting solution then flows from bottom to top through the thermostated cylindric rock (diameter: 1 inch, length: 2 inches), a cooler, a filter and a needle valve, which is used to maintain a constant pressure after the rock sample. At the outlet, the fluid drips into a container on a scale allowing the total mass flow to be determined.

The rock specimen is contained in a tight-fitting silicone tube (see fig. 1), which allows the cones of the pressure flanges above and below it to be pressed tightly against the top and bottom of the specimen. From the outside, a jacket pressure is applied to the silicone hose that is higher than the pressure acting on the rock sample. This ensures that the fluid flows through the rock and does not bypass it. Along the system pressure sensors (Digibar II PE 300 by HBM) and thermocouples (type K) are installed. The needle valve at the outlet of the plant is controlled by a PI controller, which regulates the opening of the valve via a stepping motor. A PLC ensures that the system is shut down when predefined pressures and temperatures are reached, which allows experiments to be run for several days without supervision. The measurement data acquisition system OPAL (Daubner and Krieger, 2010) registers the plant pressures, temperatures and the scale signal.

The relevant pressures for the assessment of the HydRA experiments are: p2.0 (pressure in front of the specimen), p3.0 (pressure after the rock specimen) and p1.3 (jacket pressure), see fig. 1. At the beginning of an experiment, the pressures p2.0 and p3.0 are almost equal. The jacket pressure p1.3 is set to 40 bar higher and kept constant during the experiment. If there are precipitations in the rock sample that clog the pores, at first increasing fluctuations of p3.0 (pressure after the rock) will occur. This is because it is more difficult for the PI controller to keep the pressure p3.0 constant when the permeability of the rock is reduced. Then, the pressure in front of the rock sample (p2.0) increases. In case p2.0 reaches 95 % of p1.3, the system switches off automatically, since otherwise it is no longer ensured that the jacket pressure can press the hose tightly against the sample. If no large fluctuations occur and if there is no pressure rise of p2.0, this indicates that no or only slight precipitation occurs.
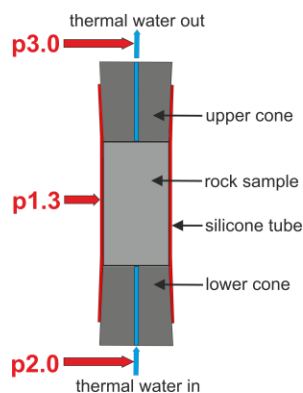

Figure 1: Rock sample in a silicone tube with applied pressures, description in the text.

3. EXPERIMENTAL PROCEDURE

First, the amount of scale inhibitor required to prevent the precipitation of barium-strontium sulfates was investigated. On the basis of this concentration, the combination product was formulated. The objective of this work was to prove that the efficiency of the scale inhibitor is not impaired by the use of the corrosion inhibitor. For this reason, the experiments focused on the precipitation of barium-strontium sulfate. Therefore, the other elements detected in the fluid and in the scales (Pb, As and Sb) were not taken into account.

3.1 Applied Solutions

3.1.1 Na-Ca-Sr-Cl-brine (model solution)

1.393 mol/L NaCl (p. a., Fisher Scientific GmbH), 0.206 mol/L $CaCl_2 \cdot 2H_2O$ (p.a., Carl Roth GmbH + Co. KG) and 5 mmol/L $SrCl_2 \cdot 6H_2O$ (p. a., Fisher Scientific GmbH) were used to form a background electrolyte. For simplifying the ion diversity in the original solution (example of a typical brine from a UGR geothermal plant in Germany), the concentrations of all monovalent ions were converted into a Na-ion concentration. Hence, one total concentration of Na was generated. Correspondingly, all bivalent ions except for strontium and barium were converted into Ca-ion concentrations and represent a total Ca concentration. Strontium correlates with the original fluid concentration. The model solution has an ionic strength of 2.03 mol/L with a total mineralization of 105 g/L like the original brine of the plant.

3.1.2 Test Solutions

Before carrying out the flow through experiments with the HydRA facility, different saturation indices (SI) for barium sulfate in the model solution were modeled at a constant molar ratio n (Ba^{2+}) / n (SO_4^{2-}) and a temperature of T = 60 °C using the freeware program PhreeqcI version 3.7.1.15876 (Charlton and Parkhurst, 2002, Parkhurst and Appelo, 2013 and 1999). The calculations were done with the integrated Pitzer database because it is appropriate for saline sulfate-rich solutions (Appelo, 2015).

For the HydRA experiments two different receiver tank solutions were prepared prior to the experiments. Receiver tank solution 1 contained half the volume of the model solution plus a corresponding amount of barium chloride solution. In receiver tank solution 2, the second half of the model solution was supplemented with the desired sodium sulfate solution.

When the contents of the two receiver tanks are mixed in a volume ratio of 1:1, this generates the test solution which flows through the rock sample inside the HydRA facility. As long as they are separated, both the receiver tank solutions remain undersaturated. Mixing the receiver tank solutions leads to oversaturation and precipitation of barium sulfate according to the following reaction equation:

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2\,Na^+ + 2\,Cl^-$$

For inhibitor experiments, the necessary amount of inhibitor is added to the sodium sulfate containing receiver tank solution.

3.1.3 Inhibitor Solutions

In this work commercial inhibitors were used. The scaling inhibitor is a formulation containing DTPMP, which is known to have an inhibitory effect on the formation of $Ba(Sr)SO_4$. The corrosion inhibitor contains a polyamine (PA) whose anti-corrosive properties have been proven in preliminary tests. The inhibitor combination is a self-made product mixture of the scale and the corrosion inhibitor. Flow through experiments were carried out without inhibitor, with the scale inhibitor in different DTPMP concentrations and with the combination product.

3.2 Experimental Conditions

For the experiments red sandstone coming from Lahr, south west Germany, was used as an analog rock. A characterization of this rock can be found in chapter 4.2.

The temperature in the test section was chosen to be 60 °C, because this is a typical re-injection temperature for thermal water. The PhreeqcI modeling showed that the precipitation of barium sulfate is strongly dependent on the temperature, whereas the pressure hardly plays a role in the range of 20 to 100 °C. Hence, to make the experiments easier, a low pressure can be applied. In the framework of investigations concerning barite precipitation in a model solution roughly similar to the present case and with the same type of rock it could be shown that a pressure of 60 bar is sufficient to get a homogeneous distribution of barite in the rock sample. A pressure of 20 bar was found to be too low for this purpose (Baur et al., 2020 and 2022). A flow rate of 2 g/mL was used, which has proven to be appropriate in previous experiments (Baur et al., 2020). The maximum duration of the experiment was 72 hours in order to be able to complete an experiment with preparatory and follow-up work within one working week. Experiments without and with inhibitor were carried out.

In the first experiments, the concentrations of barium and sulfate in the test solution were chosen to be by a factor of 2.5 higher than in the real thermal water (i.e. exaggeration factor of 2.5, constant barium to sulfate ratio of 0.170). This is done in order to achieve a high degree of precipitation and hence pressure difference in the experiment without inhibitor in the intended maximum test duration. Since clogging occurred at the cone below the specimen (experiment URG-02) and below the reaction zone (experiment URG-04), the exaggeration factor was reduced to 2.0. Table 1 shows an overview of the performed experiments.

Table 1: Overview of the HydRA Experiments.

Test designation	ß (DTPMP | PA) in test solution [mg/L]	Exaggeration factor	c (Ba) in test solution [mmol/L]	c (SO_4^{2-}) in test solution [mmol/L]	Test duration [h]	Δp across the rock sample at the end of the experiment [bar]
URG-02	0.0. | 0.0	2.5	0.688	4.060	18.7	34
URG-04	0.0 | 0.0	2.5	0.688	4.060	50.7	34
URG-06	0.0 | 0.0	2.0	0.551	3.248	72.0	30
URG-07	3.0 | 0.0	2.0	0.551	3.248	72.0	5
URG-10	5.0 | 0.0	2.0	0.551	3.248	72.0	0
URG-12	5.0 | 2.0	2.0	0.551	3.248	72.0	0

During a 72 hour experiment, 6 aqueous samples were taken at the outlet of the HydRA facility. At a designated time, a sample was taken and immediately diluted 1:100. For this purpose, 0.2 mL of the undiluted sample was pipetted into a reservoir containing 19.8 mL

nitric acid (1 %, suprapur). After several weeks of standing and regular mixing of the samples during this time, they were filtered through nylon syringe filters (0.2 µm). The samples were then analyzed via ICP-OES.

The reason why the sample is first diluted and later filtered can be explained as follows: The 60 °C hot thermal water in the test section then flows through the cooling section, where it is cooled down to 25 °C. This reduces the solubility of the $BaSO_4$ and enables clusters and / or small crystals to be formed. By filtering immediately, these crystal formations due to temperature reduction would be removed and thus the solubility at 25 °C instead of 60 °C would be determined. Due to the rapid dilution of the suspension, the standing time and the periodical mixing, it is possible for small crystals to redissolve in the 100-fold increased solvent volume, namely those that were dissolved at 60 °C but precipitated when cooled down to 25 °C.

After the experiments, the rock samples were sawed through lengthwise, stabilized with epoxy resin and polished for subsequent SEM - EDX measurements.

4. RESULTS

4.1 Pressure Curves
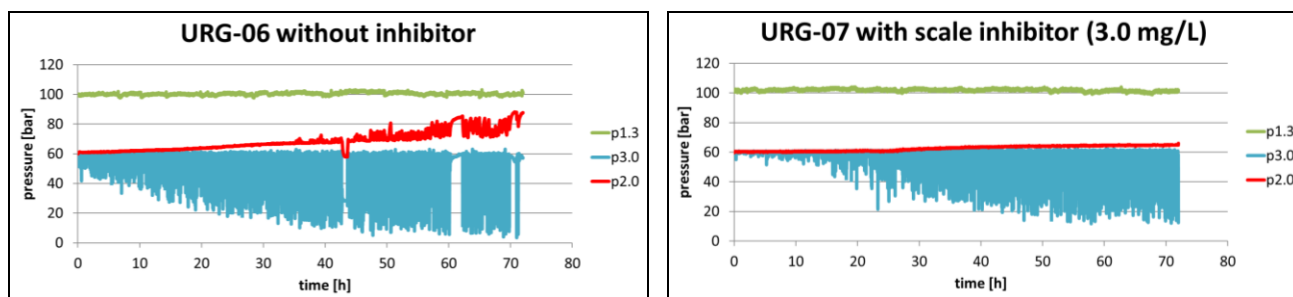The figures 2 and 3 show the pressure curves of the most conclusive experiments.

Figure 2: Left side: pressure curves in experiment URG-06 without inhibitor; right side: pressure curves in experiment URG-07 with the scale inhibitor (3.0 mg DTPMP/L test solution).

As expected, in the experiment without inhibitor (URG-06, see fig. 2 left side), the pressure after the rock sample (p3.0) fluctuates increasingly over time. After about 20 h, the pressure in front of the sample increases until a value of 30 bar is reached after 72 h. In the subsequent experiment URG-07 with 3.0 mg DTPMP per liter of test solution (see fig. 2 right side), p3.0 also fluctuates to an increasing extent. However, after 72 h, there is only a pressure increase of 5 bar in front of the sample. This indicates that the inhibitor concentration is too low. Therefore, in experiment URG-10, the DTPMP mass concentration is increased to a value of 5.0 mg per liter of test solution. This procedure resulted in no strong fluctuations of p3.0 and no pressure increase of p2.0, as can be seen in the left part of fig. 3. In Experiment URG-12 (see fig. 3 right side) the pressure curves are almost the same. For this experiment, the inhibitor combination was used (contains 5.0 mg DTPMP and 2 mg PA per liter of test solution).
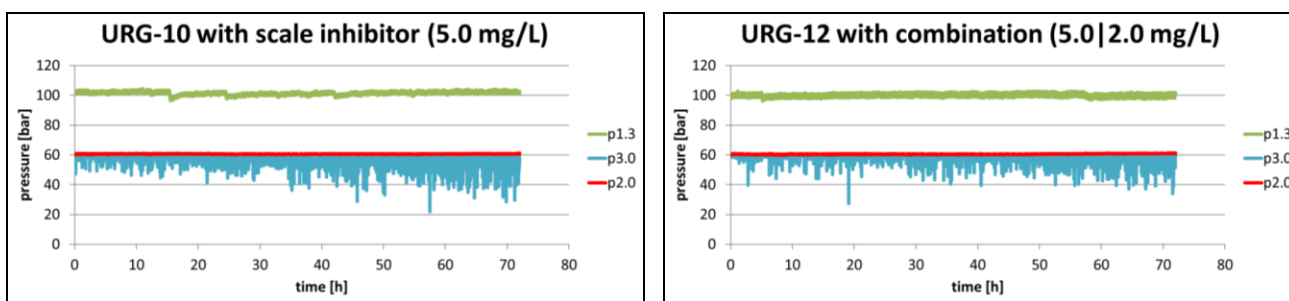

Figure 3: Left side: pressure curves in experiment URG-10 with 5.0 mg DTPMP per liter test solution; right side: pressure curves in experiment URG-12 with the inhibitor combination (contains 5.0 mg DTPMP and 2 mg PA per liter of test solution).

4.2 Rock Analysis (SEM/EDX)
The analysis of rock material was done on a *Zeiss Evo 10* SEM with an *EDAX Element* EDX system. The sample material is a feldspar bearing sandstone with an average grain size of 200 to 500 µm. The proportion of feldspar is around 10 %. Mineralogically the feldspar is orthoclase, sometimes with small amounts of sodium. As accessories, heavy minerals like hematite, barite, pyrite, and zircon were

observed. Hematite was observed in the pore space in the shape of skeletal-like crystals and is the reason for the red coloring of the rocks. By means of image processing, the free pore volume was determined to be about 28 %. Within the pore volume and especially in nooks and gussets in addition to hematite the clay minerals illite and kaolinite were seldomly found. Fig. 4 shows an overview of the untreated sandstone sample from backscattered electrons (BSE). The brightness of particles can be used to differentiate them mineralogically. Within the image, black areas represent the pore space, dark grey particles are quartz, medium grey particles are feldspars and light grey to white particles are heavy minerals, hematite in this case.
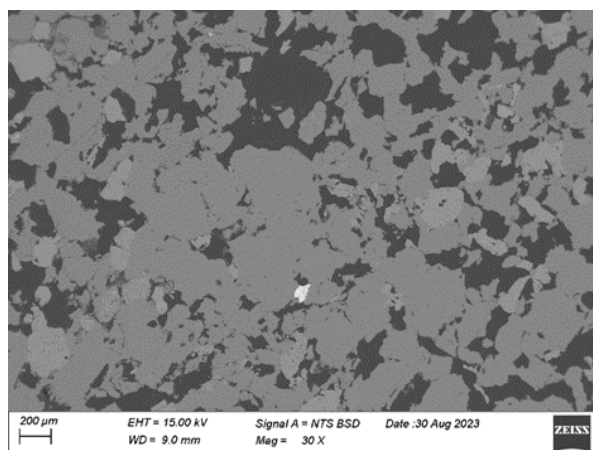

Figure 4: Overview image of untreated sandstone.

In the BSE images, newly formed minerals can easily be recognized by their bright colors (light grey to white). By means of EDX they can also be distinguished from the heavy minerals that are naturally present in the source rocks based on their chemical composition.

Based on EDX analysis, the newly formed phases are chemically a compound made up from barium, strontium, sulfur and calcium in traces. They are barite-celestine solid solutions. The strontium in these newly formed sulfates helps to distinguish between two generations of sulfates that were observed in the rock samples. On the one hand there is pure barite, which is a primary mineral within the rock, on the other hand there are newly formed barite-celestine solid solutions (see fig. 5).
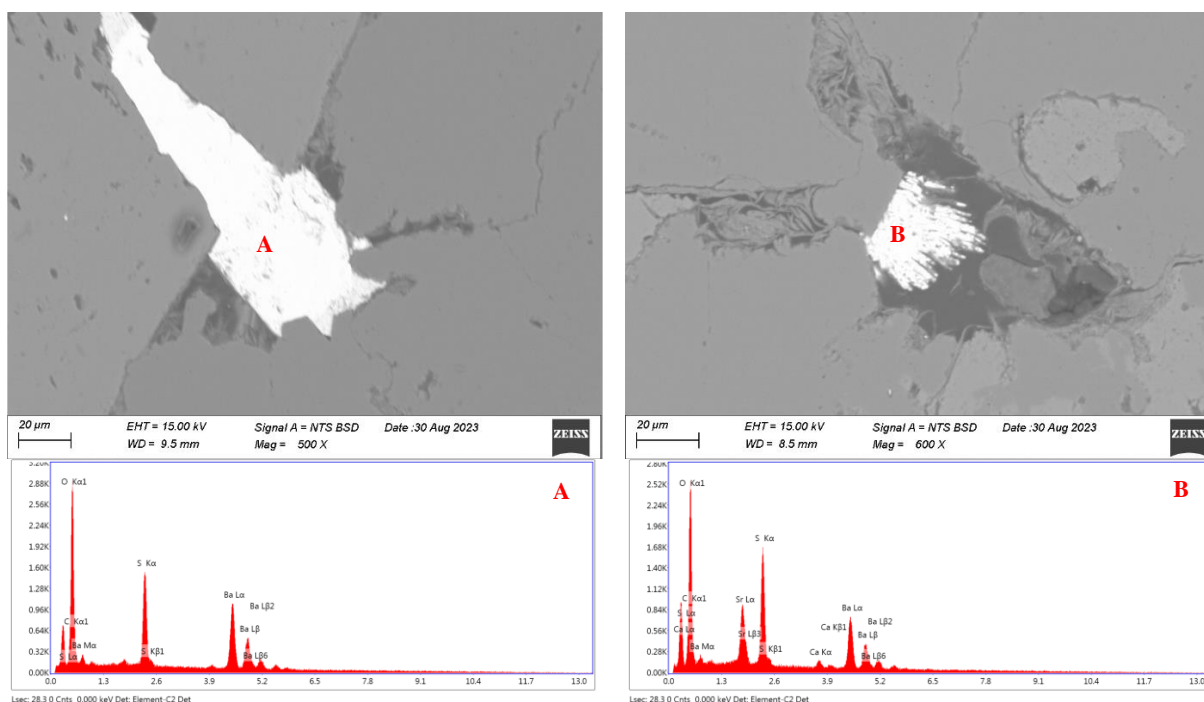

Figure 5: Sulfate minerals in the rock samples from the HydRA experiments: left side: primary barite from the source rock (point A); right side: newly formed barite-celestine solid solution (point B).

The two generations of sulfates can also be distinguished by their morphology. The primary barites form massive crystals that completely fill single pores. In contrast, the newly formed crystals have a needle-like shape and often appear in radial shaped bundles (see fig. 5). In addition, they usually do not fill the whole pore. Crystal growth starts in nooks, pore throats or on grain surfaces, the crystals then grow inwards to the center of the pore or seal pore throats. The observation that newly formed crystals do not grow large enough to fill out the whole pore is likely related to the testing time. It is also noticeable that new crystal growth seemingly favors spots where there is already growth of hematite or clay minerals (illite, kaolinite). These filigree minerals likely act as crystallization nuclei.

During the experiments without inhibitor (URG-06) or with the low concentration of the scaling inhibitor DTPMP (URG-07) a thick crust formed on the inlet side of the samples. The pore space on the inlet side also showed high amounts of newly formed crystals (see fig. 6). These findings are consistent with an observed pressure increase at the inlet side of the core plugs during the experiments.
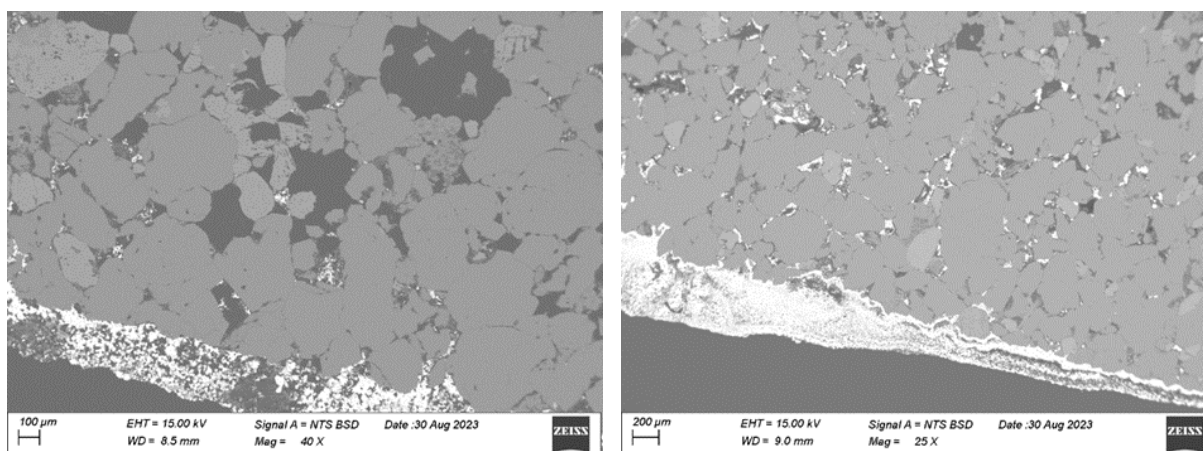

Figure 6: Left side: SEM image of the inlet side from experiment URG-06 without inhibitor with crustation and precipitation in the pore space; right side: SEM image of the inlet side from experiment URG-07 with 3.0 mg DTPMP/L with crustation and seams from barite-celestite solid solution growth in the pore space.

In the experiments with higher concentrations of scaling inhibitor (URG-10 and URG-12) no crust formation on the inlet side of the core plugs occurred, only some crystal growth within the pore space was observed. Experiment URG-12 had the lowest amount of newly formed phases (see fig. 7, right side). This again is consistent with observations during the HydRA experiments, where no significant pressure build up at the inlet side of the samples occurred.
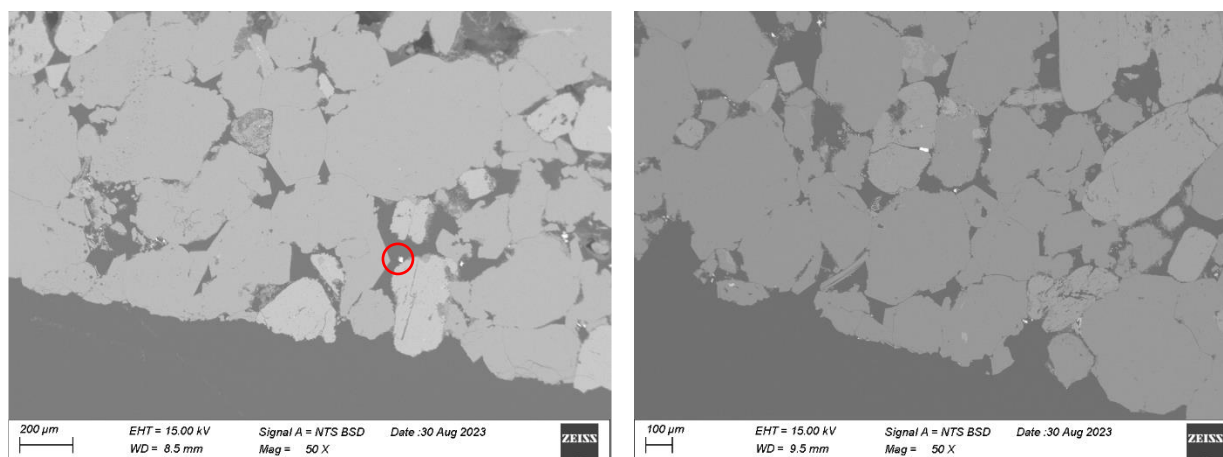

Figure 7: Left side: SEM image of the inlet side from experiment URG-10 with 5.0 mg DTPMP/L without crustation, and sporadic precipitation with radially grown crystals in the pore space (red circle); right side: SEM image of the inlet side from experiment URG-12 with an inhibitor combination, newly formed phases appear only seldomly (white spots in the image).

The proportion of strontium sulfate in the newly formed phases varies between 25 and 50 % and variations occur within the same sample on a small scale so that an influence of the inhibitors on the strontium to barium ratio cannot be assumed.

Interactions between the inhibitors and the grain structure of the samples made up from quartz and feldspar could not be detected in any of the experiments. Grain surfaces are smooth and do not show any signs of dissolution. Also, the original minerals that occur within the pore space (hematite, clay minerals) are unaffected even at high inhibitor concentrations.

4.3 Eluate Analysis (ICP-OES)

The flow through experiments simulate the conditions in the area close to the borehole. A large amount of liquid flows through the rock sample. Therefore, the analytical error is expected to be greater than the analytically determined concentration changes after the rock sample. However, barium and strontium are an exception here. In the case of the formation of barium, however, they are determined as they are components of the test solution and can precipitate in the form of sulfates, which leads to lower results in the eluate compared to the test solution.

The analyses of the eluates concerning barium and strontium were performed with the ICP-OES *iCAP 7000* by *ThermoFisher Scientific*. Fig. 8 shows the concentrations of the ions barium and strontium in the eluates in percent relative to the inlet concentration (= 100 %). A percentage concentration of > 100 %, i.e. an excess finding, indicates a re-solving of precipitations, a percentage concentration of < 100 %, on the other hand, indicates a deposition or precipitation of the ion.

Since the two membrane pumps used in the experiment are operated in the lowest flow range, deviations in throughput of up to 10 % may occur. In addition, there are also fluctuations caused by sampling, sample preparation and analysis. Total deviations in the range of ± 10 % are therefore considered to be realistic. For this reason, in the following, only variations of more than 10 % are regarded as significant. The range of 100 % ± 10 % is marked by a brown frame in fig. 8.
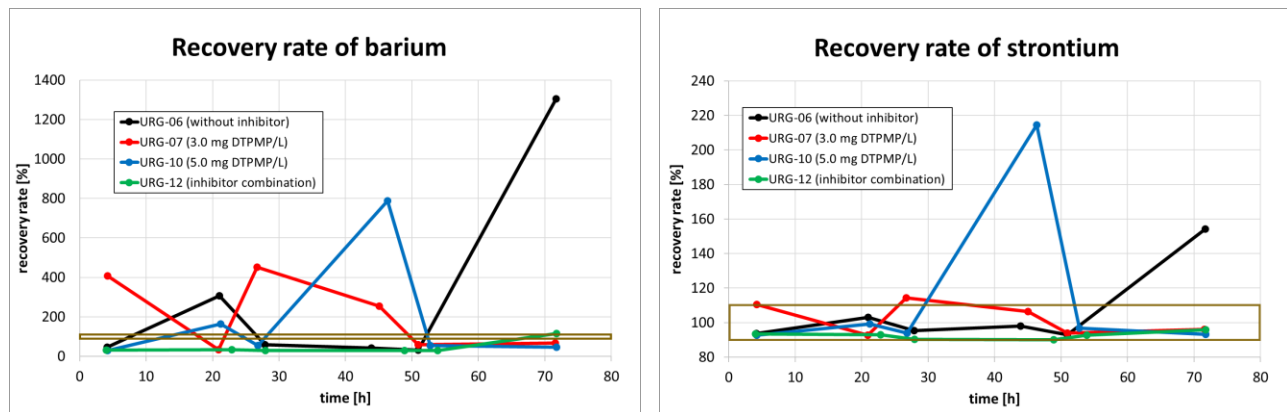

Figure 8: Recovery rate of barium and strontium (outlet concentration in relation to inlet concentration, inlet concentration set equal to 100 %). The brown frames highlight the range from 90 to 110 %.

The results show that the barium concentrations in the fluid samples are highly fluctuating (see fig. 8 left side) and partly exceed considerably the solubility of barium calculated with PhreeqcI. In this figure, the recovery rate of barium does not correlate with the use of an inhibitor. If barium sulfate particles that had already precipitated on the rock are rinsed out occasionally, due to the dilution of 1:100, they can resolve in the higher amount of solvent. The same happens with particles that are formed in the cooling zone. Both can lead to additional barium findings, so it is not possible to distinguish where the particles originate from.

The strontium concentration curves behave similarly to the ones for barium, with the difference that the upward outliers are less pronounced for strontium than for barium. An exception to this is the experiment URG-12, in which the inhibitor combination was used. Here, all measured strontium and barium concentrations remain below 100 % and no outliers occur.

The simultaneous occurrence of upward peaks for barium and strontium in fig. 8 could be an indicator for the fact that the outliers consist of already deposited barium-strontium sulfate solid solutions, which were flushed out. For all experiments, in SEM-EDX measurements barite-celestine solid solutions, coming from precipitates, can be detected in the pore spaces of the rock samples (see chapter 4.2).

5. SUMMARY AND CONCLUSIONS

One of the problems with the use of geothermal energy is the precipitation of barium-strontium sulfate when the water is cooled. As a result, the rock pores can gradually become clogged during re-injection, which affects the injectability and performance of the reservoir. This paper shows that flow through experiments with the HydRA laboratory facility are suitable for demonstrating the effectiveness of an inhibitor combination, i.e. the prevention of rock clogging. Both the assessment of the pressure increase during the flow through the

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rock sample in the HydRA facility and the analysis of the precipitates in the subsequent SEM-EDX investigations provide consistent indications of the appropriate inhibitor concentration in the geothermal plant.

The precipitates within an experiment are barite-celestine solid solutions with varying barium to strontium ratios. The inhibitors have no influence on this ratio. The growth of new sulfates begins preferentially at spots where there is already growth of hematite or clay minerals. They probably act as crystallization nuclei.

In all experiments, SEM imaging shows no evidence of inhibitor-induced dissolution reactions at the rock contact surfaces. This shows that the inhibitors have no negative effects on the rock-fluid interactions.

REFERENCES

Appelo, C. A. J.: Principles, Caveats and Improvements in Databases for Calculating Hydrogeochemical Reactions in Saline Waters from 0 to 200 °C and 1 to 1000 atm. Applied Geochemistry, 55, (2015), 62-71.

Baur, S., Neuberger, A-K., Kuhn, D. and Seibt, A.: Measurements on Fluid-Rock-Interaction of Thermal Water-Inhibitor-Mixtures with the HydRA Facility. Proceedings of the World Geothermal Congress 2020, Reykjavik, Iceland (2020).

Baur, S., Seibt, A. and Kuhn, D.: Laboratory flow-through experiments to determine the effect of inhibitors in the injection of fluids supersaturated with barium sulfate. Proceedings of the European Geothermal Congress 2022, Berlin, Germany (2022).

Charlton, S. R. and Parkhurst, D. L.: PhreeqcI — A Graphical User Interface to the Geochemical Model PHREEQC: U.S. Geological Survey Fact Sheet FS-031-02, (2002), 2 p., https://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/fs/FactSheetFS-031-02.html.

Daubner, M. and Krieger, V.: Betriebsmessdatenvisualisierung und -erfassung mit OPAL (OPC-Panel Livegraph) https://edocs.tib.eu/files/e01fn11/633077852.pdf, Online-Ressource. KIT Scientific Publishing, Karlsruhe (2010).

Hettkamp, Th., Baumgärtner, J., Parades, R., Ravier, G., Seibel, O. and Chouet, P.: Industrial Experiences with Downhole Geothermal Line-Shaft Production Pumps in Hostile Environment in the Upper Rhine Valley, Proceedings of the World Geothermal Congress 2020, Reykjavik, Iceland (2020).

Jähnichen, S., Degering, D., Seibt, A., Scheiber, J., Mouchot, J., Buse, Ch. and Heberling, F.: Inhibition of scales in geothermal plants in Upper Rhine Graben: Monitoring of fluids and scales, Proceedings of the European Geothermal Congress 2019, Den Hague, Netherlands (2019).

Scheiber, J., Nitschke, F., Seibt, A. and Genter, A.: Geochemical and Mineralogical Monitoring of the Geothermal Power Plant in Soultz sous Forêts, (France), Proceedings of the 37th Workshop on Geothermal Reservoir Engineering 2012, Stanford, CA, USA, (2012).

Scheiber, J., Seibt, A. Jähnichen, S., Mouchot, J., Baumgärtner, J., Hettkamp, T. and Uhde, J.: Scale and Corrosion Mitigation: Economic Feasibility of Combined Mitigation Measures. Proceedings of the World Geothermal Congress 2020, Reykjavik, Iceland (2020).

Parkhurst, D. L., and Appelo, C. A. J.: Description of Input and Examples for PHREEQC Version 3 — A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Techniques and Methods (2013).

Parkhurst, D. L., and Appelo, C. A. J.: User's Guide to PHREEQC (Version 2) — A Computer Program for Speciation, Batch Reaction, one Dimensional Transport, and Inverse Geochemical Calculations. Water-Resources Investigations Report 99-4259. U.S. Geological Survey, Denver, Colorado (1999).

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