Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Measurements on Fluid-Rock-Interaction of Thermal Water-Inhibitor-Mixtures with the HydRA Facility

Sabine Baur[1], Ann-Kathrin Neuberger[1], Dietmar Kuhn[1] and Andrea Seibt[2]

[1]Karlsruhe Institute of Technology, IKET, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

[2]BWG – Geochemische Beratung GmbH, Seestrasse 7A, D-17033 Neubrandenburg, Germany

E-mail: dietmar.kuhn@kit.edu

Keywords: barite oversaturation, saline fluid, water-rock-interactions, inhibitor

ABSTRACT

Generally, geothermal water in the reservoir is mostly close to the saturation equilibrium of the included salts. By pumping the water to the surface and extracting the heat, some minerals become supersaturated and precipitate. Therefore scaling occurs within the pipes of the thermal water cycle and in the reservoir at the injection well. The precipitation of supersaturated salts can lead to clogging of the pipes and to blockage of the rock pores or joints. The currently favored approach in the industry is to add complexing agents (inhibitors) to the thermal water before it is reinjected back into the reservoir.

The HydRA facility (= hydrothermal reaction apparatus) allows experiments to investigate the interaction of brine with reservoir rock samples under realistic reservoir conditions up to 420 bar and 250 °C. The facility offers the possibility of mixing two undersaturated solutions, which are supersaturated after mixing. In the test section the fluid mixture is pumped through a cylindrical rock specimen (1 inch in diameter, 2 inches in height) to interact with the reactive surface in the pores. Pressure probes at the inlet and outlet of the test section allow the detection of precipitation and dissolution of scales in the pore spaces. Thus, the phenomena during reinjection of thermal water into the reservoir rock can be investigated in the HydRA facility.

The topic of this work was to investigate how geothermal water supersaturated with barite (artificially made according to the composition of geothermal water of the Upper Rhine Graben) behaves when it flows through a red sandstone sample. Experiments without the inhibitor DTPMP and with different concentrations of this inhibitor were carried out. Also the stimulation and reactivation of already blocked pore spaces by injecting inhibitor solutions have been investigated. Furthermore the effect of injecting undersaturated water to enhance flow rate and reduce pressure drop in the rock sample was investigated. The experiments show that the performance of a geothermal well possessing a decreased permeability cannot be increased by injecting high inhibitor concentrations. The results show the importance of using inhibitor right from the start when exploiting a geothermal reservoir.

1. INTRODUCTION

During the operation of a geothermal plant hot thermal water is extracted by a production well, cooled down by a heat exchanger and reinjected into the rock layers from which it was taken. Due to the cooling many salts contained in the thermal water are less soluble. In particular, barium sulfate is problematic because it has only a low solubility in water (Monnin and Galinier, 1988 and Templeton, 1960). Precipitation can occur in the pipelines or heat exchangers of the power plant, but the crystallization of barium sulfate can also take place with a time delay close to the bottom of the reinjection well. As a result, its permeability is reduced, which requires higher and higher pressures to maintain a constant flow for the reinjection of the cooled thermal water.

Although it is state of the art that sulfate scales are successfully inhibited in plants in the Upper Rhine Graben (Jähnichen et al., 2019 and Seibt et al., 2018), more information about the inhibitor-rock-interactions is still needed.

Flow tests are carried out by laboratory experiments with the HydRA facility. Under practical conditions (T and P) red sandstone is flowed through by oversaturated $BaSO_4$ model brines (Na-Ca-Sr-Cl) with and without scale inhibitor.

2. MODELING AND SELECTION OF OPERATING CONDITIONS

The freeware program PhreeqcI Version 3.4.0 (Charlton and Parkhurst, 2002) was used to model the experiments. It is a graphical user interface for the geochemical computer program PHREEQC (Parkhurst and Appelo, 1999 and 2013). For the calculations the included Pitzer database was selected because it is appropriate for saline sulfate-rich solutions (Appelo, 2015).

The objective was to illustrate the solubility and the saturation index of barium sulfate in the artificial thermal water to be used for the experiments in this work (= test solution, see chapter 3.2.5) depending on temperature and pressure. By this way the operating conditions of the HydRA experiments should be selected.

A synthetically prepared solution, which is referred to in this work as the primary solution (see section 3.2.1), is used for modeling with PhreeqcI. In the first modeling the amount of barium sulfate is calculated that can be added to this solution until a saturation index of 0 is reached at different temperatures and pressures. The result can be seen on the left side of Figure 1. For comparison, the solubility of barium sulfate in demineralized water is plotted in the right part of Figure 1.

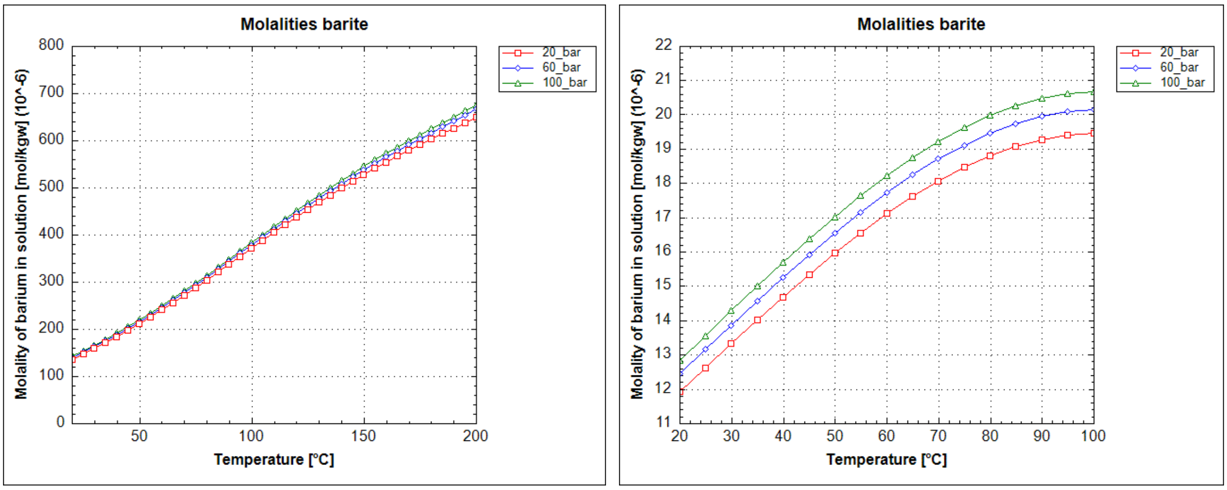

Figure 1: Left: Solubility of barium sulfate in the primary solution as a function of pressure and temperature. Right: Solubility of barium sulfate in demineralized water depending on pressure and temperature

The difference in the solubility of barium sulfate is low at different pressures between 20 and 100 bar. The left side of Figure 1 shows that at 20 bar and 60 °C the solubility of barium is 0.240 mmol Ba/kgw = 32.9 mg Ba/kgw, while at 60 bar and 60 °C the solubility of barium is 0.244 mmol Ba/kgw = 33.6 mg Ba/kgw. Higher pressures in the reservoir show only a little influence on the kinetics of the barium sulfate precipitation. In a geothermal power plant, the thermal water has to be exposed to at least 20 bar, to ensure that the gases contained remain dissolved. In some experiments rock specimens loaded with barium sulfate have to be made. Therefore the pressure in the experiments has to be adjusted in a way that the barium sulfate precipitating during the experiment is distributed homogeneously in the rock sample. If 20 bar is too low, higher pressures can also be applied.

The temperature has a considerable influence on the solubility. In the saline solution (left) significantly more barium sulfate dissolves than in pure water (Figure 1, right). For the experiments a temperature of 60 °C is selected because it is a realistic temperature for the reinjection of thermal water.

The left side of Figure 2 shows the saturation index of barite as a function of pressure and temperature, if the artificial thermal water contains exactly the mass concentrations of barium and sulfate included in the real thermal water (0.276 mmol Ba/kgw and 1.722 mmol sulfate/kgw). The right-hand illustration similarly plots the saturation index that results when these two concentrations are doubled.

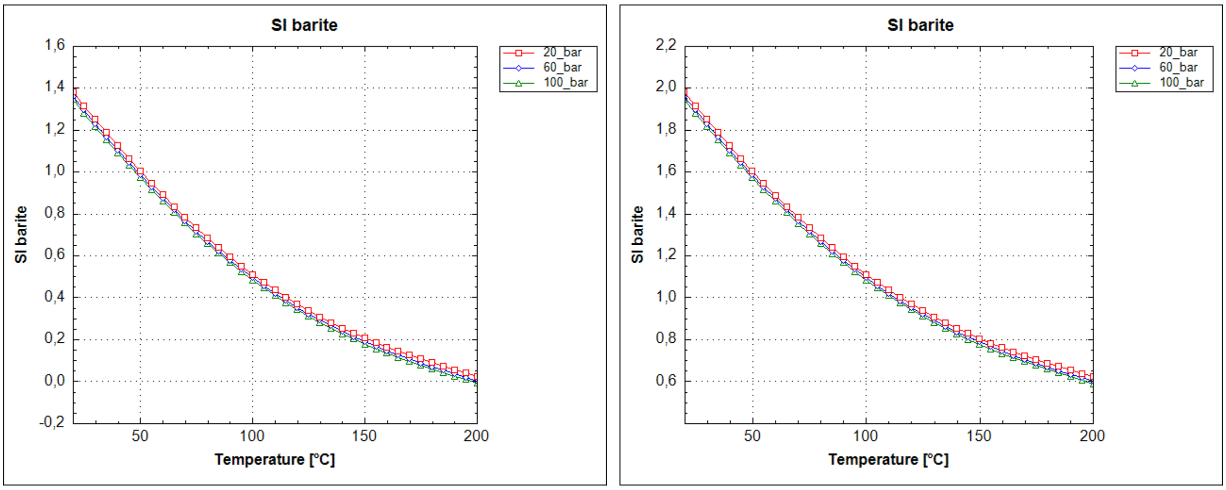

Figure 2: Saturation index (SI) of barite based on the barium and sulfate concentrations in the artificial thermal water used in this work. Left: Mass concentration of barium and sulfate as they occur in the real thermal water. Right: Mass concentration of barium and sulfate doubled.

With the real barium and sulfate concentrations, an SI (barite) of 0.888 results at a pressure of 20 bar and a temperature of 60 °C. As expected the SI for barite is only slightly smaller (0.871) at P = 60 bar and T = 60 °C. If the mass concentrations of barium and sulfate in the solution are doubled the SI increases from 0.888 to 1.488 and from 0.871 to 1.471, respectively.

To reflect almost real conditions in the precipitation experiments the initial concentrations of barium and sulfate were adjusted to a saturation index of about 0.9 to 1.5 at a temperature of 60 °C in a pressure range from 20 to 100 bar.

3. EXPERIMENTAL SETUP

3.1 Description of the HydRA Facility

HydRA is a test facility that can be used to recreate the conditions that can occur during the reinjection of thermal water in a geothermal power plant after its use. The system can be operated at pressures of up to 420 bar and temperatures of up to 250 °C. HydRA offers the possibility to pump two different undersaturated solutions and transport them separately into the test section where the mixture then becomes supersaturated and precipitation occurs. The main components of HydRA are shown in Figure 3.

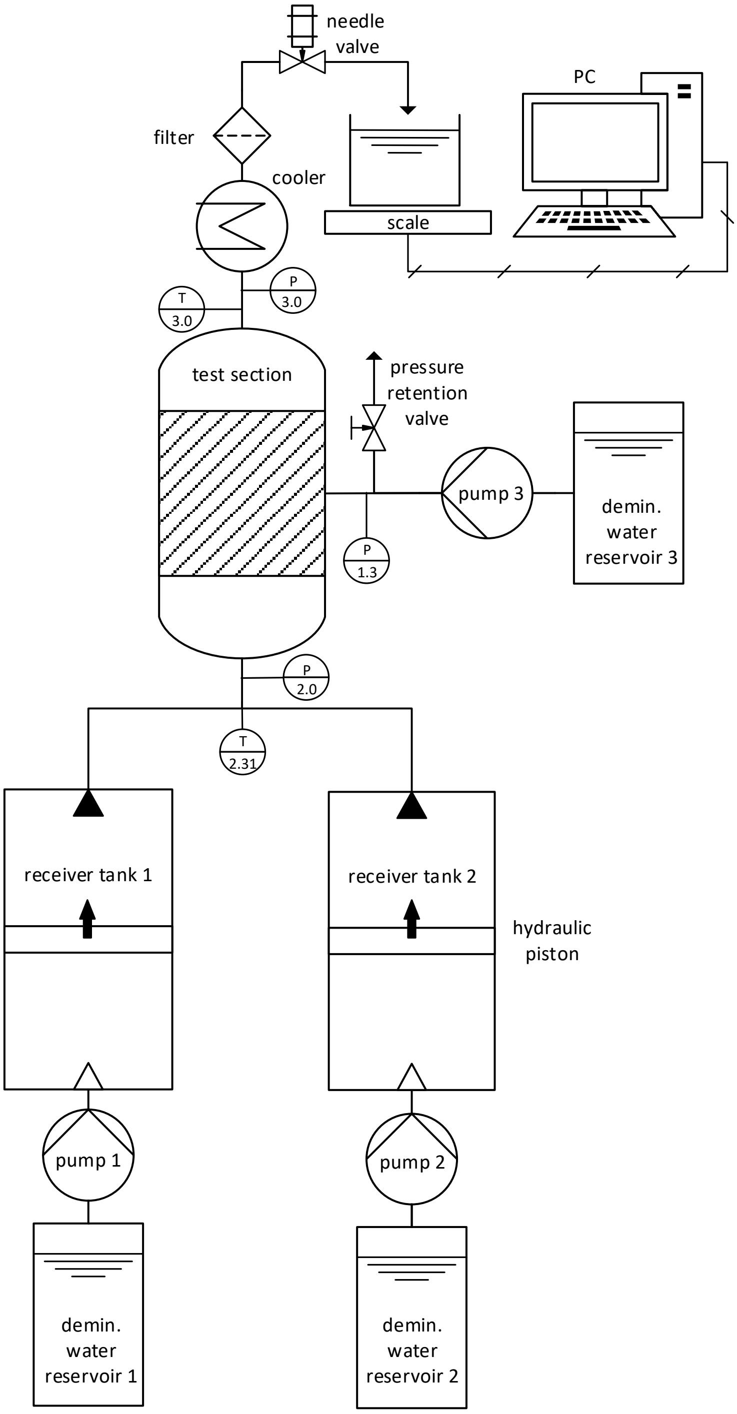

Figure 3: Main components of the HydRA facility and their connection.

Each cylindrical receiver tank contains a piston which separates its volume into an upper and a lower part, with the saline thermal water being stored in the upper part. The two pumps 1 and 2 (LEWA membrane pumps) convey demineralized water into the lower parts of the tanks, thus pushing the pistons upwards. In this way the potential corrosive thermal water is transported to the experimental plant without any contact to the internal parts of the pumps.

In the mixing section, the two solutions are mixed in equal portions by a mixing tee and then enter the reaction zone, where the mixture flows through the rock specimen. The fluid is then cooled and passes through a filter and a needle valve. Via a PLC, a pecking motor is controlled that adjusts the operating pressure by regulating the opening of the needle valve at the outlet. Both supply lines as well as the mixing and reaction zones can be heated separately.

At the outlet of the plant, the fluid drips into a reservoir on a scale, which is connected to the data acquisition system OPAL (Daubner and Krieger, 2010). The test facility is equipped with several pressure cells (Digibar II PE 300 by HBM) and thermocouples (type K), that are also recorded by the OPAL system. The most important sensors of the experimental set-up are: P2.0: pressure in front of the rock specimen, P3.0: pressure after the specimen (= operating pressure regulated by the needle valve), T2.31: temperature in the mixing section, T3.0: temperature shortly after the specimen (in the specimen no measurement is possible).

A typical red sandstone rock of the Upper Rhine Graben was chosen for the experiments and cylinders with a diameter of 1 inch and a length of 2 inches were fabricated from it. For a detailed characterization of the red sandstone used see Orywall et al. (2017). To saturate the pores of the rock samples with water they were placed into demineralized water prior to the experiments, until an almost constant weight was achieved.

To prevent the fluid from flowing laterally alongside the rock sample, it is enclosed in a silicone tube. From the outside pressure is applied (= jacket pressure, P1.3), which has to be kept larger than P2.0 and P3.0, so that the hose is always pressed firmly against the outside of the sample cylinder.

3.2 Applied Solutions

The following solutions were produced for the HydRA experiments:

3.2.1 Primary Salt Solution: Na-Ca-Sr-Cl Sole (Model Solution)

1.446 mol/L NaCl (ROTH, p.a.), 0.221 mol/L $CaCl_2 \cdot 2H_2O$ (ROTH, p.a.) and 5.0 mmol/L $SrCl_2 \cdot 6H_2O$ (VWR International, AnalaR NORMAPUR) were used as background electrolytes for simplifying the ion diversity in the original solution. The molar concentrations of all monovalent cations of the original thermal water were summed up and the result is included in the primary solution in the form of NaCl. The molar concentrations of all bivalent cations of the original thermal water, except for barium and strontium, were also summed up and the sum is mapped in the primary solution in the form of $CaCl_2$. The strontium content corresponds to the original fluid concentration. The total amount of dissolved solids in the model solution was 110 g/l.

3.2.2 Inhibitor Solutions

Dilutions of the commercial scale inhibitor DTPMP (diethylenetriamine pentamethylene phosphonic acid) were used in this study. For this purpose a commercial product by ZSCHIMMER & SCHWARZ MOHSDORF GmbH & Co KG was taken, having a concentration of DTPMP of about 50 %.

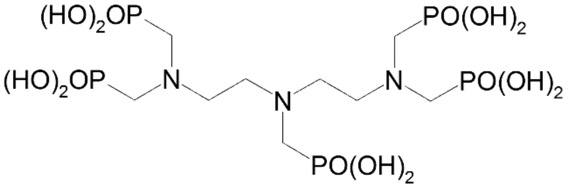

Figure 4: Molecular structure of DTPMP

Generally, inhibitors can act in two different ways: Either the inhibition of crystal nucleation takes place by complexation of corresponding cations (e.g. Ba) to soluble complexes. Or the crystal growth can be reduced by chemisorption at actively growing crystal surfaces (e.g. Ba or sulfate). For complexation a stoichiometric amount of inhibitor is needed whereas in the case of chemisorption substoichiometric amounts are sufficient for scalings to be inhibited (threshold-effect). For DTPMP, the crystal growth-blocking mechanism is more pronounced (Shaw and Sorbie, 2012).

3.2.3 Secondary Solution: $BaCl_2 \cdot 2H_2O$ and Na_2SO_4 Solutions

Diluted $BaCl_2 \cdot 2H_2O$ (MERCK, p.a.) and Na_2SO_4 (MERCK, p.a.) solutions were produced with regard to the volume of the primary salt solution that will be filled into the receiver tanks.

3.2.4 Receiver Tank Solutions

To the primary solution for the first receiver tank the required amount of barium chloride containing secondary solution is added. To the primary solution for the second receiver tank the necessary amount of sodium sulfate containing secondary solution is added. Both resulting receiver tank solutions are undersaturated as long as they are separated. But when they are mixed in the test facility in the same volume ratio to produce the test solution, an oversaturation of barium sulfate occurs according to the following reaction equation:

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2\,Na^+ + 2\,Cl^- \qquad (1)$$

This procedure is necessary to avoid precipitation of $BaSO_4$ during storage or in the supply lines.

In case of inhibitor experiments, the necessary amount of inhibitor is added to the second receiver tank which contains the sulfate solution.

3.2.5 Test Solutions

The mixture of both receiver tank solutions forms the test solution that flows through the rock sample. This test solution contains 0.257 mmol Ba/L combined with 1.614 mmol sulfate/L or 0.514 mmol Ba/L combined with 3.227 mmol sulfate/L. In the experiments with inhibitor the test solution contains 2.5, 5, 25 or 100 mg DTPMP/L. Two further experiments were performed with demineralized water flowing through the rock sample.

4. PLANT OPERATION AND HYDROCHEMICAL ANALYSES

4.1 Loading of the Rock Specimen

The PLC-controlled needle valve (see Figure 3) ensures that the pre-set pressure at the outlet of the test facility (P3.0) is kept constant. If continuous precipitations occur in the rock specimen, the pressure in front of it (P2.0) steadily increases. However, the pressure after the sample (P3.0) is still kept constant at the preset value, which leads to a pressure difference. If the pressure in front of the rock reaches 95% of the jacket pressure (P1.3), the system switches off automatically (= immediate shutdown criterion). In the following experiments this is defined as status "rock sample blocked". The aim is a uniform distribution of the precipitated barium sulfate inside the rock.

4.2 Sampling and Chemical Analytics of Barium

The barium concentration in the solution discharged from the facility is determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, OPTIMA 4300 DV by PerkinElmer). To enter the metering range of the ICP-OES, the water samples had to be first diluted 1:5 with nitric acid solution (5 mL concentrated HNO_3 to 1 liter of demineralized water), thoroughly mixed and shaken from time to time. The samples were then filtered via 0.2 µm nylon filters and analyzed by ICP-OES. The reason why the solutions were diluted prior to the filtration was that the 60 °C hot thermal water flows through the 25 °C cold cooling section after the test section in which the insoluble barium sulfate content at 60 °C precipitates. This reduces the solubility of $BaSO_4$ and new crystals and/or clusters can be formed. If the resulting suspension is filtered subsequently after sampling, the barium concentration dissolved in the thermal water at 25 °C would be determined. The crystals which have precipitated after the 60 °C zone can be dissolved again by the dilution at an early stage and the successional waiting period.

5. EXPERIMENTS

The aim of the blocking experiments (chapter 5.1) is to load a red sandstone specimen homogeneously with barium sulfate crystals according to the description in chapter 4.1. The subsequent inhibitor experiments (chapter 5.2) attempted to resolve the previously precipitated barium sulfate. The inhibitor-blocking experiments (chapter 5.3) are intended to determine the concentrations of the DTPMP inhibitor which are needed to prevent precipitations of barium sulfate in the rock right from the beginning.

The temperatures of the mixing and reaction sections (T2.31 and T3.0 respectively) are set to 60 °C and the flow rate of both receiver tank solutions is 1 mL/min each in all experiments.

Table 1: Overview of the experiments.

Chapter	Kind of experiment	Test designation	Pressure regulated by needle valve [bar] = P3.0	Jacket pressure [bar] = P1.3	Temperature of mixing section [°C] = T2.31	Temperature of test section [°C] = T3.0	Total flow through the rock sample [mL/min]	Barium concentration in test solution [mmol/L]	Sulfate concentration in test solution [mmol/L]	Inhibitor concentration in test solution [mg/L]	Test duration [h]
5.1	Blocking experiment	Be_04	60	112	63,5	65,6	2	0.514	3.227	0	50
5.2	Inhibitor experiment after blocking	In_03	60	109	65,3	56,8	2	0.257	1.614	25	74
	Inhibitor experiment after blocking	In_04	60	127	68,5	58,4	2	0.257	1.614	100	78
	Inhibitor experiment after blocking	In_05	60	105	56,6	58,0	2	demineralized water		0	136
	Inhibitor experiment after blocking	In_06	60	114	53,4	57,7	2	demineralized water		0	170
5.3	Inhibitor-blocking experiment	IBe_01	60	107	63,5	65,4	2	0.514	3.227	5	127
	Inhibitor-blocking experiment	IBe_02	60	104	61,3	62,0	2	0.514	3.227	5	137
	Inhibitor-blocking experiment	IBe_07	60	107	59,5	58,7	2	0.514	3.227	2.5	139

5.1 Blocking Experiments

Blocking experiments in the HydRA facility showed that the real concentrations of barium and sulfate in the test solution are not sufficient to reach a precipitation of $BaSO_4$ that is fast enough to load or block the specimen to an extent, that pressure P2.0 approaches the value of the jacket pressure P1.3 (see chapter 4.1). Therefore, in the further blocking experiments, the concentrations of barium and sulfate in the test solution are doubled. The experiments also showed that for a homogeneous distribution of barium sulfate in the rock an operating pressure of P3.0 = 60 bar is required. The initially used pressure of P3.0 = 20 bar proved to be insufficient. The jacket pressure P1.3 is set to 110 bar, so the shutdown criterion and thus the blocking of the rock as defined in chapter 4.1 is reached at a pressure value of approx. 105 bar for P2.0. In experiment Be_04 specimen blocking was reached after 50 hours. The pressure increase in front of the rock sample (P2.0) is shown as a red curve in Figure 5.

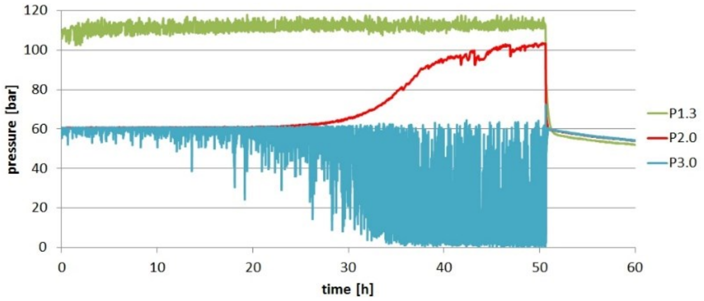

Figure 5: Pressure profile in blocking experiment Be_04

By opening the needle valve at the outlet of the system, the pressure after the specimen (P3.0) is reduced. If the pressure drop across the rock sample is low, the fluid flows well, and can quickly compensate this pressure difference. Increasing loading of the rock sample increases the resistance, which leads to a deteriorated delivery of the solution. The pressure loss due to the opening of the needle valve can thus be compensated increasingly worse and becomes more and more pronounced. Instead of the initial pressure fluctuation of about 3 to 5 bar, a pressure fluctuation of almost 60 bar occurs after the rock sample by the end of the experiment.

The pressure curve of the experiment Be_04, as well as the distribution of the barium sulfate precipitations inside the rock and the duration of the experiment are ideal. Therefore, this experiment is taken as reference blocking experiment and further rocks were loaded with barium sulfate under analog operating conditions.

5.2 Inhibitor Experiments after Blocking

Following blocking experiments, the respective specimens are used for inhibitor flushing experiments. These are intended to show whether a rock that has already been blocked by barium sulfate can be made usable again by subsequent addition of inhibitor. For this purpose, the concentrations of barium and sulfate that naturally occur in the thermal water were added to the primary solutions.

To prevent barium sulfate precipitation usually inhibitor concentrations in the low mg/L range are used. In the inhibitor experiments after blocking, significantly higher concentrations of 25 mg/L (experiment In_03) or 100 g/L (experiment In_04) are used since it is intended to resolve already precipitated barium sulfate. In further experiments (experiment In_05 and In_06), it is investigated whether a rock that is already blocked by barium sulfate can be made permeable again by purging with an undersaturated solution. For this purpose in the current work demineralized water was chosen.

All following inhibitor experiments took place immediately after the respective blocking experiment with operating parameters according to Be_04 (see Table 1).

5.2.1 Inhibitor Experiments with Addition of Inhibitor

For these experiments the pressure after the specimen was regulated to 60 bar by the needle valve. But instead of reducing the pressure drop over the rock sample, which would indicate a dissolution of the precipitated barium sulfate, the pressure P2.0 in front of rock sample continues to rise (see Figure 6, red curve), which indicates that the permeability of the rock becomes rather worse during the experiment.

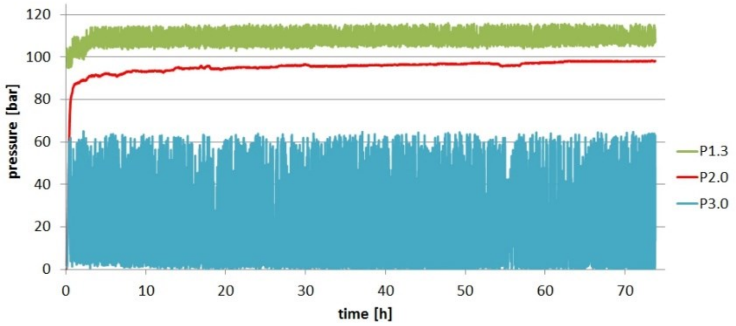

Figure 6: Pressure profile in inhibitor experiment In_03

The mode of action of the inhibitor is based on an attachment on crystals and thus the prevention of their further growth. The resulting enlargement of the crystals could be the reason that the flow paths were further blocked by the inhibitor and thus an increase in pressure in front of the rock sample occurs. Also an addition of barium sulfate to existing crystals is conceivable. Due to the already existing loading of the rock sample, the surfaces are already covered with many barium sulfate crystals. If these sites are not blocked by inhibitor, further barium sulfate could attach despite the added inhibitor.

Compared to experiment In_03, the concentration of inhibitor is increased four times to 100 mg/L in experiment In_04. However, no reduction of the pressure difference across the rock sample is observed within a test duration of 78 hours. The pressure curve is analogous to In_03 with an inhibitor concentration of 25 mg/L.

5.2.2 Inhibitor Experiment with Demineralized Water

In principle, precipitated salts can be dissolved by being rinsed with an undersaturated solution. Thus it should be possible to redissolve precipitated barium sulfate in demineralized water.

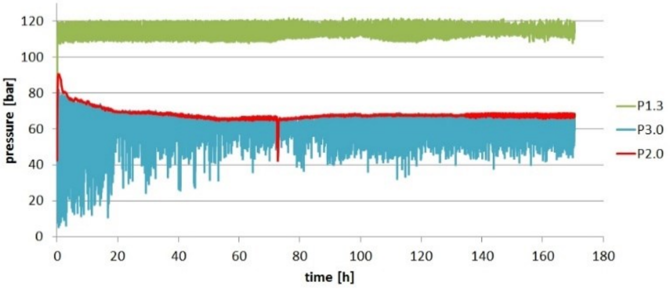

Figure 7: Pressure profile in inhibitor experiment In_06

To get an indication whether the decrease in pressure in front of the rock sample (P2.0, red curve in Figure 7) is due to dissolution of $BaSO_4$ crystals or mechanical purging, ICP-OES was used for hydrochemical analyses of barium in the artificial thermal water discharging the facility. The procedure of sampling and the sample conditioning are described in chapter 4.2.

Barium was detected in all samples taken during experiment In_06, and often the measured value was above the calibrated range of 5 mg/L. In these samples significantly more barium was detected (up to the range of approx. 32 mg/L), than is soluble in pure water at 60 bar and 60 °C according to the PhreeqcI calculations (2.43 mg/L, see Figure 1 right). The reason for this high barium content in the ICP-OES analysis could be that small barium sulfate crystals were flushed out of the rock and dissolved completely or partially due to the 1:5 dilution. So these results would rather indicate a mechanical flushing of the rock sample loaded with $BaSO_4$, than an exclusive purging due to solubility.

5.3 Prevention of Precipitation by the Inhibitor (Inhibitor-Blocking Experiments)

These test series are designed to show which concentration of inhibitor is required to prevent the rock from becoming blocked. All inhibitor-blocking experiments were carried out analogously to the loading experiment Be_04, but in contrast to this inhibitor was added from the very beginning. Due to the otherwise identical composition of the water both experiments, and thus the effectiveness of the inhibitor, are well comparable.

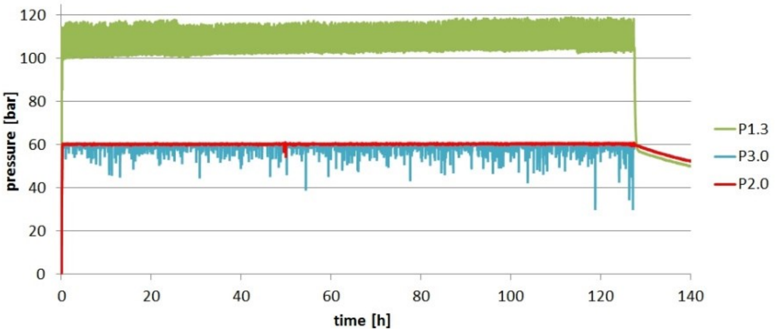

Figure 8: Pressure profile in inhibitor-blocking experiment IBe_01

In the experiment IBe_01, which was carried out with 5 mg DTPMP per liter of test solution, there is no significant increase in the pressure drop across the rock sample (= P2.0 – P3.0) even with a considerably longer test duration than in experiment Be_04 (127 h versus 50 h). Since no scaling could be detected, the effectiveness of the inhibitor was shown (see Figure 8). In experiment Be_04, after a test duration of approx. 25 hours a first pressure increase in front of the rock sample was observed (see P2.0 in Figure 5). In experiment IBe_02, a repetition of IBe_01, the same result is obtained: no pressure increase in front of the rock sample is detected for 137 hours. Even with a reduced inhibitor concentration of 2.5 mg/L no pressure difference across the specimen occurs within 139 hours in experiment IBe_07.

6. RESULTS

To obtain results that can be transferred to reality, experimental conditions as natural as possible should be pursued. Experiments showed that 60 °C (a typical reinjection temperature) as operating temperatures for the mixing and reaction zones are suitable to obtain good results in all kind of experiments.

As far as the blocking experiments are concerned, a doubling of the barium and sulfate concentration and an increase in operating pressure from 20 bar to 60 bar yielded the desired result: In experiment Be_04, the rock sample could be blocked within 50 hours, with a homogeneous distribution of the crystals. Therefore, the experimental conditions of Be_04 were used in all further blocking experiments.

In all other types of experiments (In and IBe) a pressure of 60 bar is applied as well and the concentrations of barium and sulfate are set to the values in real thermal water.

In experiment In_03 it was intended to rinse a previously blocked rock sample by resolving the scalings of barium sulfate with a concentration of 25 mg of inhibitor per liter of thermal water. In experiment In_04 100 mg of inhibitor per liter were applied. Both approaches did not lead to a reduction but to an increase in pressure in front of the rock sample.

In an attempt to free the blocked sample from barium sulfate with demineralized water (experiment In_06), a reduction in the pressure loss was observed. But this behavior is not necessarily due to dissolution of the crystals.

In the final test series on the prevention of scaling it was shown, that an amount of 5 or 2.5 mg DTPMP per liter of solution right from the beginning is sufficient to prevent an increase in pressure in front of the rock sample.

7. SUMMARY AND CONCLUSIONS

One of the problems that arise when using geothermal water is the precipitation of dissolved salts, in particular $BaSO_4$, due to the cooling of the thermal water. By these precipitations, the pore spaces of the rock can be reduced or ultimately blocked. As a result, for operating the power plant higher and higher pressures are necessary to reinject the extracted thermal water.

Laboratory experiments with the HydRA facility indicate that the addition of the inhibitor DTPMP can prevent such blockage of the pores of red sandstone. As demonstrated in the experiment, already an inhibitor concentration of 2.5 mg/L is efficient under practical conditions. So the HydRA facility is able to make estimates concerning the concentration needed to prevent precipitations.

The experiments have shown how important it is to apply precipitation inhibitors permanently right from the start when using a geothermal well to avoid blockages of the reservoir. The process of blocking can not be reversed by addition of high concentrations of inhibitor. A possible explanation for this is that the inhibitor attaches to existing crystals, thereby enlarging them and thus worsening the flow. Flushing an already blocked reservoir with undersaturated water (in our experiments demineralized water) is also not helpful. Although the differential pressure across a blocked rock sample drops, precipitated barium sulfate crystals are rather mechanically removed than chemically dissolved.

In the HydRA facility realistic geothermal conditions can be simulated to investigate rock samples. Therefore the investigation of the following research areas are of interest: Interaction phenomena between rock and thermal water and inhibitor can be studied. Further research could also lie in the decomposition products of the inhibitor. Also the efficiency of inhibitors at higher temperatures could be examined.

8. ACKNOWLEDGEMENTS

The authors would like to thank Dr. Thomas Bergfeldt, KIT, IAM-AWP-CA for his constructive support in sample analysis using ICP-OES. We are also grateful to Dr. Andreas Friedrich, Pro Science for proofreading.

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.

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).

Jähnichen, S, Degering, D., Seibt, A., Scheiber, J., Mouchot, J., Buse, Ch., and Heberling, F: Inhibition of scale in geothermal plants in Upper Rhine Graben: Monitoring of fluids and scales, EGC 2019.

Monnin, C., and Galinier, C.: The Solubility of Celestite and Barite in Electrolyte Solutions and Natural Waters at 25°C: A thermodynamic study. *Chemical Geology*, **71**, (1988), 283-296.

Orywall, P., Drüppel, K., Kuhn, D., Kohl, T., Zimmermann, M., and Eiche, E., 2017: Flow-through Experiments on the Interaction of Sandstone with Ba-Rich Fluids at Geothermal Conditions. *Geothermal Energy*, **5**, 20 p.

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).

Seibt, A., Jähnichen, S., and Wolfgramm, M.: Inhibitoren bei der geothermischen Nutzung hochmineralisierter Fluide, *Zeitschrift Geothermische Energie*, Heft 89/2018/2.

Shaw, S. S., and Sorbie, K. S.: The effect of pH on static barium sulphate inhibition efficiency and minimum inhibitor concentration of generic scale Inhibitors, *Society of Petroleum Engineers*, SPE 155094, (2012).

Templeton, C. C.: Solubility of Barium Sulfate in Sodium Chloride Solutions from 25° to 95°C. *Journal of Chemical & Engineering Data*, **5**, (1960), 514-516.