Application of a Scaling Inhibitor System at the Geothermal Power Plant in Soultz-sous-Forêts: Laboratory and On-site Studies

Julia Scheiber[1], Andrea Seibt[2], Johannes Birner[3], Albert Genter[1], Wilfried Moeckes[1]

[1] GEIE, “Exploitation Minière de la Chaleur”, Route de Soultz, 67250 Kutzenhausen, France

[2] BWG Geochemische Beratung GmbH, Seestraße 7A, 17033 Neubrandenburg, Germany

[3] GTN Geothermie Neubrandenburg GmbH, Seestraße 7A, 17033 Neubrandenburg, Germany

scheiber@soultz.net

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ABSTRACT

At the geothermal power plant in Soultz-sous-Forêts, France, geothermal brine (100 g/l TDS) is produced from a fractured granite reservoir, which is a natural radioactive rock. The formation of scalings affects negatively the efficiency of the heat exchangers and the injection well performance. Those scalings are formed mainly at the cold part of the plant and consist of solid solutions of strontium rich barite ($Ba_{1-x}Sr_xSO_4$) and minor amounts of sulfide minerals like galena (PbS). Within the Organic Rankine Cycle (ORC) heat exchanger act those scalings as isolation material and decreases the efficiency of the heat transfer between geothermal and organic fluid. As a consequence, cleaning operations for scale removal are required in regular time intervals to keep up the efficiency of the energy production. During cleaning and disposal operations, strict regulations for safety at work have to be followed due to radioprotection rules, related to the presence of ^{226}Ra and ^{210}Pb in the scalings. In the injection wells, the inner diameter of the casing decreases slowly but continuously by deposition of scales. Moreover, a progressing precipitation front exists in the injection wells versus depth which can reach the open-hole section in the future as a function of the injected volume of geothermal brine.

For reasons of safety at work and long term operation of the injection wells in Soultz, the formation of barite needs to be inhibited continuously. Therefore, 4 different products based on phosphonic acid were tested in laboratory experiments. These study included tests for calcium tolerance, effectiveness, dose rate adjustment, thermal stability and the interaction with reservoir rocks. Artificial solutions and original Soultz brine was utilized. All four inhibitors showed a high calcium tolerance. Three of them inhibit successfully the formation of barite with both, artificial solutions and original brine. One of the products triggered barite precipitation instead of blocking it. Only two products were able to suppress co-precipitation of iron-silica compounds.

Finally the DTPMP based product was selected for injection at the geothermal power plant in Soultz and an injection system was installed. Concentrated phosphonic acid is added dropwise to the production stream at 433 K (160˚C) and 2 MPa (20 bars) before entering the heat exchanger. The on-site injection test worked out very well and the Ba^{2+} concentration in the brine kept a constant level from the production to the injection well. Besides the successful blocking of barite precipitation, a slight dissolution of the galena was observed.

1. INTRODUCTION

The deep geothermal project at Soultz is located 50 km NE of Strasbourg in the north of France at the western part of the Upper Rhine Graben (UGR). This tertiary rift system is connected with a geothermal anomaly showing a higher temperature gradient (Fig. 1).

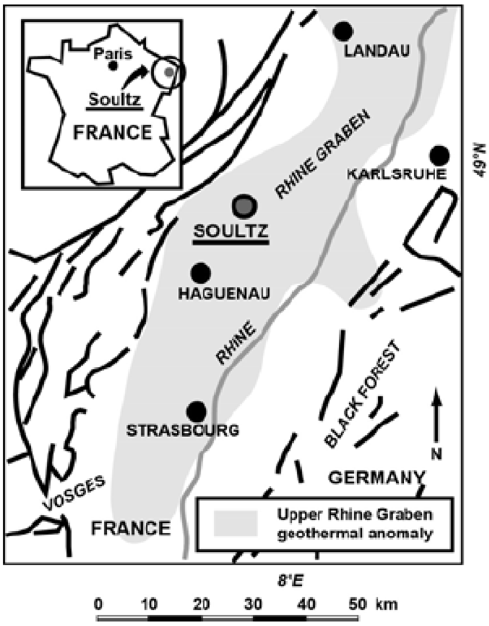

Figure 1: Location of the geothermal project of Soultz-sous-Forêts. The grey area marks the geothermal anomaly of the Upper Rhine Graben (Hurtig et al., 1992).

Within this anomaly are a few locations where the temperature gradient is even higher than in the surrounding areas. Temperature measurements in oil wells of the Pechelbronn oil field indicated one of these very local anomalies to be at the Soultz Horst (Haas and Hoffman, 1929). The crystalline basement is covered by 1400 m of sediments, mainly made of clays, sands, marls, lacrustine limestone and sandstone (Schnaebele et al., 1948).

Originally in 1984, the Soultz project was planned as a Hot Dry Rock (HDR) project (Gérard and Kappelmeyer, 1987) but in fact, permeable and native brine-bearing fractures were discovered during reservoir development down to over 5000 m depth. From 1987 to 2005, five wells were deepened into the crystalline basement: One exploration well, EPS-1 (2227 m), and four geothermal wells, GPK-1 (3590 m), GPK-2 (5077 m), GPK-3 (5111 m) and GPK-4 (5270 m). The openhole sections of all wells are located in a fractured and altered granite reservoir (Genter et al. 2010). Permeability of the existing fracture zones was improved successfully by several hydraulic and chemical stimulations (Nami et al., 2008, Portier et al. 2009). The former HDR project consequently turned into one of the first EGS projects in Europe.

After stimulation, several short and long-term circulation tests were successfully conducted in 2005 (Nami et al., 2008). The power plant, equipped with an Organic Rankine Cycle (ORC) unit, was designed and installed between 2007 and 2009 with an estimated gross capacity of 2.2 MWe. The 4 geothermal wells were originally planned to act as two doublets, involving two production wells, GPK-2 and GPK-4, and two injection wells, GPK-1 and GPK-3. For the circulation period in 2013 however, the following setup was chosen: production from GPK-2, equipped with a Line Shaft Pump (LSP), and injection into GPK-4 and GPK-3. GPK-4 is performed as injection well for this circulation period but could be re-used as production well in the future.

The formation of scalings in the surface and subsurface installations of the Soultz geothermal power plant, are connected with circulation and cooling of the geothermal brine due to the high salt content (97 g/l) of the Na-Cl-Ca brine (Sanjuan et al., 2010). The scaling formation in Soultz is strongly connected to the cold part of the power plant due to the significant temperature decrease from 433 K (160˚C) to 343 K (70˚C) in the ORC tube heat exchanger. By decreasing the temperature of the geothermal brine, the saturation state of several minerals is exceeded and strontium rich barite ($Ba_{1-x}Sr_xSO_4$), galena (PbS) and minor fractions of mixed sulfides ($((Fe,Sb,As)S_x)$) are formed (Sanjuan et al., 2011; Scheiber et al., 2012 and Nitschke, 2012), (Fig, 2 and Fig. 3). The sulfate and sulfide scalings are deposited in the heat exchanger system, inside of the equipment downstream to the injection well and even inside of the injection wells.

Figure 2: Barite scaling cover the inner surface of a pipe of the surface installations. The deposit has a thickness of 0.5 to 0.7 mm (Picture: GEIE)**.**

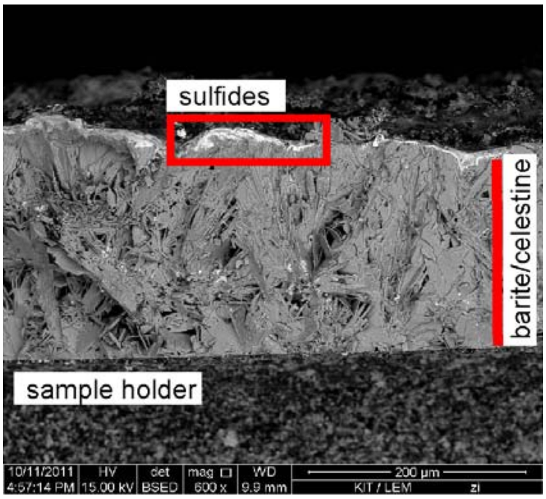

Figure 2: Electron microscopy exposure of the cross section of a scaling layer in the back scattered mode (BSED). A thin layer of sulfides, approximately 5-10 µm, covers the surface of the dominating barite layer, average thickness of 200 µm. The deposit was sampled from the main ORC heat exchanger (Scheiber et al., 2012)

Those scales are known to accumulate the radionuclides ^{226}Ra in barite/celestine and ^{210}Pb in galena by chemical substitution during the formation of the minerals (e.g. Doerner and Hoskins, 1925, Ceccarello et al., 2004, Zielinski et al., 2001, Kudryavskii and Rakhimova, 2007 and Curti et al., 2010). Geothermal fluid is circulating within fractured granite which is a natural radioactive rock. The geothermal fluid is in equilibrium with the rock and by rock-fluid interactions radionuclides are transferred into the brine.

Three serious issues are connected with the precipitation of industrial scalings, classified as Naturally Occurring Radioactive Material (NORM) in the surface installations of the Soultz power plant: First, scalings act as an isolation material in the heat exchanger which leads to a significant efficiency decrease in the heat transfer from the geothermal to the organic fluid (isobutane). In consequence, extensive costs and time consuming cleaning procedures had to be applied. Second, specific protection regulation for the workers and for scale disposal needed to be followed due to the presence of radionuclides in the scales. Those scales are considered as radioactive waste deposits and had to be evacuated with ANDRA (French National Agency for Radioactive Waste Management). Third, within the injection well casing, the inner diameter decreases slowly but continuously due to deposition of scales. Moreover, it is assumed that a progressing precipitation front exists in the injection wells versus depth which can reach the open-hole section in the future as a function of the injected volume of geothermal brine.

To avoid the formation of scales and thereby the radioactive contamination of deposits, several measures were developed in the past in the oil and gas industry. Most common method is the addition of scale inhibitors like phosphonates, polyphosphates and polycarboxylates (He et al., 1994). Therefore, a scaling inhibitor, based on phosphonic acid, was selected and tested in laboratory experiments for its compatibility with the Soultz brine as well as the reservoir rocks. At the power plant an injection system was installed and tested for efficiency and dose rate adjustment. The injection of a scaling inhibitor is expected to decrease the total amount of scalings at the cold part of the power plant and as a consequence, the time periods between the cleaning procedures can be significantly elongated.

2. LABORATORY TESTS OF SCALING INHIBITOR EFFICIENCY

Strontium rich barite is the dominating precipitate in the Soultz scalings. For inhibition of this kind of sulfate mineral, chemical products based on phosphonates were chosen to be tested for their effectiveness of scaling avoidance at the Soultz geothermal power plant.

2.1 Efficiency of Phosphonates

Phosphonates are well known inhibitors which are widely used in oilfield applications (Black et al., 1991 and He et al., 1994). They act in two different ways: On one hand they complex specific cations by forming water soluble complexes. On the other hand, they inhibit the growth of crystals by adsorption on growth-active surfaces which leads thereby effectively to retardation or blocking of the growth rate.

The degree of efficiency of an inhibitor is influenced by several physical-chemical parameters: pH, coordination number of the complex, thermal stability, adsorption affinity, and the presence and concentration of co-ions like Ca^{2+}, Mg^{2+}, Sr^{2+} or Pb^{2+} in solution, the degree of supersaturation of barite as well as of the degree of supersaturation of the inhibitor and the thermal stability of the phosphonate.

With decreasing pH the inhibiting effect of phosphonates of sulfate mineral growth, like barite and gypsum, also decreases (Van Rosmalen et al., 1980, He et al., 1994 and Rosenberg et al., 2012). Phosphonates are very effective at very low concentrations. This type of threshold inhibition is related to adsorption of phosphonates or their dissociated compounds on growth-active surfaces (Weijnen and Van Rosmalen, 1986, He et al., 1996 and Pina et al., 2004). As a consequence of these adsorption processes the crystal morphology changes from typically idiomorphic crystals to smoothed and rounded surfaces (Black et al., 1991 and Pina et al., 2004). A high concentration of co-ions can trigger the precipitation of metal-phosphonates (Nowak, 2003). With increasing temperature a higher amount of inhibitor is required (He et al., 1994) and also thermal induced decomposition of phosphonates needs to be considered. Thermal stability depends on the specific properties of the product in use.

2.2 Scaling Inhibitor Selection for the Soultz site

Four products were tested for their calcium tolerance and their effectiveness for blocking the barite formation in the Soultz brine. The products are described in the following as Inhibitor Green, Inhibitor Orange, Inhibitor Blue and Inhibitor Red.

Calcium Tolerance

The produced fluid in Soultz is a Na – Cl – Ca based brine with a calcium concentration of 6.5 g/l. All four products were tested for the formation of Ca-phosphates after addition of the inhibitors in three different concentrations to *artificial brine (1)*.

Therefore, the four inhibitors were added in different concentrations to a Ba^{2+} and Sr^{2+} free artificial brine. Coloration of the solutions was due to the original color of the respective product.

Composition of the artificial brine, the inhibitor concentration and the results are listed in Table 1.

Table 1: Test of the calcium tolerance: Composition of the *artificial brine (1)*, inhibitor concentration and results of the test.

Artificial Brine (1)		
Na in mg/l	Cl in mg/l	Ca in mg/l
25900	51520	6530
Results		
Product	Concentration	Ca-Tolerance
Inhibitor Green	0.5, 3 and 5%	good
Inhibitor Orange	0.5, 3 and 5%	good
Inhibitor Blue	0.5, 3 and 5%	good
Inhibitor Red	0.5, 3 and 5%	good

All four products showed a good calcium tolerance and all brines kept a transparent state after the addition of the inhibitors (Fig. 4).

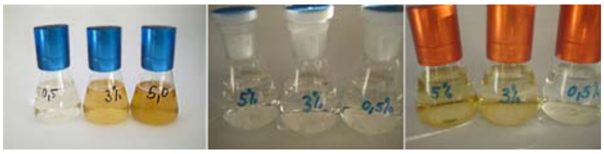

Figure 4: Artificial Soultz brine mixed with different concentrations of inhibitors. No precipitation of Ca-Phosphate was observed. Inhibitor Blue (left), Inhibitor Green (middle) and Inhibitor Red (right) (Picture: BWG)**.**

Suppression of the Barite Formation in Artificial Brine

To test the efficiency of the four products in the laboratory, they were mixed with *artificial brine (2)*. Within this brine, the Ba^{2+} concentration was six times higher than in the original Soultz brine. Composition of the *artificial brine (2)* is listed in Table 2.

Table 2: Composition of the *artificial brine (2)*

Artificial Brine (2)	
Electrolytes	Concentration in mg/l
Na	25430
Ca	6340
Ba	60 (overdose)
Sr	400
Cl	50770
SO_4	1010 (overdose)

Active content of 5 and 15 mg/l respectively, of Inhibitor Green, Orange, Blue and Red were tested for the inhibition of barite formation. The mixtures were shook continuously for 48 h at 333 K (60°C). Barite formation was detected in form of turbidity measurements and additionally the Ba^{2+} concentration was measured after 6 and 48 h. The effectiveness of Inhibitor Green (green line), Inhibitor Blue (blue line) and Inhibitor Red (red line) are compared to the barite formation in brine without the addition of any inhibitor (black line) (Fig. 5).

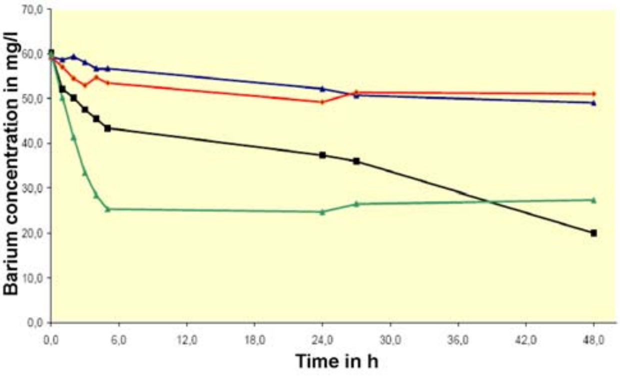

Figure 5: Ba^{2+} concentration as a function of time after the addition of Inhibitor Green (green line), Inhibitor Blue (blue line) and Inhibitor Red (red line). The black line represents the barite formation in inhibitor-free brine.

Suppression of the Barite Formation in the Soultz Brine

After determination of the calcium tolerance and a first inhibition test, the remaining three products (Inhibitor Orange, Blue and Red) were tested for their inhibition effectiveness in the Soultz brine. Therefore, closed bottle tests were performed. This experiment was already described in detail in Scheiber et al. (2012). This paragraph summarizes the findings.

Original Soultz brine was sampled at the production well GPK-2 by cooling the brine from 433 K (160°C) to 343 K (70°C) in a cooler. The Inhibitors were added directly with an active content of 5 mg/l and bottles were stored at room temperature. After 8 days the inhibitor/brine samples were filtrated and the filters residues investigated visually and by electron microscopy. Additionally, the filtrate was analyzed concerning the Ba^{2+}, Sr^{2+}, Ca^{2+} and SO_4^{2-} concentration. In the non-treated brine sample, the Ba^{2+} concentration decreases to half of the original concentration. In the presence of the three inhibitors no decrease of the Ba^{2+} concentration was monitored in the fluid and no barite deposits were detected on the filter surface. Figure 6 shows the filter residues on the filter surfaces. Most deposits, including barite crystals, were found after filtration of the non-treated fluid sample (Fig. 6a). The Inhibitor Orange suppressed the formation of barite but allowed co-precipitates like iron oxides and hydroxides to be formed, (Fig. 6b). Inhibitor Red (Fig. 6c) and Inhibitor Blue (Fig. 6d)) inhibit both, the formation of barite and co-precipitation of other minerals.

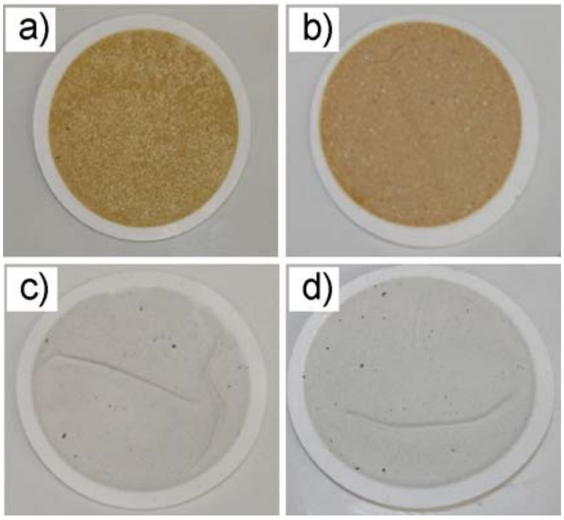

Figure 6: Filter residues of the closed bottle tests a) reference sample (brine without inhibitor), b) Inhibitor Orange/brine mixture, c) Inhibitor Red/brine mixture and d) Inhibitor Blue/brine mixture (Scheiber et al., 2012).

Finally, Inhibitor Red was selected for the inhibition of barite at the Soultz geothermal power plant. This product showed a slightly better performance than Inhibitor Blue and will be added continuously to the production stream of the geothermal power plant in Soultz for scale inhibition. It is based on DTPMP (Diethylenetriaminepentakis (methylenephosphonic acid)).

2.3 Dose rate adjustment: Dynamic Tube blocking tests

For dose rate adjustment, dynamic tube blocking test were performed to determine the required dose rate for the Soultz brine. For this type of test, brine/inhibitor mixtures flow continuously through capillary tubes of small diameters. If scalings are formed at the tube surface, the inner diameter decreases and the pressure rise. The differential pressure is monitored by measuring the pressure before and after the capillary tube. Every experiment starts with a pre-scale test. Inhibitor-free brine flows through the capillary tube and the blocking time was detected. This is the minimal blocking time which should be elongated significantly by adding different concentration of inhibitor.

All experiments were conducted at 333 K (60˚C) which is the minimal injection temperature of the Soultz injection wells. The barite solubility decreases with decreasing temperature (Blount, 1977) which means that for the Soultz injection conditions the lowest solubility will be reached at this temperature and the inhibitor has to operate at its maximum efficiency. Artificial brine was used for the tube blocking tests and barium, strontium and sulfate concentration were adjusted to a supersaturated state of the strontium rich barite to decrease the nucleation time. Composition of the *artificial brine (3)* is listed in Table 3.

Table 3: Composition of the *artificial brine (3)* for dynamic tube blocking tests

Artificial Brine (3)	
Electrolytes	Concentration in mg/l
Na	28380
Ca	7800
Ba	300 (overdose)
Sr	2050 (overdose)
Cl	58090
SO_4	1860 (overdose)

Inhibitor Red was used for the inhibitor/brine mixtures. With increasing concentration of the inhibitor the blocking time of the capillary tube increases (Fig. 7). At a concentration of 5 and 25 ppm of Inhibitor Red, scalings are formed immediately and tubes get blocked within 25 min. With increasing inhibitor concentration, the dynamic operation time increases significantly. The best performance was observed at an inhibitor concentration of 45 ppm. Here, scaling was inhibited for 2 h (Fig. 7).

Based on the degree of supersaturation of *artificial brine (3)*, the optimal dosage for the Soultz conditions was calculated to be 4 mg/l active content of Inhibitor Red per liter of geothermal brine.

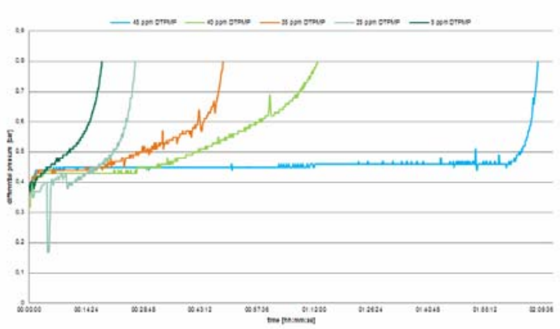

Figure 7: Dynamic tube blocking tests: active content of 5 ppm (dark blue curve), 25 ppm (light blue curve), 35 ppm (orange curve), 40 ppm (green curve) and 45 ppm (blue curve) are displayed as a function of the differential pressure (y-axis) versus time (x-axis).

2.4 Interaction between reservoir rocks and inhibitor

Investigations of the inhibitor performance at the surface installations are important for the best effectiveness adjustment for scale inhibition at the heat exchanger system. One thing one has to keep in mind is what happens during the re-injection inside of the injection wells and in the near wellbore region of the openhole section of the injection well: During long term circulation cold brine will be injected for several month or years in the injection wells. Thereby, a cooling front in the well and around the openhole section will spread out as a function of injection volume and time. In Soultz the reservoir permeability is related to fracture zones with thicknesses of µm to cm in the deep reservoir.

After passing the heat exchanger the inhibitor has to keep up its good performance in the injection wells and in the cooling region around the wellbore until the injected brine is heated up and the supersaturation of the dissolved barite decreases. Moreover, secondary mineral formation by interaction of the inhibitor with the granitic host rock has to be avoided.

Both parameters, long term effectiveness and secondary mineral precipitation by inhibitor–host rock interactions were investigated in laboratory experiments.

Material selection

Two different host rocks of the Soultz granitic reservoir were selected: one piece of core of the exploration well EPS-1 from a shallow and hydrothermal altered part of the reservoir (depth: 1674 m) and cuttings from the openhole section of GPK-2 which is dominated by a fractured two mica granite (several samples between 4767 and 4780 m depth) (Fig. 8). The cutting samples were selected based on the presence of fracture zones. Host rock and fracture fillings can show a very different mineralogy, therefore, the interaction of the inhibitor with host rock and fracture fillings needs to be investigated.

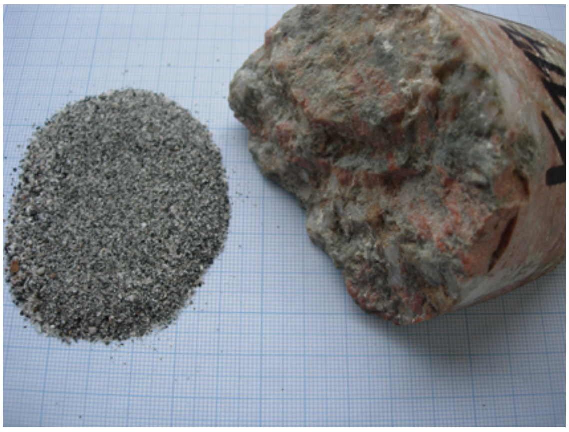

Figure 8: Host rock material of the Soultz granitic reservoir: Cuttings from GPK-2 (appr. 4775 m depth) and a piece of core from EPS-1 (1674 m depth) (Picture: GEIE).

For the batch experiments *artificial brine (4)* was mixed with grinded powder of reservoir rocks. The composition of this brine is listed in Table 4.

Table 4: Composition of the *artificial brine (4)* for host rock – inhibitor interaction experiments

Artificial Brine (4)	
Electrolytes	Concentration in mg/l
Na	28390
Ca	7800
Ba	60 (overdose)
Sr	400
Cl	57930
SO_4	370 (overdose)

Batch Experiment

The barite formation and reservoir rock mineralogy was investigated in the presence of Inhibitor Red as well as in the absence of the inhibitor.

Therefore, host rock material from two different depths of the Soultz reservoir was grinded to powder. Respectively 10 g of powder was mixed with 150 ml *artificial brine (4)* at 333 K (60°C) in tinplate capsules (5 per experiment) which were sealed and immediately heated up to 363 K (90°C). The samples were regularly mixed by shaking.

As a function of time, (2, 6, 24, 72, 168 h) tinplate capsules were removed from the experiment, unsealed and filtrated (Fig. 9). Filter residues were dried and investigated by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Ba, Sr, Si, SO_4 and ortho-phoshate concentrations were determined in the filtrate.

Figure 9: Fluid sampling from tinplate capsules as a function of the experimental duration (Picture: BWG).

Results of the batch experiments

In the absence of Inhibitor Red, the Ba^{2+} concentration starts to decrease immediately after start of the experiment and reaches after 3 days a constant level of 6 mg/l (Fig 10, dashed lines). In the presence of Inhibitor Red, the Ba^{2+} concentration is constant during the first 24 h and decreases continuously but slowly during the experiment (Fig 10, solid lines).

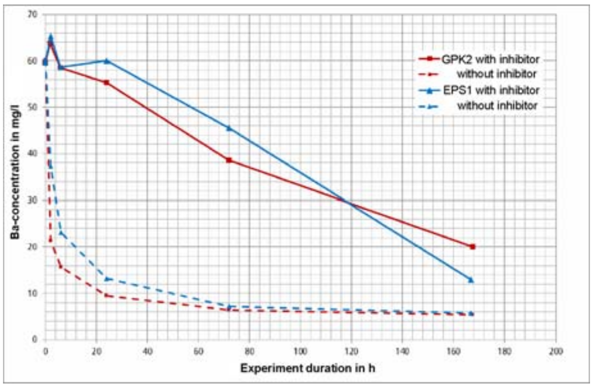

Figure 10: Batch experiments for reservoir rock-inhibitor interaction with artificial brine (4). Ba^{2+} concentration as a function of time in the presence of Inhibitor Red (solid lines) and in the absence of the inhibitor (dashed lines).

The two reservoir rocks show the same behavior with or without inhibitor, they have no direct impact of the Ba^{2+} concentration. Mineralogical composition did not change in the presence of the inhibitor. Secondary mineral formation by inhibitor-reservoir rock interaction was only observed for barite but not for phosphate minerals, nor by XRD neither by SEM analysis. Table 5 shows the mineralogical characterization of reservoir rock powder by XRD after 7 days of exposure to *artificial brine (4)*/inhibitor mixture.

Table 5: Mineralogical composition of the reservoir rock samples EPS-1 and GPK-2 after 7 d in *artificial brine (4)*/inhibitor mixture.

Core EPS-1 (1674 m depth)	Cuttings GPK-2 (appr. 4775 m depth)
Quartz (dominant)	Quartz (dominant)
Muscovite (dominant)	Albite (dominant)
K-feldspar	K-feldspar (intermediate)
	Chlorite
	Muscovite
	Calcite
	Pyrite

Ortho-phosphate concentration in the filtrate was analyzed as a function of time. By thermal decomposition of the phosphonic acid, the ortho-phosphate is formed and can be used as an indicator for decomposition processes. No significant increase of the ortho-phosphate concentration was observed during the batch experiment. Nevertheless, the decrease of the Ba^{2+} concentration and precipitation of barite start after 24 h (Fig. 10, solid lines). Two theories could explain this effect. First, the growth of barite crystals takes place at surfaces with non preferred adsorption sides for the phosphonic acid but the growth rate is very low. Second, a part of the phosphonic acid is adsorbed at minerals surfaces of the reservoir minerals and growth-active surfaces of the barite start to growth. Further investigations needs to be done to clarify this point.

3. ON-SITE TEST OF INHIBITOR INJECTION

After the successful selection of the inhibitor in laboratory experiments, the product was tested on-site at in-situ conditions for its efficiency of scale avoidance.

3.1 Installation of the Inhibitor Injection System

An injection of the inhibitor at the production side at approximately 433 K (160°C) is necessary to guarantee appropriate mixing with the geothermal fluid before entering the heat exchangers. Therefore, the inhibitor is injected at the hot side of the production side approximately 8 m downstream of the production well and 20 m before entering the heat exchangers. The selected product for scaling inhibition, Inhibitor Red, has a boiling point of 383 K (110°C). The addition of the inhibitor at the production side risks decomposition of a fraction of the injected inhibitor. Nevertheless, a complete mixing of the inhibitor with the brine before entering the heat exchanger (before nucleation of barite seeds) is necessary to guarantee best results.

A flange-mounted pipe is connected to the main production pipe. Within this flange, a hastelloy coiled tubing is installed and its tip goes to the center of the production pipe (Fig. 11). Here the inhibitor is added dropwise to the geothermal fluid at 2 MPa (20 bars) and 428 K (155°C).

Figure 11: Injection system of the scaling inhibitor located 5 m downstream of the production well GPK-2 (Picture: GEIE).

3.2 On-site Efficiency Test of the Inhibitor Injection

The inhibitor was added continuously to the production stream of the geothermal brine. The optimum dosage for the Soultz conditions was determined by dynamic tube blocking tests as 4 mg/l active content at 333 K (60°C). However, the doserate of the inhibitor was adjusted to an active content of 7.6 mg/l to compensate partly decomposition of the inhibitor due to its boiling point, which is below the production temperature.

The operation conditions of the Soultz geothermal power plant at the time of inhibitor injection are listed in Table 6. The power plant was still in the restart phase after a maintenance period, so temperature and flow rate of the production stream were not at their maximum.

Table 6: Operation conditions of the geothermal loop during inhibitor injection.

Geothermal loop	Pressure in MPa (bar)	Temp. in K (°C)	Flow rate Q in l/s
Production GPK-2 $_{\text{Wellhead}}$	2.1 (21)	428 (155)	15.3
Injection GPK-3 $_{\text{Wellhead}}$	1.8 (18)	343 (70)	15.0

For the efficiency test, geothermal fluid was sampled at production and injection side. At production side, the sampling point is placed in front of the injection of the inhibitor. No inhibitor is present in the brine sample of GPK-2. Physico-chemical parameters of the sampled brines are summarized in Table 7.

Table 7: Composition of the Soultz brine at the production and injection side during the injection of Inhibitor Red

Physico-chemical parameters	Production well GPK-2 06.02.2013	Injection well GPK-3 06.02.2013
$T_{(sampl.)}$ in K (°C)	293 (20.0)	295.4 (22.4)
pH	4.88	4.82
EH (SHE) in mV	5	117
Conductivity in mS/cm	122	122
Na (mg/l)	25200	24150
Ca (mg/l)	7440	7420
K (mg/l)	3360	3270
Sr (mg/l)	418	406
Li (mg/l)	169	169
Mg (mg/l)	142	141
Ba (mg/l)	26	26
NH_4 (mg/l)	24	24
$Fe_{(total)}$ (mg/l)	30	29
Mn (mg/l)	18	18
Cs (mg/l)	11	11
Rb (mg/l)	18	24
$As_{(total)}$ (mg/l)	11	11
Zn (mg/l)	3	2
Cl (mg/l)	57300	54400
Br (mg/l)	237	249
SO_4 (mg/l)	228	208
HCO_3 (mg/l)	184	183
F (mg/l)	6	6
PO_4 (mg/l)	4	5
B (mg/l)	174	189
SiO_2 (mg/l)	41	37
Al (µg/l)	66	65
Pb (µg/l)	66	96
Cd (µg/l)	14	15
Cr (µg/l)	5	2
Cd (µg/l)	14	15
Cu ((µg/l)	<1	<1

The Ba^{2+} concentration kept a constant level of 26 mg/l from production to re-injection. Sr^{2+} and SO_4^{2-} concentration decreases slightly which can be related to the analysis error of the applied methods. Based on these results no precipitation of strontium rich barite takes place by cooling the geothermal fluid in the heat exchangers. Inhibitor Red successfully suppresses the growth of barite crystals. One interesting observation was that the Pb^{2+} concentration increases from 66 mg/l at the production side to 96 mg/l at the re-injection side. It is possible that due to the slight overdose of the inhibitor, pre-existing scaling of Galena (PbS), which is attached to pipe surfaces, was partly dissolved. This finding has to be re-produced to confirm this theory.

A slight decrease of the pH from 4.88 to 4.82 can be related to the injection of the phosphonic acid which has a pH >2 at its concentrated state. The Eh value increases from 5 to 117 mV (SHE) which can be caused by electrochemical processes like corrosion.

Immediately after fluid sampling, a filter station was connected to the sampling station and in-situ filtration at 0.4-0.6 MPa (4- 6 bar) was applied. Brownish and very fine grained particles covered the full filter surfaces after filtration of 1 liter brine (Fig. 12). Filters and filter residues were washed with demineralized water and dried at room temperature for analysis by Scanning Electron Microscopy (SEM).

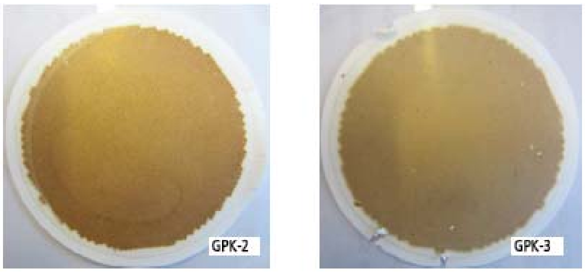

Figure 12: Filter residues after on-site filtration at the production well GPK-2 and the injection well GPK-3 (Picture: BWG).

Scanning Electron Microscopy (SEM) combined with an EDX system for elemental analysis was applied in order to detect newly formed barite precipitates if present. Elemental analysis was conducted at filter sections of 1100 x 880 µm, Table 8.

Table 8: Comparison of the elemental composition of filter residues of production and injection side after in-situ filtration

Filter residues production side GPK-2	Filter residues injection side GPK-3
oxides/sulfides of Cu (38%) Pb (25%), As (17%), Sb (11%), Fe (9%)	*oxides/sulfides of* Cu (53%) Fe (11%), As (13%), Ba (13%)

The comparison of elemental analysis showed that at production side the oxide/sulfide matrix is dominated by Cu, Pb, As and Sb whereas the filter residues at the injection side are dominated by Cu, Fe, As and Ba. Based on the oxygen to sulfur ratio, the matrix is dominated by oxides and contains a minor amount of sulfides. Either the oxide/sulfide particles are produced from the well and transported as suspended matter through the surface installations of the power plant or the particles precipitated during filtration in case of oxygen pollution during sampling. Very interesting is the high amount of Cu inside of both filter residues and the low Pb concentration at the injection side. A precipitation of Cu-oxide/sulfide during filtration is not very likely due to the low amount of dissolved Cu in the production brine (Table 7). Inside of the LSP some parts are installed which can release Cu particles by abrasion and/or corrosion processes and it is possible that those particles were trapped during filtration.

As already discussed, dissolution processes of suspended Pb particles of the production brine could take place in the surface installations because the Pb concentration in the brine of the injection side is significantly higher than at the production side. The low concentrations of Pb in filter residues at the injection side support this theory.

Very few particles of barite were found in filter residues of the injection side (Fig. 13), particle number 3, 4 and 9. Here it is not clear if particles were formed during the current circulation or if they are related to former production periods where no inhibitor was injected. Based on the fluid analysis, Table 7, no decrease of the Ba^{2+} concentration was monitored. The barite crystals in the filter residues show an idiomorphic morphology. Phosphonic acid changes the morphology of barite crystals but this change of morphology was not observed. In correlation with the findings of the fluid chemistry it is concluded that the particles were formed during earlier production periods.

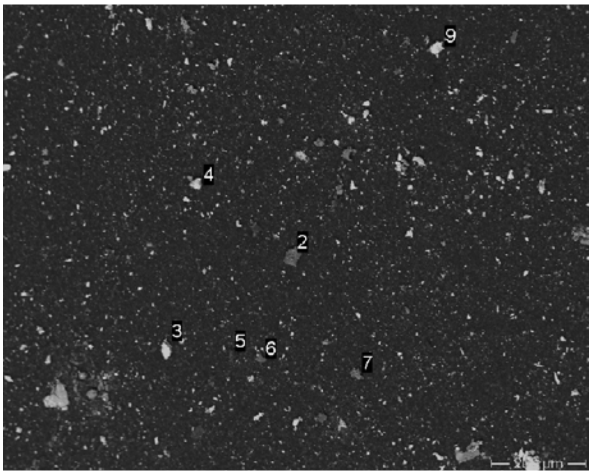

Figure 13: Scanning Electron Microscopy: Filter residues after on-site filtration of brine, injected into GPK-3. Picture size 1100x880 µm (Picture: GTN).

4. CONCLUSIONS

Scalings are formed in the surface installations of the geothermal power plant in Soultz-sous-Forêt due to the temperature decrease at the heat exchanger system. Strontium rich barite ($Ba_{1-x}Sr_xSO_4$) dominates the deposits but also a minor fraction of galena (PbS) is formed. A scaling inhibitor was selected in laboratory experiments out of various products and was successfully tested for its efficiency at the power plant after installation of the injection system. Barite precipitation was successfully suppresses.

Small-scale laboratory experiments are simple but powerful tools for a successful selection of scale inhibitors for geothermal power plants. Based on the respective brine composition the optimum product can be selected. The methods of the laboratory experiments involved pre-test with artificial brines and a final test with original brine from the Soultz site. Parameters like calcium tolerance, effectiveness, dose rate adjustment, thermal stability and the interaction with reservoir rocks have been successfully investigated with artificial brines. Those brines were mixed based on the main components of the original Soultz brine and were adjusted to the Total Dissolved Solids (TDS). For the final product selection, original brine was used. Here, the real effectiveness and the capability to avoid co-precipitation were tested. All in all, four different inhibitor products were tested. The most successful one for the Soultz location is based on DTPMP (Diethylenetriaminepentakis (methylene-phosphonic acid)). The injection test at the power plant worked out very well. Barite formation will be significantly decreased and the time periods between cleaning operations of the heat exchangers can be expected to increase. Moreover, tests of long term efficiency and thermal stability showed very promising results. The injection wells and the near region of the openhole section in the reservoir could be protected by inhibitor injection at the surface installations.

Besides the successful blocking of barite precipitation, a slight dissolution of the galena was observed. This fact becomes of great significance by thinking of long term circulations of month and years. Sulfide scales can be expected to become the dominating deposits the surface installations of the power plant after efficient retardation or blocking of barite formation. Further tests have to be conducted if this type of phosphonic acid can be used for leaching the sulfide scalings.

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