

GEOCHEMICAL AND MINERALOGICAL MONITORING OF THE GEOTHERMAL POWER PLANT IN SOULTZ-SOUS-FORÊTS (FRANCE)

Julia Scheiber¹, Fabian Nitschke^{2,3}, Andrea Seibt⁴, Albert Genter¹

¹GEIE Exploitation Minière de la Chaleur/ EEIG Heat Mining
Route de Soultz, BP 40038, 67250 Kutzenhausen, France
e-mail: scheiber@soultz.net

²Karlsruhe Institute of Technology (KIT) – Institute of Mineralogy and Geochemistry (IMG)
Adenauerring 20b, 76131 Karlsruhe, Germany

³EnBW Energie Baden-Württemberg AG
Durlacher Allee 93, 76131 Karlsruhe, Germany

⁴BWG Geochemische Beratung GbR; Zur Untersuchung von Wasser und Gas
Seestraße 7a, 17033 Neubrandenburg, Germany

ABSTRACT

At the Soultz-sous-Forêts EGS site, a three year programm, dealing with a scientific and technical monitoring of the Soultz power plant, is ongoing between 2010 and 2012. Several hydraulic circulation tests have been running that have involved the production well, GPK-2, and two injection wells, GPK-1 and GPK-3: a long term circulation test for about 11 months in 2010 and two short-term tests in 2011. Within this research programm, a geochemical and mineralogical monitoring concept is included: Physico-chemical parameters of the geothermal fluid, sampled from the production well and the injection wells, are determined regularly. Additionally, deposits in the surface installations of the plant, inorganic and organic, are also sampled regularly and characterized in detail.

At the Soultz-site, scales are formed mainly at the cold part of the power plant due to the significant temperature decrease of 90°C by passing the heat exchanger. These scales consist mainly of barium/strontium sulfates, lead sulfide and trace amounts of mixed sulfides (Fe, Cu, Sb and As). They are known to accumulate radionuclides by chemical substitution during the crystal growth: ²²⁶Ra in barium/strontium sulfates and ²¹⁰Pb in lead sulfide. Therefore, the equivalent dose and the surface activity of the ORC heat exchanger scales were determined. A correlation between the mineralogical composition (sulfates and sulfides) and the incorporated radionuclides (²²⁶Ra, ²¹⁰Pb) was found. To assure safety at work and reduce the costs of the cleaning procedure and the scale disposal, the setup of an inhibitor system for scale avoidance has been defined. Therefore, several phosphonic acids were tested in laboratory experiments for their ability to suppress scale formation in the Soultz brine. Based

on these experiments, the product with the best performance for the Soultz site was chosen. The inhibitor will be injected continuously during circulation of the brine.

For testing the effectiveness of the inhibitor injection on-site, the geochemical and mineralogical monitoring concept of Soultz includes the characterization of brine and deposits in the surface installations of the power plant before and during the continuously addition of the inhibitor.

INTRODUCTION

The geothermal power plant of Soultz-sous-Forêts is located in the NE of France, 50 km NE of Strasbourg, at the western part of the Upper Rhine Graben. The Graben structure was formed by a Tertiary rift system and is connected with a geothermal anomaly, Figure 1.

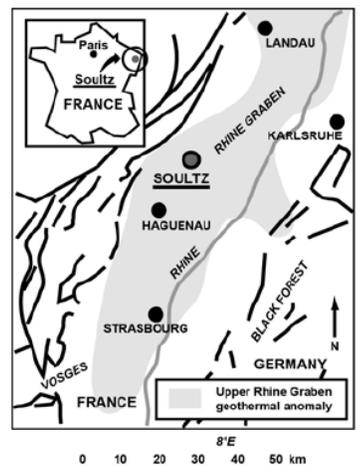


Figure 1: Geothermal anomaly of the Upper Rhine Graben, grey area and location of the Soultz-sous-Forêts geothermal site (Hurtig et al., 1992).

In this anomaly are a few areas located where the temperature gradient is higher in comparison to the surrounding areas. Old petroleum wells in the Pechelbronn oil field indicated one of these very local anomalies at the Soultz horst first mentioned by (Haas and Hoffmann, 1929). Here 1400 m of sediments, lacustrine limestone and sandstone, cover the crystalline, granitic basement (Schnaebele et al., 1948).

The Soultz-sous-Forêts project started in 1987, with the aim to develop heat exploitation of deep reservoirs (Gérard and Kappelmeyer, 1987). Therefore, four deep wells, GPK-1 to GPK-4 were drilled between 1987 and 2005 down to the crystalline basement of the Rhine Graben, made of altered and fractured granites (Genter et al., 2010)

The initially low permeability of the reservoir was improved by hydraulic and chemical stimulations, creating an Enhanced Geothermal System (EGS), (Gérard et al., 2006). 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 net capacity of 1.5 MWe. 4 wells are available to act as two doublets: GPK-2, equipped with a Line Shaft Pump (LSP) and GPK-4, equipped with an Electric Submersible Pump (ESP) as production wells and GPK-1 and GPK-3 as injection wells. After the ESP breakdown in GPK-4 in December 2009, GPK-2 remained as the main production well.

Until October 2010 the main fraction of the geothermal fluid was injected to the reservoir with a maximum pressure of 60 bar in GPK-3 by using an injection pump. Only minor fractions were injected in GPK-1. In this period, several hundred microseismic events per year were detected in the reservoir. From January 2011 the injection of the fluid stream was splitted to nearly equal parts to the injection wells GPK-1 and GPK-3 without the use of an injection pump. Since this time, the number of microseismic events, measured in the reservoir, decreases significantly. The present day's status and use of the wells of the Soultz power plant are shown in Figure 2.

Due to the high salt content, 95 g/l, of the Na-Cl-Ca brine (Sanjuan et al., 2010) several issues, concerning the formation of scales, are connected with circulation and cooling of the geothermal brine at the surface: Cuttings are transported from the reservoir to the surface and cause significant damage on the LSP. Furthermore, they were deposited in the complete surface installations of the plant.

Another type of deposit is strongly connected to the surface equipment at the cold part of the plant, the heat exchangers, pipes and filters which are in contact with the fluid on the way to the injection well.

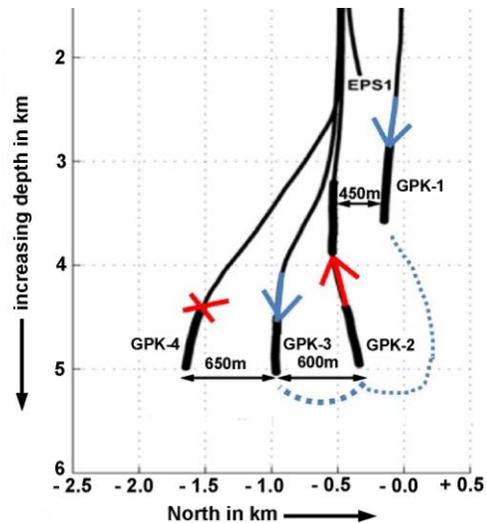


Figure 2: Today's state and use of the geothermal wells of the Soultz-sous-Forêts power plant.

The deposits consist mainly of solid solutions of barium/strontium sulfates (barite/celestine), minor amounts of lead sulfide (galena), trace amounts of other sulfides and iron oxides and hydroxides (Sanjuan, 2011). 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, Kudryavskii and Rakhimova, 2007, Curti et al., 2010, Ceccarello et al., 2004 and Zielinski et al., 2001). Two serious issues are connected with the precipitation of industrial scales, classified as Technically Enhanced Naturally Occurring Radioactive Material (TENORM) in the surface installations of the Soultz power plant:

First, the scales act as an isolation material in the heat exchanger which leads to a significant efficiency decrease in the heat transfer from the geothermal fluid to the organic fluid. In consequence, extensive costs and time consuming cleaning procedures had to be applied.

Second, due to the presence of radionuclides in the scales, specific protection regulation for the workers and for scale disposal needed to be followed. Those scales are considered as radioactive waste deposits and had to be evacuated with ANDRA (French National Agency for Radioactive Waste Management).

To solve these problems, a concept for the application of an inhibitor system for scale avoidance has been designed. It includes the selection of an appropriate inhibitor for the Soultz brine based on phosphonates. Those chemicals are well known as inhibitors used in oilfield applications (He, 1994). The inhibitor injection system has been designed and its installation is on-going.

FORMATION OF DEPOSITS IN THE SURFACE INSTALLATIONS OF THE SOULTZ-SITE

Deposits in the surface installations of the power plant are made of particles like cuttings which were raised from the reservoir during fluid production and scales which are formed directly in the surface installations of the power plant.

With increasing flow rate the amount of cuttings, extracted from the reservoir, increases. Main fraction of them settled in the filters of the production side before entering the heat exchanger system. Minor fractions were observed in the complete surface equipment. The amount of cuttings decreases along the transport through the surface installations.

The scale formation in Soultz is strongly connected to the cold part of the plant due to the significant temperature decrease from 157°C to 70°C by passing the heat exchanger. Scales occur in the heat exchanger systems and in all of the following equipments like pipes and filters on the injection side. They were found to exist even in the injection pipe of GPK-1: This well was inspected visually with a camera system down to 500 m depth in cooperation with the Leibniz Institute of Applied Geophysics (LIAG). Scales form compact grayish deposits on the surface of the injection pipe (Figure 3).



Figure 3: Deposit, visible on the internal section of the injection pipe of GPK-1 in 80 m depth. Picture size: 5 cm x 4 cm, with the courtesy of the Leibniz Institute of Applied Geophysics (LIAG).

For investigations of the formation conditions of the scales, the operating conditions of the power plant (T, P and flow rate), physico-chemical parameters of the brine, elemental and mineralogical composition of the scales were taken into account. In this paper, the scale formation of the heat exchanger system of the ORC unit was analyzed in detail.

This heat exchanger was cleaned in April 2011 and was thereafter one week in use in April before power production was stopped, caused by the breakdown of

the LSP. After restart of the power production it was two weeks in use before the next cleaning event took place in September. During the cleaning procedure the scales are nearly completely removed because the scale adherence on the walls of the heat exchanger is weak due to the polymercoating; only minor fractions of the scales remain after cleaning in the ORC heat exchanger system. Therefore it can be expected that the scale formation took place in two growth periods: One week in April and two weeks in September 2011.

Main Physical Parameters of GPK-1, GPK-2 and GPK-3

Within a few days after restart of the well in August 2011, the production temperature of 157°C was reached. Fluid was injected with 65 to 70°C in GPK-1 and GPK-3. To avoid degassing of CO₂, the pressure in the surface installations was kept at 18 to 20 bars. Only the pressure of GPK-1 with 5-6 bars is significantly lower in comparison to GPK-3. The flow rate of the brine was stepwise increased to 25 l/s and the production stream was splitted after passing the ORC heat exchanger system to nearly equal amounts for injection in GPK-1 and GPK-3 (Figure 4).

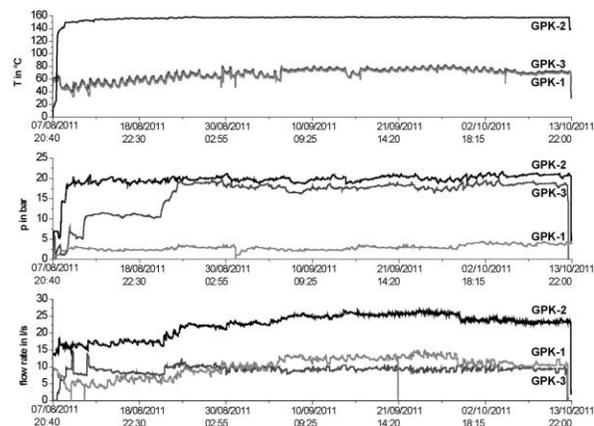


Figure 4: In-situ measurement of T, P and flow rate of the production well GPK-2 and the two injection wells: GPK-1 and GPK-3 between August and October 2011.

Physico-Chemical Parameters of the Geothermal Fluid

The long term circulation of deep brines in the Soultz EGS reservoir produced a geothermal fluid with TDS (Total Dissolved Solids) of 95 g/l. Main electrolytes in this fluid are Na⁺, K⁺, Ca²⁺, Cl⁻ and SO₄²⁻. Trace amounts of alkali metals, alkaline earth metals, transition metals and post transition metals in the µg to mg range are present, Table 1. The alkalinity of the brine, sampled from GPK-2 in 2011, ranges from 2.7 - 3.2 meq/l. The average conductivity was 125 mS/cm and the pH ranges between 4.9 and 5.3.

Table 1: Physical parameters and electrolyte concentrations of the Soultz brine, sampled from the injection well GPK-1 and from the production well GPK-2 in 2011. Data from February after Sanjuan, 2011.

Fluid samples	Date	T _{Meas.} °C	Cond. 25°C	pH	TDS g/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	SO ₄ mg/l	SiO ₂ mg/l
GPK-1 INJ	23/02/11	40.2	129	5.2	95	26100	3200	6850	124	57500	183	189
GPK-2 PROD	22/02/11	40.1	129	5.5	97	26677	3220	6880	124	58271	177	226
GPK-2 PROD	17/08/11	25	134	5.3	92	21340	3540	7588	155	58132	188	197

Fluid samples	Date	Sr mg/l	Li mg/l	Br mg/l	NO ₃ mg/l	F mg/l	PO ₄ mg/l	B mg/l	NH ₄ mg/l	Fe mg/l	Mn mg/l	Ba mg/l	As mg/l
GPK-1 INJ	23/02/11	402	152	267	<0.5	2.1	0.5	34.5	21.6	68.9	15.6	16.1	8.1
GPK-2 PROD	22/02/11	397	152	264	<0.5	1.9	1.4	34.7	21.4	27.6	14.8	19.4	8.3
GPK-2 PROD	17/08/11	479	150	239	n.d	3.7	n.d	37.6	n.d.	28.5	15.8	9.6	8.7

Fluid samples	Date	Rb mg/l	Cs mg/l	Ge µg/l	Al µg/l	Zn µg/l	Pb µg/l	Cd µg/l	Co µg/l	Cr µg/l	Cu µg/l	Ni µg/l	Ag µg/l
GPK-1 INJ	23/02/11	23.4	14.8	50	55	2091	112	5.6	6.7	2.5	1.9	2.6	0.9
GPK-2 PROD	22/02/11	23.5	14.6	50.2	42	2163	254	5.8	2.0	1.0	3.7	1.9	0.8
GPK-2 PROD	17/08/11	26.4	14.8	n.d	<0.3	2590	416	9.3	2.8	2.0	12.1	37.3	1.1

The Cl⁻ concentration is 53 g/kg brine (56 g/l). SiO₂ is present with 225 mg/l. All values are in good accordance to former measurements (Sanjuan et al., 2010). Results of the on-site monitoring of the GPK-2 brine, sampled during the production period August to October 2011, are presented in Figure 5.

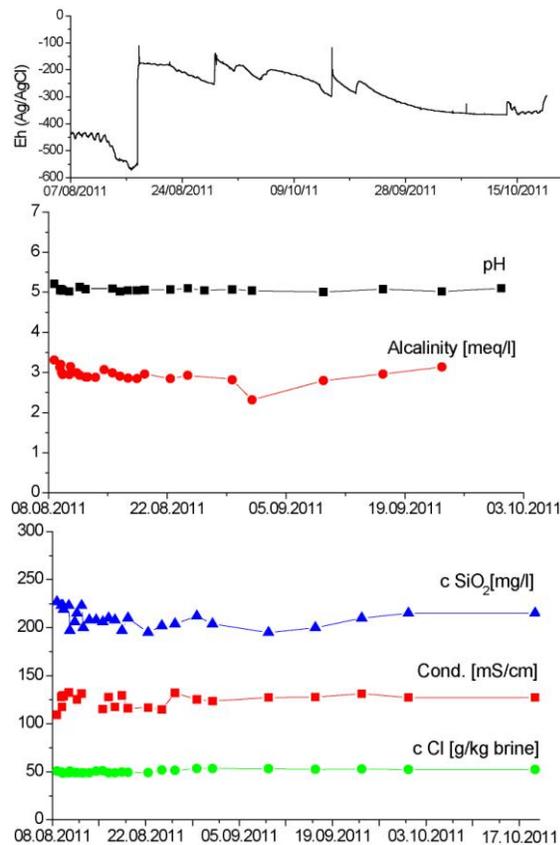


Figure 5: Results of the on-site measurements of Eh, alkalinity, pH, conductivity and SiO₂ and Cl⁻ concentration in the fluid of GPK-2 between August and October 2011.

Elemental and Mineralogical Characterization of the Deposits

The mineralogical and elemental composition of scales was investigated as a function of the formation temperature.

Sampling and sample preparation

For this purpose, deposits of the ORC system, the ORC Evaporator (front) and the Preheater 1 and 2 (front and back) were sampled in the middle of September 2011 (Figure 6). The solids were washed with demineralized water and dried at 40°C. Thereafter, scales and cuttings were separated manually and a small fraction of the scales were removed for investigation by electron microscopy. The main fraction of the scales was grinded and homogenized for further investigation by X-ray Diffraction, measurement of the equivalent dose and the surface activity.



Figure 6: ORC heat exchanger system of the Soultz power plant: ORC Evaporator, Preheater 1 and 2.

Mineralogical characterization by X-ray diffraction (XRD)

Powder samples of the scales were analysed by using a Bruker Advanced D8 equipped with a LynxEye-Detector. Diffractograms were recorded at 30kV/35mA, step size 0.009° and time/step 0.5s between 5 and 70° 2Theta

All the samples of the ORC heat exchanger system are made of barium/strontium sulfates (barite/celestine) and lead sulfide (galena), (Figure 7).

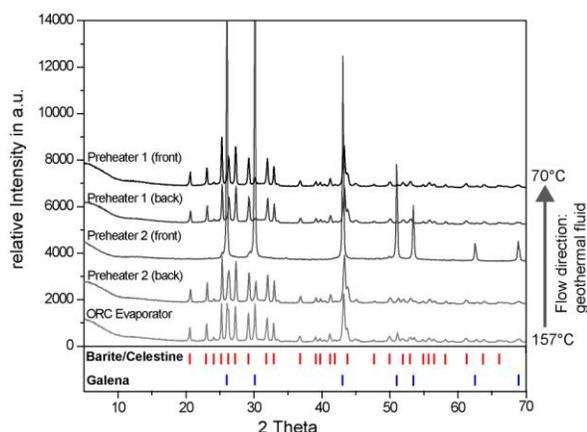


Figure 7: X-ray Diffraction (XRD) of scales, sampled from the ORC heat exchanger system.

The sulfate-sulfide ratio remains nearly constant, independent of the different temperature ranges of the ORC heat exchanger system. The only exception is sample *Preheater 2 (front)*. This sample is mainly made of galena, barite/celestine is present only in minor amounts. The ratio of barium to strontium within the solid solutions of barite/celestine was estimated by the shift of the diffraction angle as a function of the barium content in the diffraction patterns. Therefore, the diffraction patterns of the samples were compared with diffraction patterns of solid solutions of barium/strontium sulfates of the ICDD-PDF. It was found to be 58 - 64% Ba to 36 - 42% Sr.

Qualitative elemental analyses of the scales by scanning electron microscopy (SEM)

All scales of the ORC heat exchanger were analysed by Scanning Electron Microscopy (SEM) to investigate their morphology and characterize the elemental composition semiquantitatively by Energy Disperse X-Ray Fluorescence (EDX).

Therefore, small pieces of the scales were fixed with conductive silver on the sample holder and coated with a carbon film. For analyses, the FEI Quanta 650 FEG ESEM was used. The EDX Spectra were collected at 15 kV.

Exemplarily, the results of the samples *ORC Evaporator (front and back)* are presented in this paper: Investigations of a cross section of the *ORC Evaporator (back)* sample revealed that the porous bulk material is dominated by barium/strontium sulfates which form superimposed rosettes. Examination of the cross section in the back scattered mode (BSED) show two layers of sulfides (white spots) at the top of the scale and one in the bulk material (Figure 8). This may indicate two different growth cycles, which is in good agreement to the power production periods and cleaning events of the ORC heat exchanger.

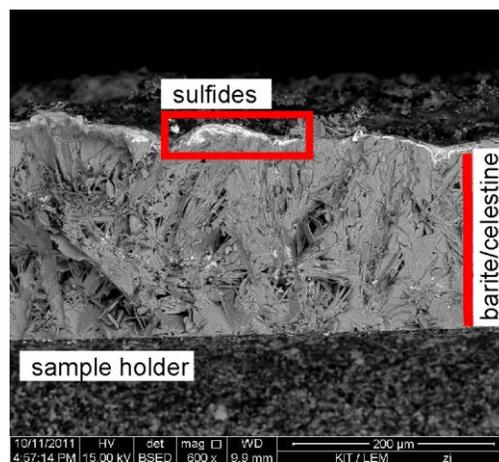


Figure 8: Cross section of the sample ORC Evaporator (back) in the back scattered mode (BSED) of the scanning electron microscopy.

EDX analyses of the tabular barium/strontium sulfates show the typical spectra of barite/celestine solid solutions (Figure 9a).

The surface of the scales is covered completely with a thin deposit of sulfides. Many thin and elongated lead sulfide crystals up to 30 µm of size overlie the bulk material. The dendritic shape indicates a fast growth of single crystals in a preferred direction (Figure 9b).

Besides the spiky lead sulfides, small crystal in a size of a few µm form spherical aggregates in the pores of the surface. They consist of mixed sulfides, mainly made of Fe, Sb, Cu and As (Figure 9c).

Also organic matter was found to exist on the scale surface: high C concentration dominates the EDX analyses. Single spots of 5 µm size to clusters of 20 µm size were detected; they are unequally distributed on the scale surface (Figure 9d). They were also found on the reverse sides of the scales, which was in direct contact with the heat exchanger. The EDX analyses give no information concerning the origin of the organic compounds. It can be made of microbiological deposits, minor fractions of crude oil from the Pechelbronn oil field or industrial oil, used by plant operation.

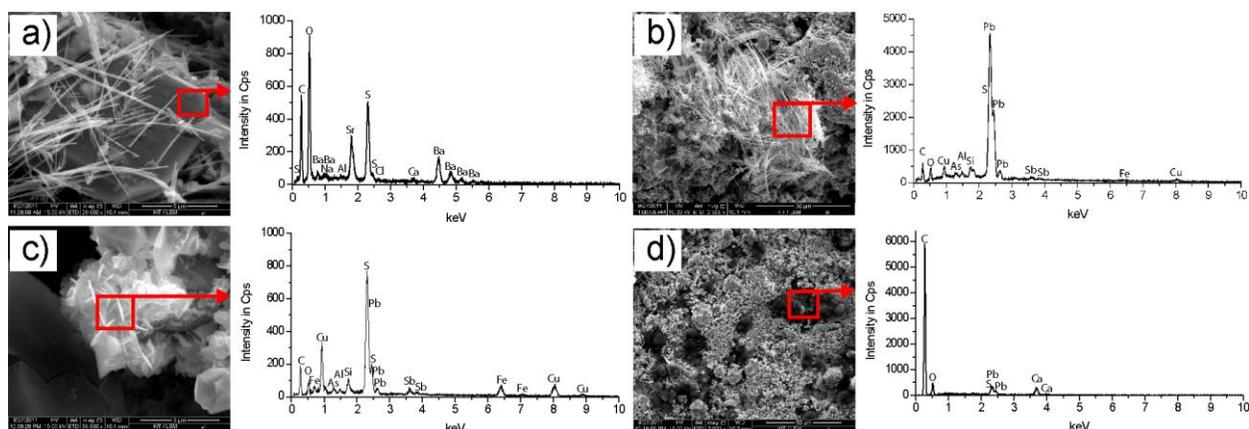


Figure 9: Electron microscopy: Morphology of the scales and semiquantitative analyses by EDX (red marked area); a) Tabular barium/strontium sulfates, showing the typical EDX spectra of barite/celestine solid solutions. b) Thin and elongated crystals of lead sulfide. The EDX analyses revealed Pb and S as main elements. c) Spherical crystals, embedded in pores of the surface are mainly made of Fe, Sb, Cu sulfides. d) Single spots on the surface of the scales are made of organic matter. High C concentration dominates the EDX analyses.

Equivalent dose and surface activity of the scale powder samples

The radioactive contamination of the ORC heat exchanger scales was detected on-site by measuring the equivalent dose and surface activity ($\alpha+\beta+\gamma$ and γ only) per gram powder. Therefore, the device Saphymo 6150 AD 6H, equipped with the sonde 6150 AD17, was used. Even though these measurements do not give the total activity of the samples and do not differentiate between the single radionuclides, they are an important indicator for the level of radioactive contamination of the samples on-site. The equivalent dose in $\mu\text{Sv/h}$ is a reference parameter, mainly used for issues of working safety and sample transportation. The surface activity is related to the surface of the Saphymo sonde, 6.5 cm^2 , not to the surface of the pulverized scales. About 94% of the emitted radiation on the scale surfaces consists of β -radiation and 6% of γ -radiation, Table 2.

Table 2: Equivalent dose and surface activity ($\alpha+\beta+\gamma$ and γ only) per gram scale powder of the ORC heat exchanger samples

Sample	Equivalent dose in ($\mu\text{Sv/h}$)/g (*1)	Surface Activity in Bq ($\alpha+\beta+\gamma$) (*2)	Surface Activity in Bq (γ only) (*2)
ORC Evaporator	0.72	180	10.5
Preheater 2 (back)	0.68	195	11.0
Preheater 2 (front)	0.13	460	1.3
Preheater 1 (back)	0.78	190	11.0
Preheater 1 (front)	0.88	170	10.0

(*1) contact measurement

(*2) surface activity of 1g sample powder in 0.2 cm distance

Only the sample Preheater 2 (front) emitted nearly 100% β -radiation and its activity is significantly higher than the activity of the other samples. In contrast, its equivalent dose is the lowest of all ORC scales ($0.13\ \mu\text{Sv/h}$). This sample is mainly made of lead sulfide and contains only minor amounts of barium/strontium sulfates. Due to the mineralogy, ^{210}Pb is present as the main radionuclide. The emitted γ -radiation in the ORC heat exchanger samples increases with increasing amount of barium/celestine sulfates, which incorporated ^{226}Ra . It should be kept in mind that using this kind of setup, self-adsorption effects had to be considered; the total activity of the samples is expected to be much higher.

Interpretation of the ORC Heat Exchanger sample analyses

The geothermal fluid produced in GPK-2, consists mainly of a Na-Cl-Ca brine with 95 g/l TDS (Sanjuan, 2011).

Several minerals, dissolved under the thermodynamic conditions of the reservoir, exceed their saturation state within the thermodynamic conditions in the surface installation of the power plant. Especially Ba^{2+} , Sr^{2+} , Pb^{2+} , Fe^{2+} , Sb^{3+} , Cu^{2+} , SO_4^{2-} and S^{2-} are involved in scale formation processes.

The mineral saturation state can be affected by changes of the temperature, the pressure, the electrolyte concentration and the Eh – pH conditions. In general, the solubility of barite (BaSO_4) and celestine (SrSO_4) in aqueous solutions is mainly affected by salt concentration, pressure and temperature. The solubility of both, barite and celestine, increases with increasing salt concentration (salting-in effect) and pressure (Strübel, 1966, Blount, 1977 and Monnin, 1999) With increasing temperature, the solubility of barite increases but the solubility of celestine decreases (Strübel, 1966, Blount, 1977 and Reardon and Armstrong, 1987).

This means that by passing the heat exchanger the solubility of barite decreases but the solubility of celestine increases. This can be a reason for the higher fraction of barium in the barium/strontium sulfates. Solubility of the end members is important for the solubility of the solid solutions of $Ba_xSr_{1-x}SO_4$ because it is a function of the strontium, respectively the barium concentration. With increasing barium concentration, the solubility of the solid solution approaches the solubility of barite and with increasing strontium concentration it approaches the solubility of celestine (Felmy et al., 1993). Based on the XRD measurements, the Ba : Sr ratio in the deposits of the ORC heat exchanger samples is nearly 0.6 : 0.4. This indicates that the solubility of these barium/strontium sulfates is closer to the solubility of barite than to the solubility of celestine. Interestingly, all ORC heat exchanger samples showed the same ratio of Ba : Sr, although the temperature decreases of about 90°C. Due to the nucleation period precipitation and deposition of scales will not take place directly by entering the heat exchanger. Seeds will be transported by the fluid stream until they come in contact with already existing growth active surfaces of barium/strontium sulfates.

The presence of sulfides in the deposits indicates that sulfate was reduced to sulfide. Still now it is not clear which reactions are involved in this process. Due to the lack of H_2S in the gas analyses (Sanjuan, 2011) it was concluded that also S^{2-} is not present in the fluid. Additionally, it was never found in chemical analyses. Geochemical calculations regarding this topic needed reliable values of the Eh. Unfortunately, the in-situ Eh measurements show strong variations and not all of the deviations can be related to a change of the production parameters of the plant. Here, the monitoring of the Eh under in-situ conditions needed to be improved during the on-going monitoring of the brine. The dendritic morphology of the lead sulfide crystals indicates a fast growth in one preferred direction. In equilibrium conditions lead sulfide forms crystals with octahedral shape. Idiomorphic lead sulfide crystals are formed in scales of the Soultz site when the brine was allowed to cool down and remained undisturbed about several weeks.

The composition of the sample Preheater 2 (front) is very different in comparison to all other samples of the ORC heat exchanger system: it is mainly made of lead sulfide. As mentioned before, the Preheater 2 is located in the middle of the heat exchanger system between the ORC evaporator and the Preheater 1. Physical parameters of the fluid had to be changed very locally for this significant change of the mineralogical composition.

Two processes can change locally the Eh-pH conditions of the brine: corrosion and microbiological activity of sulfur reducing bacteria. The ORC heat exchanger is coated by a polymer to suppress corrosion processes. Within the deposits of

the ORC heat exchanger, some iron oxides were found by SEM analyses. It is not clear if the oxides were transported by the fluid stream from uncoated pipes and settled in the ORC heat exchanger system or if parts of the coating in the heat exchanger is damaged and therefore corrosion takes place. In SEM analyses, unknown organic compounds were found attached on the scales. On one hand the round and partially elongated shape and the size of a few μm match with shape and size of bacteria deposits. On the other hand minor fractions of crude oil, extracted from the Pechelbronn oil field, can be a source of the organic matter on the scales. Some organic matter was found in cores of the EPS-1 (Ledésert et al., 1996). Also the industrial oil and grease, used for power plant operation, needed to be considered as possible source of the organic deposits. Further investigations in the framework of microbiology and organic geochemistry needed to be conducted.

Concerning the working safety and scale disposal the activity of the scales is of special interest. Investigations of the ORC heat exchanger samples showed, that the activity of a sample (decay processes per time) cannot be equalized with the equivalent dose of the scales. It mainly depends on the emitted radiations of the incorporated radionuclides and their concentration. The *Preheater 2 (front)* sample is the best example: it shows the highest activity but the lowest equivalent dose. Lead sulfide is contained as main mineral and therefore it is assumed that ^{210}Pb made up the main radionuclide in this sample. Here the lowest γ -radiation was detected. All samples, containing barium/strontium sulfates, which incorporate ^{226}Ra show lower activities but higher equivalent doses.

APPLICATION OF THE INHIBITOR SYSTEM

To avoid the radioactive contamination of barium/strontium sulfates or the formation of scales at all, 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, 1994). Scaling in the surface installation of the Soultz power plant by barium/strontium sulfates and lead sulfides leads to serious problems concerning the working safety and scale disposal due to their well-known accumulation of radionuclides. The issues, connected with this topic, were described extensively in the introduction.

To solve these problems a concept for the application of an inhibitor system for scale avoidance was designed: This concept includes the selection of an appropriate inhibitor by laboratory experiments and the design and installation of the inhibitor system.

Three different inhibitors, based on phosphonates, were tested in laboratory experiments for their ability to suppress barite/celestine formation in the Soultz

geothermal brine. Exemplarily, the results of the closed bottle test are presented in this paper.

Effectiveness of the Scale Inhibitors

Phosphonates act in two ways as scale inhibitor: on one hand they complex specific cations and keep them in solution, on the other hand they inhibit the growth of seeds by adsorption on growth-active surfaces (Nowack, 2003).

The degree of efficiency of an antiscalant is influenced by several physical-chemical parameters: pH, coordination number of the complex, temperature-resistant, adsorption affinity, and the presence and concentration of co-ions like Ca^{2+} , Mg^{2+} , Sr^{2+} or Pb^{2+} in solution and the solubility of the inhibitor in water (Nowack, 2003).

Selection of the Inhibitor by Laboratory Experiments: Closed Bottle Tests

Three phosphonic acids were tested for their potential of scale inhibition in the geothermal fluid of Soultz: For product anonymization, the following inhibitor labeling was chosen: *Inhibitor orange*, *Inhibitor blue* and *Inhibitor red*.

Sampling and sample preparation of the brine/inhibitor mixtures

Brine was sampled from the production well GPK-2 with 157°C and cooled by a chiller to 70°C. For sample preparation, 4 1L bottles were filled to the top with brine to suppress the uptake of oxygen. To three of these samples, phosphonic acid (5 mg/l active concentration) was injected directly and vigorously mixed with the brine. The fourth sample remained as a reference sample, no phosphonic acid was added. A water analysis of the reference sample was conducted directly one day after sampling and 8 days after sampling.

Bottles with brine/inhibitor mixtures and the reference sample were stored for 8 days at room temperature in a non-disturbed state. Thereafter, 50 ml of each sample was passed through a 0.45µm membrane filter. The filtrate was diluted (1:100) and mixed with nitric acid for determination of the Ca^{2+} , Sr^{2+} , Ba^{2+} and SO_4^{2-} concentrations.

Analysis of the filtrate and the filter residues

Concentration of barium in the reference sample and the brine/inhibitor mixtures after 8 days storage were compared to the barium concentration in the reference sample of the sampling date. Without inhibitor the barium concentration decreases from 26 to 16 mg/l in the reference sample. In the brine/inhibitor mixtures the barium concentration remains nearly constant at 25 mg/l. Also the strontium concentration did not change significantly (Table 3).

Table 3: Ion concentration of Ca^{2+} , Sr^{2+} , Ba^{2+} and SO_4^{2-} in the filtrates of the reference samples and the brine/inhibitor mixtures

Sample	Ca in mg/l	Sr in mg/l	Ba in mg/l	SO ₄ in mg/l
Reference 06/04/2011	7600	412	26	150
Reference 14/04/2011	7080	398	16	250
Inh. orange 14/04/2011	7380	406	25	310
Inh. red 14/04/2011	6960	394	25	300
Inh. blue 14/04/2011	6970	400	23	310

Filter residues of the reference sample and the *Inhibitor orange*/brine mixture are made of yellow to brownish precipitates of very fine grain size (Figure 10). In contrast, only a few filter residues were formed in *Inhibitor red*/brine and *Inhibitor blue*/brine mixtures.

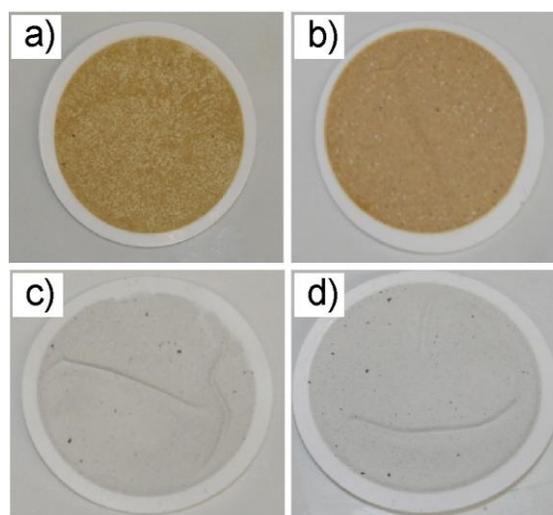


Figure 10: Filter residues of the closed bottle tests a) reference sample (brine without inhibitor), b) Inhibitor orange/brine mixture, c) Inhibitor red/brine mixture, d) Inhibitor blue/brine mixture.

All inhibitors suppress the formation of barium/strontium sulfates. Inhibitor blue and Inhibitor red additionally restrain also co-precipitation. Therefore, these products turned out to be convenient for the use as an antiscalant in Soultz brine conditions.

Outlook: Mineralogical and Geochemical Monitoring During the Inhibitor Injection

The mineralogical and geochemical monitoring concept in Soultz includes the characterisation of deposits and of the geothermal fluid in the surface installations of the plant during the continuously addition of the inhibitor.

It is expected, that the amount of deposits in the surface installations, especially at the cold part of the plant will be significantly reduced or completely blocked. Thereafter, the ORC heat exchanger system keeps its efficiency about a long term production interval and the interval of the cleaning procedures will be elongated significantly. To affirm the effectiveness of the inhibitor, the ORC heat exchanger system, pipes and filters at the cold part of the power plant will be controlled regularly. Filter residues, if present, will be characterized chemically and mineralogically. Their activity and the radionuclide content will be investigated.

During the injection of the inhibitor, geothermal fluid will be sampled regularly and characterized in detail. Especially the barium and phosphor concentration in the fluid should be in focus of this monitoring. If the inhibitor works properly, the barium concentration at the production and the injection side remains equal. Monitoring of the total phosphor concentration in the fluid could confirm if the inhibitor is recycling and accumulating with time. Decomposition of the inhibitor can be monitored by comparison of the total phosphate and the phosphonate concentration.

CONCLUSIONS

In the Soultz power plant, deposits were found in all parts of the surface installations: filter, pipes heat exchangers. At the warm part, the production side, are those deposits mainly made of cuttings which were raised from the reservoir. During cooling of the Na-Cl-Ca brine in the heat exchanger from 157 to 70°C, barium/strontium sulfates, lead sulfides and mixed sulfides of Fe, Sb and Cu precipitate and form scales with thicknesses from μm to mm. The different temperature ranges in the heat exchanger have no or only a minor impact on the mineralogical composition of the scales. Sulfate and sulfide minerals coexist in the deposits. They are not mixed but separated in different layers which indicate different growth cycles. Further investigations have to be applied to identify the chemical reaction, responsible for the formation of S^{2-} in the geothermal fluid: microbiological activity of sulfur reducing bacteria, corrosion processes or the Eh – pH conditions of the fluid.

Accumulation of radionuclides in the scales, ^{226}Ra in barium/strontium sulfates and ^{210}Pb in lead sulfide, causes significant problems during energy production: specific time- and cost-intensive restrictions for the working safety during the cleaning procedures and for scale disposal have to be applied. To solve these problems, an inhibitor system in Soultz has been designed. Therefore, several products, based on phosphonates were intensively tested in laboratory experiments. One of these products, the *Inhibitor red*, showed the best performance to suppress the precipitation of barium/strontium sulfates in the Soultz-brine and will

be injected continuously after finishing the installation of the inhibitor system. The geochemical and mineralogical monitoring of the brine and the deposits in the surface installations during injection of the phosphonate will be continued to test the effectiveness of the inhibitor.

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