IN SITU MATERIAL STUDIES AT THE HIGH TEMPERATURE SKID (HTS) BYPASS SYSTEM OF THE GEOTHERMAL POWER PLANT IN SOULTZ-SOUS-FORÊTS, FRANCE

Julia Scheiber¹, Guillaume Ravier², Oriane Sontot¹, Christina Hensch³, Albert Genter¹

¹GEIE Exploitation Minière de la Chaleur/EEIG Heat Mining
Route de Soultz, BP 40038, 67250 Kutzenhausen, France
e-mail: scheiber@soultz.net
²ES-Géothermie
3A Chemin du gaz, 67500 Haguenau, France
³Rhenotherm Kunststoffbesichtungs GmbH
Peter-Jakob-Busch-Straße 8, 47906 Kempen, Germany

ABSTRACT
The three-year research program (2010-2012) of the Soultz-sous-Forêts geothermal power plant (France) is associated with a scientific and technical monitoring during geothermal exploitation. Several hydraulic circulation tests have been performed in this time and those tests were used for intensive in-situ material studies concerning corrosion, coating and scaling which resulted in an improved design for a corrosion skid at the high temperature side of the geothermal power plant.

At Soultz, saline brine is produced from a granitic EGS reservoir at 160°C and 20 bars (wellhead GPK-2). This fluid consists mainly of a Na–Ca–Cl brine with a TDS of 97 g/l at a pH of 4.8. Measurement of the redox potential show reducing conditions.

Identification and testing of materials which are able to resist in these operational conditions became an essential part of the Soultz research program. Selection of applicable materials for this aggressive environment focuses on their stress resistance against chemical attack, on mechanical stress resistance and durability and on their cost effectiveness. Corrosion studies of metals and tests of the thermal stability of polymer coatings were also conducted over the 3 years, from the first circulation tests to the current operation state but mainly on the cold part of the surface installations at 70°C and 18 bars. A relatively low corrosion rate of 0.2 mm/year was observed.

The ongoing challenge is to conduct material tests at in-situ conditions at the hot side of the geothermal loop. Therefore, an innovative high temperature skid (HTS) has been designed, built and assembled in the hottest zone of the surface installations of the Soultz geothermal site.

This tool operates at 160°C and 20 bars. Flow, temperature and pressure are monitored continuously during skid operation and an internal window provides the direct observation of the inside flow conditions at the upper part of the skid.

Testing of metal coupons is still an important part of the corrosion experiments but the main improvement was established by integrating two different geometric setups into the skid equipment: straight pipes and T-shaped pipes. The last one reflects both, dynamic flow and stagnant flow in one sample. Different metals will be tested to investigate the corrosion rate in stagnant and dynamic flow conditions and the type of corrosion, either uniform or pitting.

Moreover, corrosion products and scaling layers on the metal surface will be characterized. Besides the corrosion study of metals, the test of different polymer coatings concerning their thermal stability, their abrasion resistance against mechanical attack by quartz and feldspar particles, produced from the granite reservoir, and the formation of scalings on the polymer surface are under investigation.

Corrosion and coating in-situ experiments at the high temperature side of the geothermal loop in Soultz provide unique opportunities to test and select materials based on their durability and cost effectiveness for geothermal applications with Upper Rhine Valley type fluids.

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. This area is one of the hottest areas in Western Europe with 110°C at 1 km depth.

Within this anomaly are a few areas located where the temperature gradient is higher in comparison to the surrounding areas. Temperature measurements in former petroleum wells of the Pechelbronn oil-field area indicated that one of these very local anomalies is present at the Soultz horst, first mentioned by Haas
and Hoffmann, 1929. Here 1400 m of sediments, lacrustine 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). In the deepest wells, at 5 km depth, a bottom hole temperature of 200°C has been observed.

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 gross capacity of 2.2 MWe.

The 4 wells were originally planned to act as two doublets. Within the last three years, different scenario of well setups were tested that involve one production well, GPK-2 and two injection wells, GPK-1 and GPK-3: a long term circulation for about 11 months in 2010, two short term circulation tests in 2011 and one in 2012 that uses GPK-3 and GPK-4 as injection wells. During the circulation period in 2013 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 but could be re-used as production well in the future.

The circulation of geothermal brine effects the material performance of equipment which is in direct contact with the fluid. The high salt content, 97 g/l, of the Na-Cl-Ca brine (Sanjuan et al., 2010) and the production of cuttings from the reservoir causes different corrosion and abrasion issues at the surface and subsurface installations of the geothermal loop. Additionally, the formation of scalings, partially related to corrosion processes, complicate proper material performance of the surface equipment, for example at the heat exchangers. Intensive mechanical cleaning procedures were required in the past in order to remove the inorganic deposits, mainly made of strontium rich barite (Ba,Sr,SO₄) galena (PbS) and minor fractions of mixed sulfides ((Fe,Sb,As,S)ₓ) (Sanjuan et al., 2010; Scheiber et al., 2012 and Nitschke, 2012).

For material protection and improving the cleaning procedure of the heat exchanger, it was decided to apply a polymer coating with beginning of the ORC operation in 2008. The anti-adhesive properties of the coating surface decrease the scaling adhesion. Those surface properties should improve the cleaning efficiency of the water jetting procedure which works out very well until the last production circle. The first damages of the coating and corrosion related deposits as well as damages of the heat exchanger tubes were observed recently and are under investigation. The first results are presented in this paper.

Another focus of the in-situ material experiments at Soultz is related to the performance of materials utilized for the downhole pump. These materials have to stand high temperature and pressure at rotation rates of 1500 – 2000 rpm which creates high flow velocities at the hydraulic part of the LSP. Based on the geochemical conditions, electrochemical corrosion due to the impact of oxygen is negligible during production due to the anoxic conditions of the geothermal brine. Corrosion issues related to carbonic acid needs further investigations. The CO₂ concentration in the gas phase at atmospheric conditions is ~85%, fluid to gas volume ratio is 1:1 (Sanjuan et al., 2011). Besides the geochemical conditions during production, also the impact of injected artificial brines for well killing and well activation causes corrosion issues if they are not treated properly with corrosion inhibitors.

Materials at geothermal power plants have to stand a wide range of operational parameters and therefore they have to be specifically selected based on the operational purpose, on their durability and cost efficiency.

SHORT SUMMARY OF FORMER MATERIAL STUDIES IN SOULTZ

Corrosion studies are conducted in Soultz since 1994. First studies involved corrosion inhibitors for casing protection during drilling. The first material study was conducted in a simple bypass system equipped with five chambers in 1997. During a 4 month circulation, metal coupons of carbon steel, stainless steel, austenitic stainless steel and Ni-based alloy...
were exposed to the geothermal brine. Uniform corrosion was observed at the carbon steel sample but no corrosion was visible at the stainless steel or Ni-based alloy coupons (Baticci and Faucher, 2008).

In 2008, the low temperature skid (LTS) bypass system was installed at the cold side of the geothermal loop downstream of the heat exchanger system, Figure 2.

![Figure 2: Low temperature skid (LTS) located downstream of the heat exchanger before injection well GPK-3 (Picture: GEIE).](image)

Corrosion experiments at this bypass system focused on material research at in situ conditions of 70°C and 18 bars. Metal coupons were exposed in three different chambers which were made of PEEK (Polyether Ether Ketone). Corrosion rate and type of corrosion were investigated on metal coupons made of carbon and stainless steels. Sample selection was based on those materials which were already in use in the surface and subsurface installations of the geothermal power plant in order to identify the weakest points at the power plant.

For mild steels uniform corrosion were observed mainly at corrosion rates up to 0.2 mm/year. Pitting corrosion dominate at stainless steel samples. The more noble the material is the minor was the impact of the geothermal brine on the metal. The formation of a strong adhesive scaling was recorded especially for carbon steels. (Baticci, 2009, Baticci et al., 2010, Mundhenk et al., 2012, Mundhenk et al., 2013)

**MOTIVATION FOR MATERIAL STUDIES AT THE BYPASS SYSTEM HIGH TEMPERATURE SKID (HTS)**

During the next phase of scientific activities in Soultz, the improvement of the heat exchanger system and the pumping system are in focus of material research. Both equipments are located at the hot part of the geothermal loop and require very specific operational demands. Chemical and mechanical attack by geothermal brine and produced cuttings from the granitic reservoir in combination with high rotation velocities at the hydraulic part of the Long Shaft Pump (LSP) create a highly aggressive environment for materials in use. Within the heat exchanger, the thermal gradient between organic fluid and geothermal fluid stresses the material. Additionally, chemical attack by geothermal brine and the mechanical cleaning procedures for cleaning from scalings are challenging for materials to be applied.

**Design of the HTS**

The HTS was calculated and designed by O. Sontot in cooperation with the scientific and technical team of GEIE in 2010 (Sontot, 2010), Figure 3.

![Figure 3: Scheme of the high temperature skid (HTS) after Sontot, 2010 (left) and the installed skid at the Soultz geothermal power plan (right) (Picture: GEIE).](image)
Samples of the HTS are a part of the pipe network of the skid itself. Metal coupons can be tested in a specific coupon sample holder system, green pipe in Figure 3. This setup is very different from former bypass systems where corrosion studies were conducted at metal coupons only which were placed in PEEK chambers.

Pipe-samples will be assembled in four different vertical lines, represented by 4 different colors in Figure 3. Three samples can be inserted in every line but in fact, every straight pipe of the skid can be replaced by a sample of similar geometry. The skid was assembled in a way that for removal and installation of pipes the skid has not to be de-installed completely.

Temperature and pressure of the geothermal fluid is measured before entering and after leaving the HTS. A flow meter measures the flow rate which can be adjusted manually to the respective production conditions of the geothermal cycle. The main objective of the skid design was to mimic the physical and geochemical conditions as close as possible. A window, placed between the first and the second line of the skid, provides direct observation of the current state of the geothermal fluid.

**CORROSION EXPERIMENTS**

Corrosion experiments in the bypass system HTS focuses on materials which are applied at the hot side of the geothermal loop at 160°C and 20 bars like the downhole pump and the heat exchanger system.

**Motivation of corrosion studies at the HTS**

The installation of the bypass system HTS for material studies on site at GPK-2 provides the opportunity to investigate the material resistance of various materials at in situ production conditions at adjustable flow rates.

**T-samples**

For corrosion experiments, a specific pipe design, T-samples, will be tested in the skid. Those T-samples mimics regular components of the power plant like installation places of sensors or dead end filtration. The shape of those samples was chosen due to the observation that corrosion rates in static systems (stagnant brine) are higher than in dynamic systems (flowing brine). The straight part of the T-sample is placed in the flow direction, simulating the dynamic conditions. In the rectangular part of the T-samples the static conditions will be formed. Two metal coupons of the same composition like the T-sample are mounted in the linear and the rectangular part. Three T-samples of the same material are installed at the same time and removed from skid as a function of the experiment duration, approximately after 3, 6 and 12 month, respectively. The first tests are carried out with 1.0425 (P265GH) and 1.4404 (316L), Figure 4.

Besides straight pipes and T-samples, pipes for tube heat exchangers will be tested at the HTS to investigate their corrosion and abrasion resistance. Investigation of the sample will be divided in the analysis of the corrosion type and corrosion rate at the inserted metal coupons. Additionally, surface analysis of the residual material and chemical and mineralogical analysis of the corrosion products will be carried out at the T-samples. In order to avoid corrosion processes after sample removal, the pipes and coupons are kept under nitrogen atmosphere until sample preparation for the analytical investigations.

**Metal coupons**

Corrosion rate will be investigated at metal coupons. Therefore, two different setups are available: First, metal coupons can be tested in static and dynamic flow conditions of the T-samples. Second, a coupon sample holder is installed after the last line, at the exit of the HTS, green pipe in Figure 3. This construction provides places for 11 coupons, coated and uncoated.

**COATING EXPERIMENTS**

**Motivation of Coating Studies at the HTS**

Coatings are already in use at the geothermal power plant in Soultz. Related to the formation of inorganic deposits in the tube heat exchangers of the Organic Rankine Cycle (ORC), a polymer coating based on a thermostetting material was applied. Scaling adhesion of the Soultz deposits on the metal surface is very strong and deposits had to be removed by milling. This type of cleaning procedure is time and cost intensive. Additionally, damages of the metal surfaces by abrasion effects like scratching can not be avoided completely.

At the Soultz site, application of coatings already proofed to be a successful tool for corrosion and abrasion inhibition. At the same time, it was observed that different products work out very differently when they are exposed to the same geochemical and
physical conditions. However, a proper material selection is essential for a long term stability of polymer coatings at geothermal power plants. Therefore, in-situ coating experiments are carried out at the high temperature skid (HTS) bypass system at the production side. After improvement of the low temperature skid (LTS), which is located downstream of the heat exchanger at the cold part of the geothermal loop, coating experiments will be carried out at the same time in both skids and results can be compared directly.

Case study: Current State of the ORC Heat Exchanger Coating

Energy production in Soultz is carried out in an Organic Rankine Cycle (ORC). The ORC heat exchanger system constitutes, of three tube heat exchangers, the ORC Evaporator, Preheater 1 and Preheater 2. Figure 5.

Repeated cleaning procedures are required due to the presence of inorganic deposits at the geothermal side of the heat exchangers. Those scalings are formed due to the temperature decrease in the heat exchanger and act as an isolation material. With increasing deposit thickness, the heat transfer between geothermal brine and organic fluid decreases significantly (Scheiber et al., 2012).

Application of coatings at the ORC heat exchanger system

The scaling formation was the main reason to apply a polymer coating on all tube exchangers at the ORC system. Based on the anti-adhesion properties of the coating surface, scaling adhesion on the polymer surface was decreased significantly. Instead of milling, high pressure water jetting was used for the cleaning procedures.

Current state of the ORC heat exchanger system

Directly after application of the coating in 2008 the cleaning procedures worked out very well. With time, the anti-adhesion properties start slowly to disintegrate and more and more of the strontium rich barite deposits could not be removed anymore. Finally, the first spalling of the coating was observed in November 2012 when the ORC heat exchanger system was opened for inspection and cleaning. The polymer coating show different signs of disintegration in the ORC Evaporator and the two Preheaters:

- loss of the anti-adhesion properties
- formation of bubbles
- mechanical spalling

Water jetting can only remove scaling which have a weak adhesion on the polymer coating. Originally, scalings were not strongly attached to the polymer surface but the poor efficiency of the water jetting cleaning implies that the anti-adhesive properties of the coating start to disintegrate. As a consequence, the scalings are much stronger attached to the surface and cleaning becomes much more difficult.

After cleaning, a thin layer of sulfate scaling cover still most of the heat exchanger surfaces, Figure 6.

Based on these observations it can be expected that the permanent scaling layer at the heat exchanger surface will grow slowly but continuously and form an inorganic isolation film on the coating. The efficiency of the heat exchange will decrease continuously as a function of the scaling thickness. Bubble formations, especially in all caps of the system indicate a loss of thermal stability of the coating, Figure 7.
Both deposits were investigated by optical microscopy (Stemi D4, Zeiss), and electron microscopy (ESEM XL 30 FEG, Philips, equipped with an EDAX system), combined with qualitative energy dispersive X-ray fluorescence.

The front side of the coating particle was in contact with the geothermal fluid and is completely covered with grey and black scalings. Morphology and elemental composition correlate with former studies, they consist mainly of strontium rich barite \( (\text{Ba}_1 \text{Sr}_x \text{SO}_4) \), galena (PbS) and minor fractions of mixed sulfides \( ((\text{Fe},\text{Sb},\text{As})_x \text{S}_4) \) (Nitschke, 2012, Scheiber et al., 2012 and Sanjuan et al., 2011).

The back side was in contact with the metal surface and is partly covered by a homogeneous and light yellow deposit. In the backscattered mode of the electron microscope two different deposits were observed, Figure 10: A dense layer of iron and oxygen rich minerals with similar morphology and single, lead and sulfur rich grains which are irregular distributed at the surface. Based on the elemental analysis, the deposit consists either of iron oxides or iron hydroxides and/or of iron carbonates, Figure 10. Both types of minerals are indicators for electrochemical corrosion of the metal surface of the heat exchanger tubes.
The corrosion type, pitting or uniform corrosion is not known right now but during the next maintenance period one damaged pipe and one non damaged pipe will be extracted from the heat exchanger in order to investigate the corrosion mechanisms. Corrosion in the heat exchanger systems of a geothermal power plant is a very serious situation which has to be avoided in any case. First, time and cost intensive maintenance procedures have to be applied to fix the damages. Second, the organic fluid at the energy production side is very often explosive and an intact circulation loop for this fluid has to be guaranteed.

The presented case study of Soultz showed that coatings do have a real potential for material protection but products have to be selected very carefully based on the specific geochemical and physical operational conditions.

**General Introduction of Materials in Use**

Coatings have a very wide range of applications. They are used for example in food industry, car industry, chemical industry and material production. For most applications, very specific surface properties are required and a huge variety of highly sophisticated products were developed in the last decades.

For geothermal applications, anti-adhesive surface properties, heat conductivity and resistivity against chemical and/or mechanical attack are the most important qualities. One of the most challenging topics for successful coating performance in industrial plants is the proper surface preparation before coating application. This can be easily handled for straight pipes and plane metal surfaces but it gets difficult for equipment with complicated geometric shape like bows or T-parts. Additionally, the coated pieces have to be handled with care after coating to avoid any damage of the surface.

**Thermosetting polymers**

This paragraph focuses on epoxy coatings which cure at room temperature by addition of catalysts. They are created by mixing two different epoxy resins or mixing of epoxy resin with a specific catalyst. After curing, the epoxy coating keeps its shape irreversibly. It is highly resistant against chemical and mechanical attack but starts to decompose if exposed to UV radiation (Schweitzer, 2001).

This type of coating can be apply on smooth and non smooth surfaces as long as no contamination like powder or deposits pollute the metal surface even if the geometry is quite complicated as it is for the metal coupon holders for T-samples (see chapter Corrosion Experiments) of the HTS, Figure 11.

**Thermoplastics**

Thermoplastic materials are formed under specific temperature conditions where the material melts but does not thermally decompose. After cooling down it keeps its certain state but can be remold after reheating (Schweitzer, 2001).

Typical examples for thermoplastics are Perfluoroalkoxy (PFA), Fluorinated Ethylene Propylene (FEP), Polytetrafluoroethylene, better known as Teflon, (PTFE) and Polyether Ether Ketone (PEEK). These polymers have excellent chemical and mechanical resistance and perform very well at high temperatures.

**In-situ Experiments at the High Temperature Skid (HTS)**

Coating experiments in Soultz focus on testing thermosetting and thermoplastic polymer coatings at the hot and the cold part of the geothermal loop.

Coating experiments at the high temperature skid focuses on testing the
- abrasion resistance
- resistance against chemical attack (fluid and gas)
- thermal stability
- functional stability (structure, porosity, pore size distribution)
- sub-surface migration in case of scaling formation
- formation and adherency of scalings on the coating surface
- performance of the anti-adhesion properties
- adherency on metal surfaces

Therefore 12 straight pipes were coated with 4 different products, 3 pipes per product respectively, based on thermoplastic and thermosetting polymers by the company Rhenotherm, Figure 12.
Sample name and the applied coatings are listed in Table 1.

**Table 1: Materials for coating experiments on straight pipes of the high temperature skid (HTS)**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Coating material</th>
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</thead>
<tbody>
<tr>
<td>Coating A</td>
<td>PFA/FEP</td>
</tr>
<tr>
<td>Coating B</td>
<td>Anti-corrosion primer combined with PFA</td>
</tr>
<tr>
<td>Coating C</td>
<td>PEEK/PFA</td>
</tr>
<tr>
<td>Coating D</td>
<td>Epoxy combined with PTFE</td>
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Two pipes per coating will be exposed at the HTS and removed after 2 and approximately 6 month of experimental duration. Evaluation of the coating performance at 160°C and 20 bars can be done by comparing the exposed coating samples with non exposed sample.

For simulation of the worst case scenario, a damaged coating surface, metal coupons will be coated with the same products and damaged by knife cuts before installation of the HTS.

**CONCLUSIONS AND OUTLOOK**

Materials which are applied in geothermal sites have to perform under specific geochemical and physical conditions. At the geothermal power plant in Soultz sous Forêts, a Na-Ca-Cl brine with a TDS of ~97 g/l and a pH of 4.8 is produced from a granite reservoir. The brine is produced at 160°C and 20 bars and injected with 70°C and 18 bars, measured at the wellheads respectively.

Based on former material studies at the low temperature skid (LTS) bypass system, an improved test skid at the hot side of the geothermal loop was designed and installed. The first experiments on this high temperature skid (HTS) start with the next production period. Physical conditions of the skid can be adjusted to the current state of the production parameters.

Corrosion studies and coating studies are carried out in pipes which are part of the HTS equipment. In fact, every linear pipe of the skid can be replaced by testing material of similar construction. Metal coupons, coated and uncoated, can be installed in two different conditions: dynamic flow and stagnant conditions. A coupon holder at the exit of the skid provides places for 11 coupons at the same time. Moreover, pipes for tubular heat exchanger can be tested directly in the skid concerning their material performance.

Characterization of material performance at samples from the HTS will be divided in analysis of corrosion type and corrosion rate (metal coupons) and surface analysis of the residual material as well as chemical and mineralogical analysis of the corrosion products on the pipe samples.

Also polymer coatings will be tested at the HTS. The wear resistance of various polymers and the heat expansion due to temperature differences will be investigated as well as their chemical resistance in the geothermal fluid at high temperatures (~160°C). The adherency of the coating to the metal surface and the formation of scalings at the coating surface which is in contact to the brine are also of interest.

The presented case study of coating performance in the Organic Rankine Cycle (ORC) heat exchanger system showed that coatings do have a real potential for material protection but products have to be selected very carefully based on the specific geochemical and physical operational conditions.

For a direct comparison of the corrosion and coating experiments at the geothermal loop, the low temperature skid (LTS) will be improved based on the current design of the high temperature skid (HTS). Experiments at high and low temperature conditions can be conducted in parallel and the results can be compared directly.

**ACKNOWLEDGEMENTS**

This work was supported by BGR, BMU and Forschungszentrum Jülich (Germany), ADEME (France) and by a consortium of French and German industrial members (EDF, EnBW, ES, Pfalzwerke, Bestec, Steag). We like to thank Dr. P. Huttenloch from EiFER and Prof. T. Kohl and N. Mundhenk (AGW, KIT) for fruitful discussions. The authors are very grateful for the support of Dr. M Schwotzer (IFG, KIT) during the ESEM measurements. The technical team of the GEIE is also greatly acknowledged for their support concerning planning and installation of the LTS and the HTS.
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