

Chemical Treatment Efficiency on Scaling and Corrosion at Rittershoffen, France, Upper Rhine Graben

Justine Mouchot¹, Guillaume Ravier¹, Clio Bosia¹, Olivier Seibel¹, Fanny Mercier², Justine Menges²

¹ ES Géothermie, 5 rue de Lisbonne, 67300 Schiltigheim, France ;

² SUEZ – Water Technologies & Solutions, Tour CB21, 16 place de l'Iris, 92040 Paris La Défense, France

justine.mouchot@es.fr

Keywords: Geothermal energy, France, Exploitation, chemicals, scaling, corrosion

ABSTRACT

The Rittershoffen geothermal plant is a deep EGS geothermal project initiated in 2011 and located in Northern Alsace, French Upper Rhine Graben. This plant, in operation since 2016, comprises the first full and direct use of an EGS thermal plant. It has a nominal capacity of 25 MW_{th}, which represents around 25% of the industrial heat demand of “Roquette Frères” bio-refinery at Beinheim, 10 km east of Rittershoffen.

The heat transfer is ensured by a tubular heat exchanger from the geothermal loop to a transport loop, reaching the industrial facility. A geothermal fluid, Na-Ca-Cl type with salinity of about 100g/L, is produced at a temperature of 170°C and is fully reinjected into the fractured granitic basement reservoir at 80-85°C. The fluid is enriched in dissolved gases, mainly CO₂. This geochemical context induces barium sulphate precipitation during the heat transfer process. These strong deposits decrease notably the heat transfer efficiency of the heat exchangers, increasing operational costs like power consumption, cleaning operation and wastes. Therefore, to ensure sustainable plant operation, a chemical treatment is required to inhibit this kind of secondary deposit. Moreover, arsenic, lead and antimony, and minor trace elements from geothermal brine, are precipitating while in contact with steel through electrochemical processes. It results in precipitations associated with sulphur. At the beginning of 2017, a plant operator team and a water treatment company built a partnership to select appropriate products tackling these operational issues, identify methodology and indicators to assess the chemical treatment efficiency of the heat exchangers.

The selected scale inhibitor contains a powerful polymeric dispersant based on patented terpolymer technology. This technology has proven its efficiency on controlling a variety of salts, particularly on barium sulphate compounds as typically encountered in the Rhine Graben. By the application of a filming agent acting as a corrosion inhibitor, the electrochemical processes leading to lead and arsenic sulphide deposition are significantly reduced, as well as contributing to the tubular heat exchanger, pipes and reinjection well casing integrity.

The quantity, the structure, and the chemistry of scaling before and after the chemical treatment are compared. From the operational point of view, the ease of cleaning and the heat transfer capacity are also monitored. After more than two years of chemical treatment at Rittershoffen geothermal plant, operational monitoring shows a good efficiency of the applied treatment. The monitoring within the following months would be focused on corrosion rate assessment. New sampling campaign of scaling will be performed to improve the understanding of chemical treatment action and to start the dosage optimization.

1. INTRODUCTION

Deep geothermal energy is developed in Upper Rhine Graben area, both in France and Germany, targeting high enthalpy fluid at depth higher than 2.5 km to produce renewable baseload energy, as heat or electricity. One geothermal site has been developed to provide superheated fluid to industrial processes, located in Rittershoffen, to the North-East of France. This plant has been commissioned in June 2016 and is operated since then under commercial conditions.

After a presentation of the geothermal site, the geochemical context is introduced as well as a designed program to control scaling and corrosion issues with the aim to manage (i) continuous energetic production, (ii) maintenance stops and (iii) waste and dismantling purposes. Performance indicators are then presented and discussed, highlighting the efficiency of applied chemical treatments and improvement perspectives.

1.1 Rittershoffen geothermal plant

The heat plant of Rittershoffen has been developed in order to supply Roquette Frères Company, a bio-refinery, with geothermal heat for their industrial processes. This industrial user, located in Beinheim, France, totals thermal needs of 100 MW_{th}. The geothermal heat plant, with an installed capacity of 24 MW_{th}, supplies the totality of its heat production to this company via an insulated heating transport loop of 15 km length (Ravier et al., 2017). The temperature of this geothermal fluid reaches 170°C (Figure 1). One production well, GRT-2 at 2700 m depth, penetrates into Triassic sedimentary layers and the top crystalline fractured basement interface, conveying about 300 m³/h of geothermal fluid to the surface under pressure induced by a Downhole production Line Shaft Pump (Baujard et al., 2015, Baujard et al., 2017). The geothermal brine flows through a system of twelve consecutive tubular heat exchangers, and is fully reinjected without additional pumps at 80°C into one injection well, GRT-1 at 2500 m depth (Ravier et al., 2016). The reinjection temperature depends on the return temperature of the transport loop.

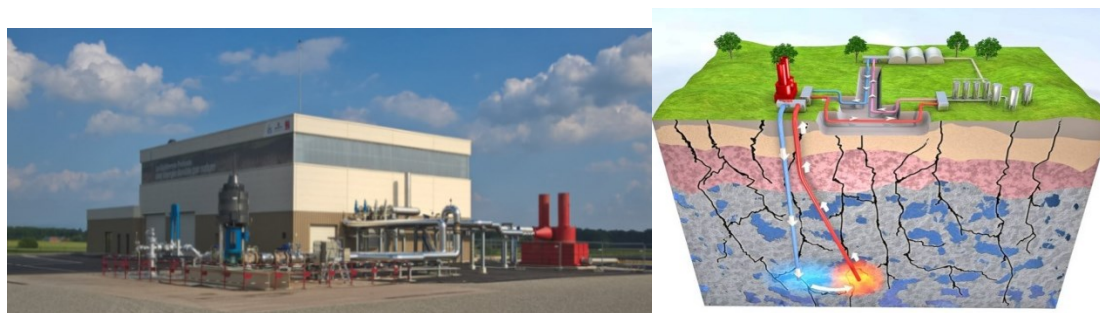


Figure 1: Rittershoffen geothermal site from surface (left) and schematic view of subsurface and surface (right)

1.2 Scaling and Corrosion context

The geothermal fluid is a highly saline brine with a Total Dissolved Solid content of about 100 g/L, Na –Ca –Cl type. Physical characteristics of the brine are also comparable to other deep geothermal plants in the same area, pH is about 5.2 and electrical conductivity is about 120 mS/cm at atmospheric pressure for a brine cooled down to 60°C (Sanjuan et al., 2016, Mouchot et al., 2018). The brine is naturally enriched in dissolved gases, with a gas-liquid ratio of 1.2 Nm³/m³ in standard conditions. The main component of the dissolved gases is CO₂ (Figure 2).

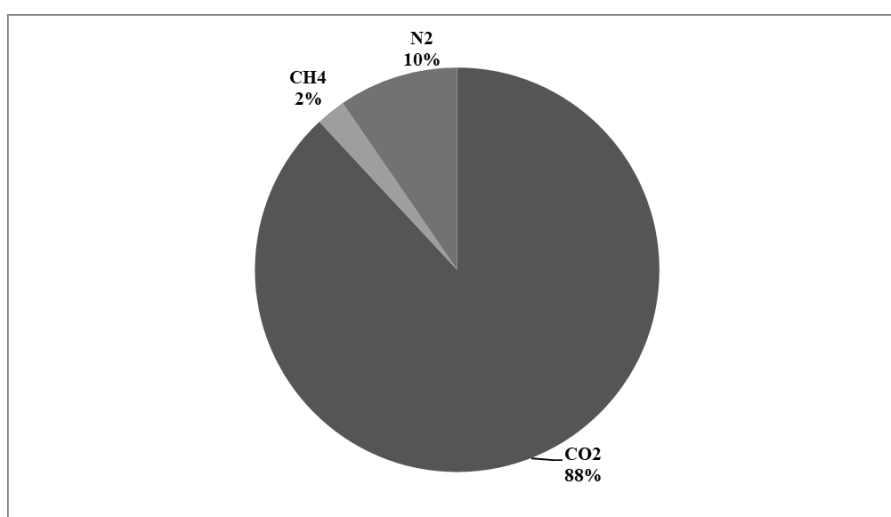


Figure 2: Dissolved gas composition of brine from Rittershoffen production well, sampled in 2018.

The chemical analysis of the brine made by ICP-MS is given in Figure 3. During the heat transfer occurring in the heat exchangers from 168°C down to 80°C, from a modelling approach with PHREEQC, barium sulphate and calcium carbonates are expected. Indeed, following the concentration in SO₄, Ca, Sr, Ba, Ca in geothermal brine, solubility curves of (Ba, Sr) SO₄ and CaCO₃ are reached.

From past experiments in the same context of deep geothermal energy in the Upper Rhine Graben (URG), a few centimetres thick scale deposit of barium sulphate clogs the tubular heat exchangers within a few months of operation. This issue leads to plant stops for cleaning, inducing a lower production, high operational costs and waste management issues. From operational feedbacks in the same area, deposition of traces of metal-rich sulphides is also expected (Scheiber et al., 2012). These metal-rich sulphides are enriched mainly in lead, arsenic and antimony. These scales are strongly attached to the pipes and tubes. Moreover, these precipitations trap natural radionuclides like ^{226/228}Ra and ²¹⁰Pb in sulphates and sulphides deposits respectively. Waste management as a NORM class induces specific regulation rules for safety and environment protection as well as high operational costs (Cuenot et al., 2013). Since the commissioning of the plants in this area, chemical treatments are applied to inhibit formation and deposition of barium sulphate. Regular inspection campaigns of the surface facilities proved the efficiency of barium sulphate inhibition but also revealed an enhanced growth of metal-rich sulphides and metals during the heat transfer in the tubular heat exchangers (Mouchot et al, 2019, Scheiber et al., 2019). Precipitation mechanisms are discussed in Haas-Nüesch et al, 2018 and Jähnichen et al., 2019, highlighting probably two processes involved: thermodynamics and electrochemistry.

Indeed, the high salinity of geothermal fluid and the operational conditions, are both corrosion enhancing factors. Different types of corrosion can occur in the surface installations: generalized corrosion, pitting corrosion, crevice corrosion, erosion-corrosion, etc. The appearance and severity of these types of corrosion depends amongst other things on the steel quality. Researches on corrosion have highlighted a generalized corrosion rate of 0.15 to 0.22 mm/year at 80°C assessed by on-site trials during carbon steel coupons exposure to the URG geothermal brine and by laboratory experiments with original URG brine and artificial brine (Baticci et al., 2010, Mundhenk et al., 2013). In the context of deep geothermal plant operation, a generalized corrosion rate of 0.14 mm/year has been measured with an LPR sensor at high temperature (Mouchot et al, 2019). Due to the presence of electrochemical processes in the scaling formation, operators and researchers identified the possibility to inject corrosion inhibitor, despite the low generalized corrosion rate, to protect even more the surface installations.

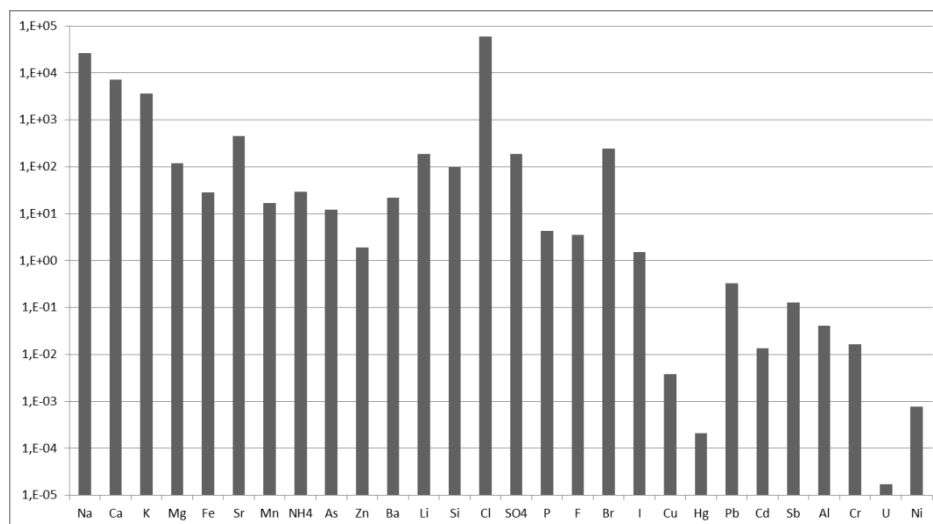


Figure 3: Chemical elements from geothermal brine (GRT2) sampled in 2018, expressed in ppm

2. SCALE AND CORROSION CONTROL PROGRAM

Within the context of scaling formation and corrosion processes involved in the crystal growth, operators and partners, researchers and a water treatment company designed a scaling and corrosion control program to protect the Rittershoffen deep geothermal plant. A lab-field test approach has been developed to identify the best chemicals combination and the appropriate strategy to inject them at controlled-costs and following environmental and safety rules.

2.1 Inhibitors selection and characteristics

With the detailed water analysis of the brine in combination with the temperature and pressure of the well, PHREEQC software was used to calculate the saturation index of different compounds. Based on the saturation index values it is possible to estimate the formation probability of the main precipitates. Scaling inhibitors were then selected based on the results these simulations. Scale inhibitor 1 was first selected. It contains a patented Co-Polymer which inhibits the crystallization of dissolved solids and is an excellent dispersant for suspended solids. This technology has proven its efficiency on controlling a variety of salts, particularly barium sulfate compounds as typically encountered in the Upper Rhine Graben. A second scale inhibitor selected is an advanced version of the previous one, formulated with SUEZ's patented Stress Tolerant Polymer (STP). It also showed efficiency against barium sulfate while it proved to inhibit crystal formation of lead sulfide. It was expected to have also a better dispersive effect on iron according to internal studies. The use of a scale inhibitor does not stop electrochemical processes from occurring. These electrochemical reactions may enhance lead and arsenic sulfide deposition (Haas-Nüesch et al, 2018). In order to stop these reactions, a corrosion inhibitor containing a filming amine was selected to form a barrier avoiding the contact between brine and the metal surfaces hindering the electrochemical reactions from occurring.

2.1.1 Compatibility test

The compatibility of the brine and the different treatment programmes were tested in the application laboratory of water treatment company. A synthetic brine was produced mimicking the Rittershoffen brine analysis. To enable a correct interpretation of test results, it was decided to remove the iron from the brine due to the coloration observed in order to allow a correct reading of the results. After de-aeration, this synthetic brine was heated, divided into individual portions then dosed with the treatment programmes at normal and high dosage. The individual brines solutions were then transferred to a pressure bomb and heated at the production well temperature for one hour. Observations were recorded along with a photograph and the pH and filterable solids content determined for each.

2.1.2 Efficiency test

The efficiency of the scaling inhibitor has been assessed in an external lab, by measuring crystal growth and kinetics of Barium Sulfate formation with a model solution based on Rittershoffen brine enriched in Barium Sulfate. Turbidity of solution with and without inhibitor are monitored and compared with time and concentration of inhibitors. The turbidity of the solution is function of crystal size of barium sulfate particles. Efficiency on corrosion inhibitor is based on operational feedbacks from water treatment companies in other sites and applications.

2.2 On-site trial performance indicators

Since the commissioning of the geothermal plant, various chemical treatments have been applied to inhibit scaling and corrosion issues within the surface facilities. Chemicals are selected based on operational feedbacks, as well as dosage and injection strategy for each product. Plant operators in partnership with a water chemical company developed a monitoring plan to assess directly and indirectly the efficiency of the applied treatment. Trial planning focused on a partnership with one water treatment company is presented in Figure 4. Indirect parameters can be monitored continuously, such as heat transfer coefficient and pressure drops in the heat exchangers. Scaling characterization, like quantity, chemistry, and radioactivity can be monitored once a year when the geothermal plant is stopped for maintenance. Regarding corrosion monitoring, two methods applied on-site to measure the generalized corrosion rate are discussed.

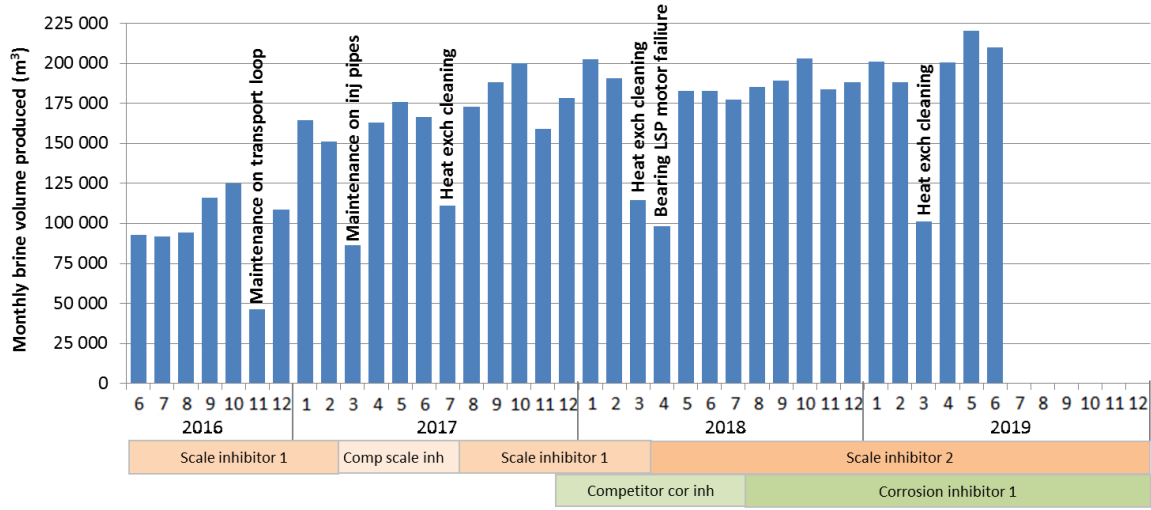


Figure 4: Trial planning of water chemical treatment since heat plant commissioning.

2.2.1 Pressure drops in the surface installations

This parameter is easy to monitor with a simple pressure difference calculation between inlet and outlet pressure of a single or a set of heat exchangers. Pressure drops of the heat exchangers give indications of scaling deposition on the inner walls of the tubes. Given a constant flow rate, an increased pressure drop suggests a thicker layer of deposits in the tubes. In the context of scaling monitoring, an analysis is made on the monthly evolution of pressure drop trends on the three sets of exchangers at Rittershoffen heat plant. Pressure drops are monitored to have a first indication of cleaning frequency of the heat exchangers and efficiency of applied chemical treatments.

2.2.2 Heat Transfer coefficient

This parameter requires more calculation than pressure drop monitoring. The heat transfer coefficient is used for calculating heat transfer between fluids separated by tubes in heat exchangers and is the inverse of thermal insulation. The heat transfer coefficient is expressed in $W/m^2.K$. Heat transfer coefficient is calculated according to equation (1) and (2).

$$\alpha = \frac{C_p \times dm \times (T_1 - T_2)}{A \times \Delta T m} \quad (1)$$

where C_p , dm , A are liquid specific heat tube side, mass flow rate, heat transfer surface.

$$\Delta T m = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln \left(\frac{T_1 - t_2}{T_2 - t_1} \right)} \quad (2)$$

where T_1 , T_2 , t_1 , t_2 are inlet tube side fluid temperature, outlet tube side fluid temperature, inlet shell side fluid temperature, outlet shell side fluid temperature.

A decrease of this coefficient in same operating conditions suggests a growing layer of scales reducing the tube's ability to allow the heat flow from its warmer surface to its colder surface. Analysis of the heat transfer coefficient also gives indicators of scales formation. The trend of the heat transfer coefficient is monitored on three sets of heat exchangers at Rittershoffen geothermal plant. These heat exchangers are designed with an oversized surface. Consequently the trend of the heat transfer coefficient indicates if the extra surface is covered by scales and gives important indications for cleaning decision and chemical treatments efficiency.

2.2.3 Scaling quantity

During the last inspection and sampling campaign on the geothermal plant surface facilities, scales have been sampled from different locations, notably in water cups and on the tubular plate of some heat exchangers. Weight and sampling surface are measured respectively in grams and square centimeters to assess and compare the scaling deposition rate in contact with the steel, for a same volume of circulated brine.

2.2.4 Scaling chemistry

The main elements are analyzed with X-Ray Fluorescence, as Pb, As, Sb, Cu, Si, Fe and are expressed in weight percentage. A deep chemical elementary analysis is performed after total digestion by Inductively Coupled Plasma Spectrometry (ICP-MS): Na, Ca, K, Fe, Sr, Mn, As, Zn, Ba, Si, S, Cu, Ti, Hg, Pb, Sb, Cd, and Th, expressed in mg/kg. Radionuclide elements as ^{226}Ra and ^{210}Pb are analyzed by gamma spectrometry, expressed in Bq/g. All these analyses are done with an external and specialized laboratory.

2.2.5 Scaling radioactivity

Due to the natural content of radionuclides in the geothermal brine and the possibility that they can be trapped in the scales in the surface installations, some radioactivity measurements are required on-site before inspection, sampling and cleaning of the surface facilities. Two devices are used for this purpose: an APVL to monitor the doserate, which measures a dose of radiation received by a body per unit of time and a Saphymo with a sensor to count nuclear disintegration per second (Cuenot et al., 2015). The doserate is expressed in $\mu Sv/h$. The maximum annual cumulative doserate admissible for public is 1 mSv. The activity is expressed in disintegration per second.

2.2.6. Corrosion rate

A Linear Polarization Resistance sensor is installed on the reinjection line to monitor the corrosion rate before and after corrosion inhibitor injection start. In addition, stainless steel corrosion holder with isolated carbon steel coupons are installed close the LPR sensor to compare corrosion rate values. Corrosion rate on coupons are assessed following the weight loss and exposure time and expressed in mm/year (ASTM standard G1-90).

2.2.7. Pitting and localized corrosion monitoring in heat exchangers

About 10% of the tubes of the heat exchangers were inspected have been characterized by Eddy-current testing (ECT) before the plant start-up in 2015. This nondestructive testing method, using electromagnetic induction on conducting materials, can identify cracks and pits of corrosion, material thickness, coating and scaling thickness. Detection limit of ECT method is about 10% of tube thickness. Tubes inspected initially are going to be inspected during operation of the geothermal plant, every 3 to 4 years with ECT methods. Results during operation will be compared to the initial status for corrosion and scaling monitoring. Figure 5 presents a picture of the tool used for Eddy-current testing method and a draft locating inspected tubes before operation.

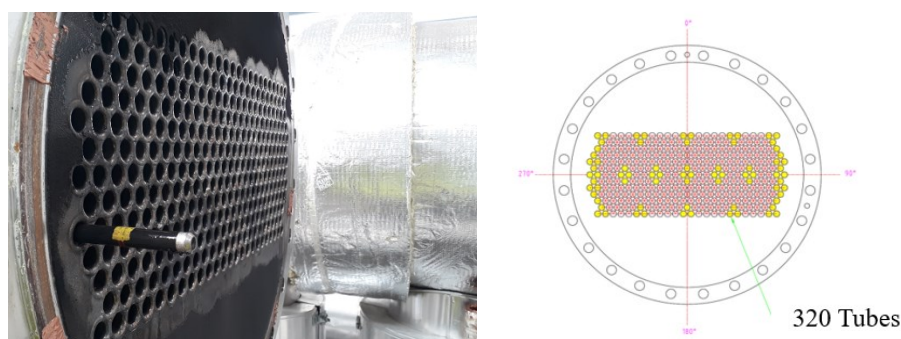


Figure 5: View of the tool used for Eddy-current testing method and a draft locating inspected tubes before operation.

3. RESULTS

3.1 Inhibitors selection and characteristics

3.1.1 Compatibility test

When the temperature was increased to 95 °C and then to 170 °C notable precipitation occurred (Figure 6). Some thin particles were observed and analyzed. They mainly consisted of iron and chloride derived from a possible corrosive reaction between the brine and the pressure vessel during the test. No other deposit has been formed. It was concluded that the corrosion inhibitor and geothermal brine at high temperature at normal dosage and above was compatible.







	Blank	Corrosion inhibitor 10 ppm	Corrosion inhibitor 100 ppm
After heating to 50 °C	brine was clear, no precipitations		
After heating to 95 °C			
After heating to 170 °C			

Figure 6: Compatibility tests with the chemical corrosion inhibitor

3.1.2 Efficiency test

From lab experiments, scaling inhibitor 1 inhibits barium sulfate formation and reduces particle size of forming crystal. Scaling inhibitor 2, as scaling inhibitor 1, inhibits barium sulfate formation. Compared to blank test, it inhibits crystal growth for three to four hours and has a dispersing effect proven by the turbidity measurements: the turbidity of the solution is more homogeneous thus having a stronger impact on light dispersion.

3.2 On-site trial performance indicators

3.2.1 Pressure drops in the surface installation

Figure 7 presents monthly trend of pressure drop in the two sets of heat exchangers from the cleaning in March 2019 to July 2019. Pressure drops in the coldest set of heat exchangers are a little bit higher, about 50 mbar, than in the hotter set because of higher

viscosity at lower temperature. If pressure drops remain constant in the hottest set of heat exchangers since the last cleaning, a slight increase of pressure drop at high flowrate can be observed in the coldest set after 4 months of operation. Pressure drop monitoring indicates in a first approach that the chemical treatment applied is working very efficiently in the hottest set of heat exchangers, but scales are still under formation at lower temperature.

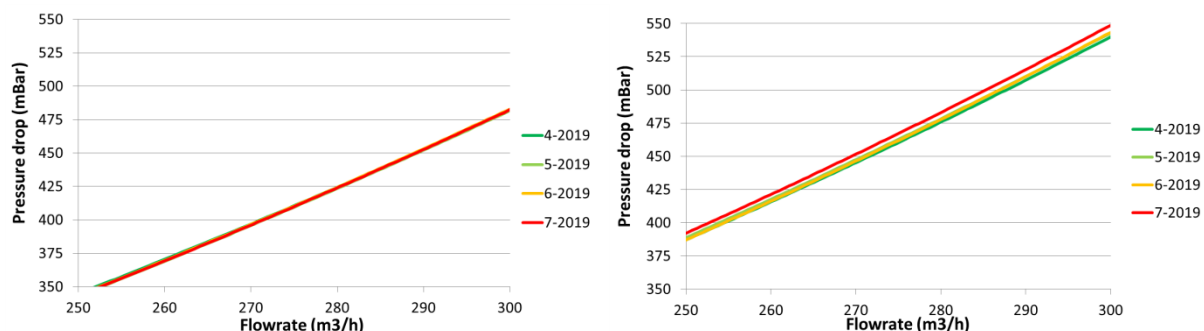


Figure 7: Monthly trend of pressure drop in the hottest (left) and in the coldest (right) set of heat exchangers since the last cleaning in March 2019 (4: April, 5: May, 6: June, 7: July)

3.2.2 Heat Transfer coefficient

Figure 8 presents the evolution of the heat transfer coefficient in the hottest (red) and in the coldest (orange) set of heat exchangers since the last cleaning in March 2019. A decrease of nearly 15%, from 2800 W/m².K to 2400 W/m².K, is observable in the coldest set of heat exchangers. Moreover, a slight decrease of the heat transfer coefficient, lower than 50 W/m².K, is measurable in the hottest set after 4 months of operation contrary to pressure drop monitoring. Heat transfer coefficient monitoring confirms that chemical treatment applied are working very efficiently in the hottest set of heat exchangers, but scales are still under formation at lower temperature. Both are starting to slightly decrease from early May, approximately one and half months after cleaning of the Heat exchangers.

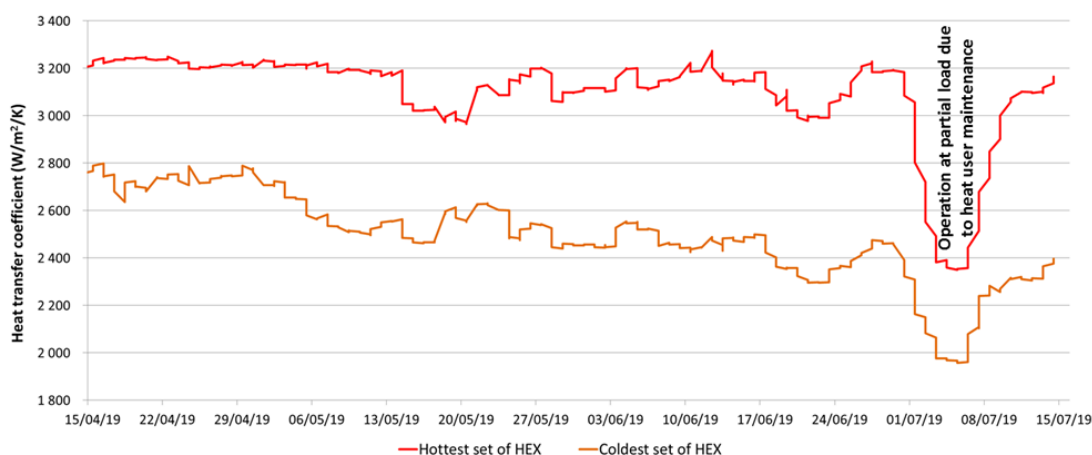


Figure 8: Evolution of the heat coefficient transfer in the hottest (red) and in the coldest (orange) set of heat exchangers since the last cleaning in March 2019

3.2.3 Scaling quantity

The inspection of the coldest heat exchanger water box is given by year in Figure 9. A strong reduction of scales is visible from year to year thanks to the applied chemical treatment. However, corrosion processes are also visible. Indeed a loss of steel has been noticed due to corrosion erosion and under deposit corrosion. On one hand, strong reduction in terms of scales quantity is appreciable, but on the other hand the protecting effect of these scales regarding corrosion processes decreases. The last inspection gives an operational feedback on the need to identify a better filming agent and probably to optimize the dosage for this product to improve the carbon steel surface facilities protection.

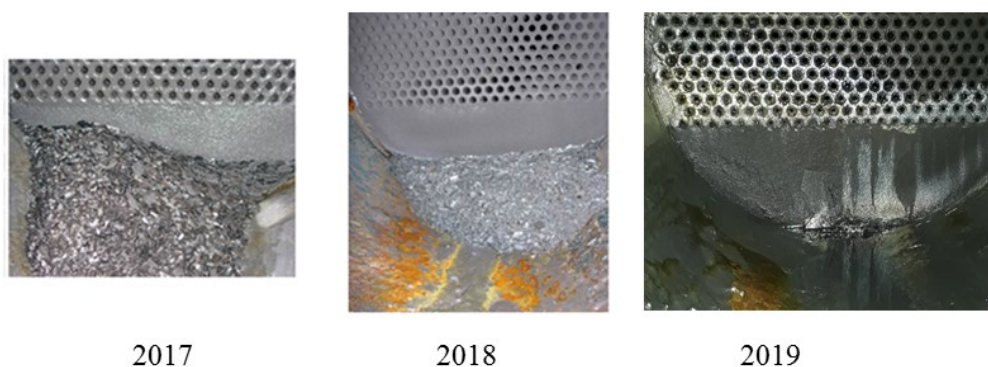


Figure 9: Observations of water box in the last heat exchanger

3.2.4 Scaling chemistry

The elementary composition of the scales varies with the temperature (Figure 10). Ca, Cu, Al, Sr, Ba and Ti concentration decrease with decreasing temperature (higher content at 146°C – heat exchanger 4), while Pb, Sb and As concentrations increase with lower temperature (higher content at 82°C – heat exchanger 12). Some elements, and in particular Mn, Fe and As, present the highest concentrations at intermediate temperature (heat exchanger 8 – 110°C). Those observations are consistent with the chemical composition of the scales formed at Rittershoffen during the previous exploitation year (Figure 11) and with the geochemical trends observed in the scales of Rittershoffen and Soultz-sous-Forêts plant in 2017 by Mouchot et al. (2018) (Figure 12).

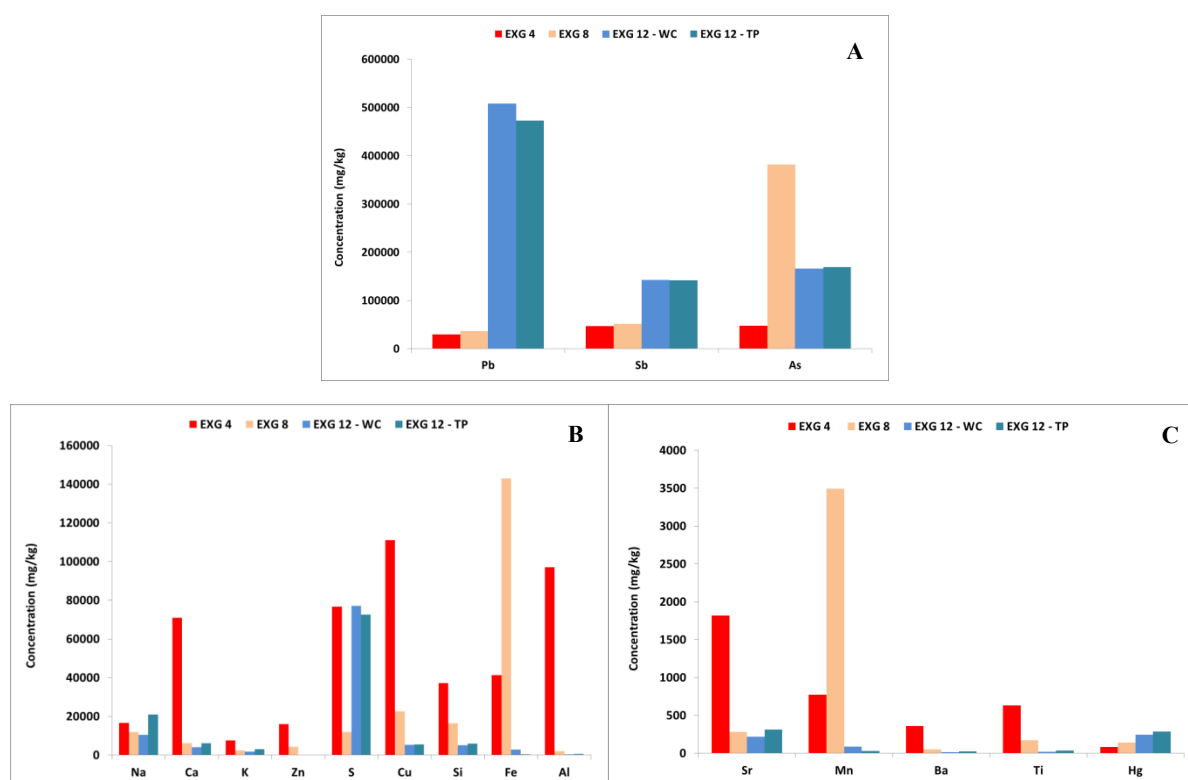


Figure 10: The composition of the scales collected in the heat exchangers (4, 8 and 12) of Rittershoffen during the inspection of 2019. WC: Water Cup; TP: Tubular Plate

The variation in the elementary composition of the scale clearly indicates the influence of thermodynamic effects, where pressure and mostly temperature variation induces elementary oversaturation, and thus mineral deposition (Scheiber et al, 2012). The data suggest that minerals such as CaCO_3 , but also Sr-BaSO_4 , which were typically observed in the geothermal installation scales of the Upper Rhine Graben (Scheiber et al., 2012 and 2015) mostly form at high temperature. On the opposite, Pb, As and Sb appear to be correlated to cold temperature. Those elements may be present in the scale on the form of metal sulfide, such as PbS , or of native metal. Metallic sulfides are likely the results of thermodynamic effects, while native metal deposition is mainly due to electrochemical corrosion processes (Scheiber et al, 2012, 2015). The lower concentration of sulfides and the presence of high Fe, Mn and As at intermediary temperatures may suggest the precipitation of As not as sulfides, but rather as native metal or associated with Fe or Mn.

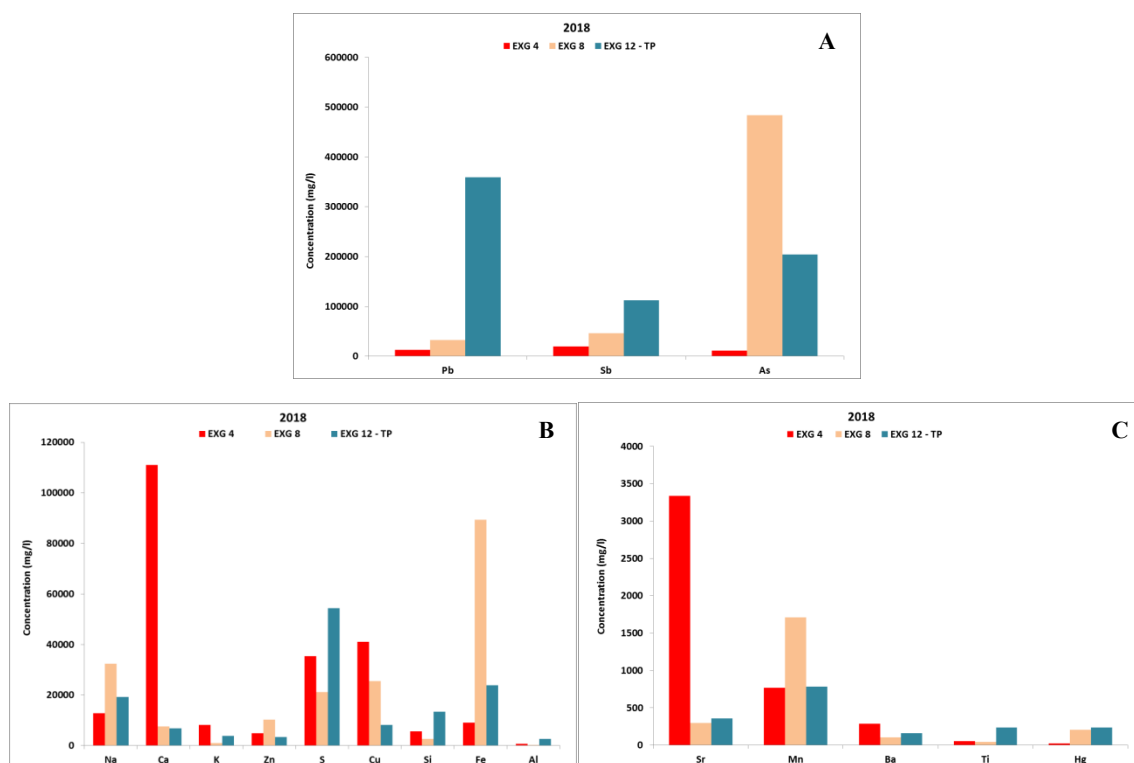


Figure 11: The composition of the scales collected in the heat exchangers (4, 8 and 12) of Rittershoffen during the inspection of 2018. TP: Tubular Plate.

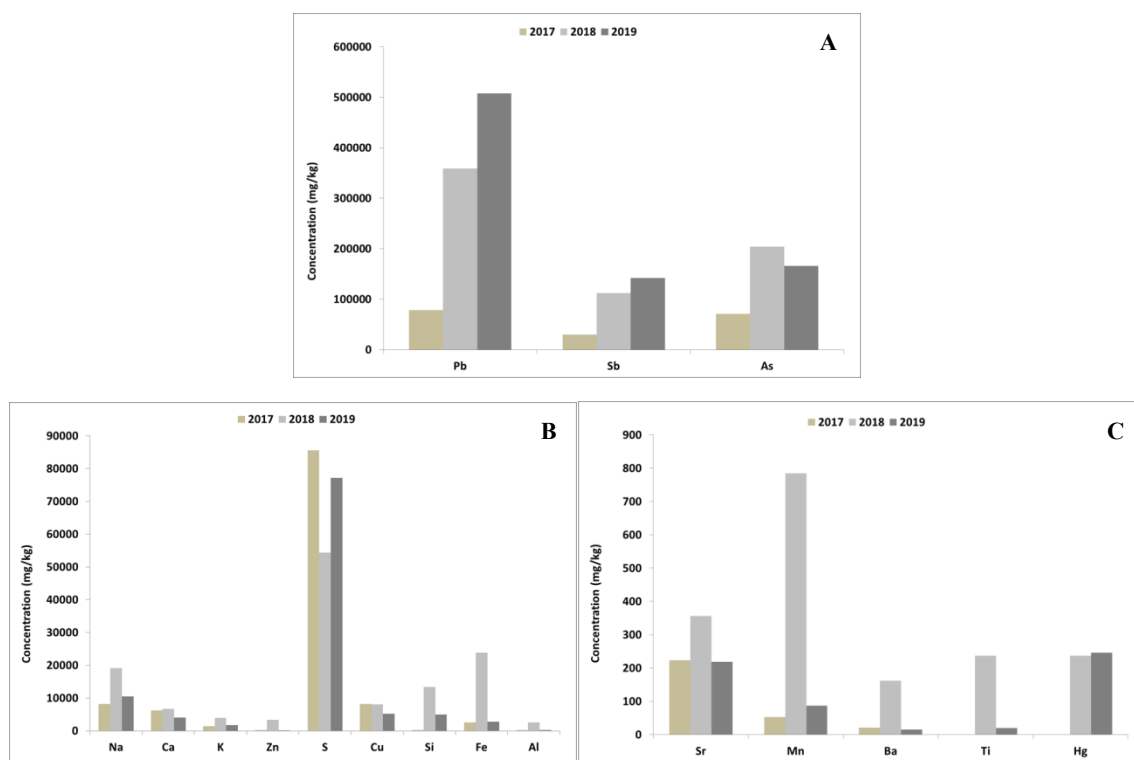


Figure 12: The composition of the scales collected in the heat exchanger 12 of Rittershoffen during the inspection of 2017, 2018 and 2019.

3.2.5 Scaling radioactivity

Figure 13 gives the annual evolution of radioactivity measurement before sampling and cleaning procedures on in the carbon steel water boxes. For the three observation years, the activity and dose rate increase with the decrease of the temperatures in the heat exchangers. When correlating the evolution of the scales radioactivity with their chemical composition, it appears that the highest activity and dose rate values are related to Pb enriched scales. While for 2017 and 2018 a minor increasing in radioactivity was

observed for intermediate temperature (114°C), in 2019 only the last heat exchanger (80°C) presents scale with significant radioactivity values. This observation confirms the efficiency of the chemical treatment.

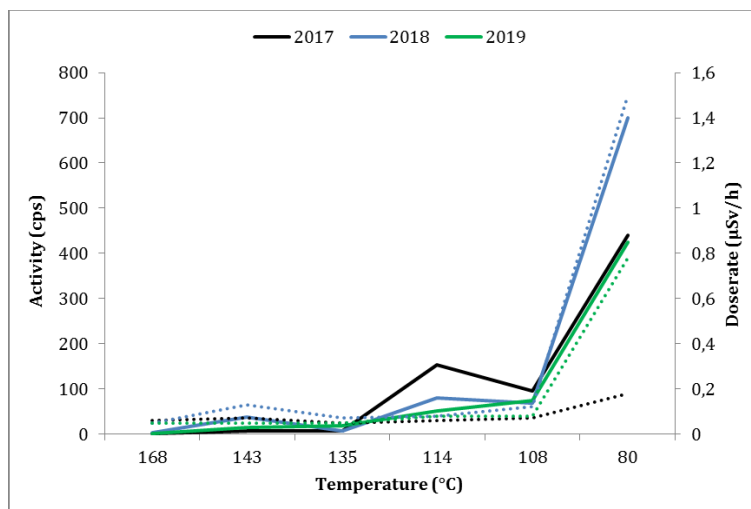


Figure 13: Evolution with the temperature of the activity and the doserate of the scales collected in the heat exchangers of Rittershoffen during the inspection of 2017, 2018 and 2019. Solid line: activity; dashed line: doserate.

3.2.6 Corrosion rate

An LPR sensor has been installed in 2017 in the reinjection line to monitor the corrosion rate before and during corrosion inhibitor injection. The measurements are purely indicative due to some troubles occurred by scale deposition on the probes and micro-degassing that could disturb the monitoring. Nevertheless, on average the corrosion rate measured without corrosion inhibitor injection ranges between 0.01 to 0.5 mm/year. When corrosion inhibitor started to be injected into the geothermal fluid, the corrosion rate decreased to 0.005 mm/year on average. To complete this first corrosion monitoring, in 2018 coupon-holders have been installed into the reinjection line close to the LPR sensor. Carbon steel and stainless steels coupons have been installed to compare measurements between LPR sensor and on the coupons after few months and a year of exposure. Only the stainless steel coupon has been removed after 135 days without uniform neither localized corrosion. All other coupons have been detached from the coupons-holder, probably due to galvanic corrosion and erosion-corrosion processes into the line. In order to have better monitoring of corrosion rate in the installation, a skid, by-pass system has been connected to the reinjection line in autumn 2019. Coupons and the LPR sensor can be then exposed and inspected frequently to assess corrosion rate monitoring techniques and chemical treatment efficiency, without disturbing the geothermal heat production.

3.2.6 Pitting and localized corrosion in heat exchangers monitoring

All the tubes initially inspected before the plant start-up have been inspected with ECT method in March 2019 after nearly three years of operation. ECT investigation didn't detect any indication above the detection limit of cracks and pits of corrosion in all inspected tubes after nearly 3 years of operation. These results confirmed that 1.4410 (UNS S32750 – F53 – 2507) stainless steel is a suitable material for the design of heat exchangers in Upper Rhine Graben brine conditions and temperature.

4. CONCLUSIONS & PERSPECTIVES

The deep geothermal plant at Rittershoffen is producing industrial heat since 2016 under commercial conditions. Since the commissioning of the plant chemical treatments are applied to control scaling and corrosion issues thanks to the operational feedbacks from other geothermal plants in the Upper Rhine Graben. Thanks to this know-how, various combinations of products have been tested for few months. A methodology has been developed to better assess the efficiency of these chemicals and in order to optimize the treatment regarding environmental footprint, costs, and efficiency on the energy production. In partnership with one water treatment company, a combination of two chemicals, a Stress Tolerant Polymer with dispersive properties, and a filming amine acting as scaling and corrosion inhibitors respectively, has been tested for more than a year. This combination gives good results compared to previous tests in terms of: (i) reduction of total scaling amount and (ii) radioactivity in the surface installations. These first conclusions can still be improved by continuing the monitoring for several more months and assess the long-term behavior of each parameter.

Surface installation inspection regarding corrosion issues highlights erosion-corrosion and localized corrosion processes in the carbon steel water boxes. ECT monitoring confirmed full integrity of Super-Duplex alloy used for the heat exchangers tubes after three years of operation. Thanks to the key-performance indicators identified, efforts would be put on chemical reaction time, kinetics of scales formation, as well as deposition and dosage optimization. A new trial considering Stress Tolerant Polymer scaling inhibitor and a more efficient filming agent is planned within the following months. Efficiency of the new treatment on corrosion and also scaling could be better assessed thanks to the installation of a dedicated skid at reinjection line by-pass system. Within the following months, efforts will be put on scaling formation mechanisms comprehension and kinetics. A periodic-monitoring is then designed to assess action on chemicals with time and their repeatability.

Acknowledgements

The authors acknowledge ECOGI for the Rittershoffen geothermal site access and the involved SUEZ - Water Technologies & Solutions team for its technical support. This work was done in the framework of the EGS Alsace project cofunded by ADEME and Electricité de Strasbourg. This work is partly cofunded by the Geothermica – ZoDrEx project supported by the European Unions’ Horizon 2020 research and innovation program under grant agreement N°731 117. The ZoDrEx project is also supported at the French level by the “Investments for the Future” managed by ADEME.

REFERENCES

- ASTM standard practice G1-90: Standard practice for preparing, cleaning, and evaluating Corrosion test Specimens, Annual Book of Standards Vol. 03.02 American Society for Testing and Materials, s.35-41
- Baticci F., Genter A., Huttenloch P., Zorn R., 2010. Corrosion and Scaling Detection in the Soultz EGS Power Plant, Upper Rhine Graben, France. Proceedings World Geothermal Congress 2010. Bali Indonesia, 25-29 April 2010 11pp
- Baujard C., Genter A., Maurer V., Dalmais E., Graff J-J., 2015. ECOGI, a new deep EGS project in Alsace, Rhine Graben, France. In: World Geothermal Congress, Melbourne, Australia 19-25 April 2015.
- Baujard C., Genter A., Dalmais E., Maurer V., Hehn R., Rosillette R., Vidal J., Schmittbuhl J., 2017. Hydrothermal characterization of wells GRT-1 and GRT-2 in Rittershoffen, France: Implications on the understanding of natural flow systems in the Rhine Graben, *Geothermics*, 65, 255-268.
- Cuenot, N., Scheiber, J., Moeckes, W., Guéry, B., Bruzac, S., Sontot, O., Meneust, P., Maquet, J., Orsat, J. and Vidal, J.: Evolution of natural radioactivity within the Soultz geothermal installation, Proceedings of the European Geothermal Congress 2013, Pisa, Italy, (2013).
- Cuenot, N., Scheiber, J., Moeckes, W., and Genter, A.: Evolution of the natural radioactivity on the Soultz-sous-Forêts EGS power plant and implication for radiation protection, Proceedings, World Geothermal Congress 2015, Melbourne, Australia, (2015), 12 pp.
- Haas-Nüesch R., Heberling F., Schild D., Rothe J., Dardenne K., Jähnichen S., Eiche E., Marquart C., Metz V., Schäfer T., 2018. Mineralogical characterization of scalings formed in geothermal sites in the Upper Rhine Graben before and after the application of sulfate inhibitors. *Geothermics* 71, 264-273.
- Jähnichen S., Degering D., Seibt A., Scheiber J., Mouchot J., Buse C., Heberling F., 2019. Inhibition of scales in geothermal plants in Upper Rhine Graben: Monitoring of fluids and scales. European Geothermal Conference 2019, Den Haag, Netherland, 11-14 June 2019.
- Mouchot J., Cuenot N., Bosia C., Genter A., Seibel O., Ravier G., Scheiber J.: First year of operation from EGS geothermal plants in Alsace, France: scaling issues, Stanford Geothermal Workshop 2018, Stanford, California, USA, 12-14 February 2018.
- Mouchot J., Scheiber J., Florencio J., Seibt A., Jähnichen S., 2019. Scale and Corrosion control program, Example of two geothermal plants in Operation in the Upper Rhine Graben, European Geothermal Conference 2019, Den Haag, Netherland, 11-14 June 2019.
- Mouchot, J., Ravier, G., Seibel, O., Pratiwi, A.: Deep Geothermal Plants Operation in Upper Rhine Graben: Lessons Learned, European Geothermal Congress 2019, The Hague, Netherlands (2019).
- Mundhenk N., Huttenloch P., Sanjuan B., Kohl T., Steger H., Zorn R., 2013. Corrosion and scaling as interrelated phenomena in an operating geothermal power plant. *Corrosion Science* 70, 17-28 pp
- Ravier G., Huttenloch P., Scheiber J., Perrot V., Sioly J-L., 2016. Design, manufacturing and commissioning of the ECOGI’s heat exchangers at Ritterhsoffen (France): a case study. European Geothermal Conference 2016, Strasbourg, France, 19-24 Sept. 2016.
- Ravier G., Harders V., El Aoud M., 2017. Rittershoffen geothermal heat plant. First geothermal heat plant for industrial uses worldwide, *EuroHeat&Power*, 3/2017 (9973).
- Sanjuan B., Millot R., Innocent C., Dezayes C., Scheiber J., Brach M., 2016. Major geochemical characteristics of geothermal brines from the Upper Rhine Graben granitic basement with constraints on temperature and circulation, *Chemical Geology*, 428, 27-47
- Scheiber J., Nitschke F., Seibt A., and Genter A., 2012. Geochemical and mineralogical monitoring of the geothermal power plant in Soultz-sous-Forêts (France). Proceedings, Thirty-Seventh Workshop on Geothermal Reservoir Engineering. SGP-TR-194.
- Scheiber J., Ravier G., Cuenot N., Genter A.: In-Situ Material and Corrosion Studies at Soultz-sous-Forêts (France) EGS Site (2015). Proceedings World Geothermal Congress, Melbourne, Australia.
- Scheiber J., Seibt A., Jähnichen S., Degering D., Mouchot J., 2019. Combined Application for Scale and Corrosion Mitigation: lessons learned. European Geothermal Conference 2019, Den Haag, Netherland, 11-14 June 2019.