Scale and Corrosion control program, Example of two geothermal plants in Operation in the Upper Rhine Graben

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ABSTRACT

Geothermal plants at the Upper Rhine graben produce electricity by exploiting highly saline brines. The installations of those industrial sites are known to suffer from very particular scale, such as barium sulphate ($BaSO_4$), lead sulphide (PbS) and metal rich scales which contain As, Pb and Sb but also from uniform and localized corrosion. While it has been shown that thermodynamic conditions are responsible for BaSO4 scale formation hydraulic conditions trigger localized corrosion. It has been believed that, since no sulphide or SRB (sulphur reduction bacteria) has ever been measured on the brine from this area, sulphide concentration is either below detection limit or scale formation and uniform corrosion were somehow related by way of an electrochemical mechanism.

In the last four years, a group of scientists and engineers have been cooperating on solving those problems in the Soultz-sous-Forêts (France) geothermal plant and other geothermal plants of the Upper Rhine Graben (URG). For this purpose, chemical treatments as scaling and corrosion inhibitors, were applied on-site and monitored for efficiency assessment. In particular, a joint monitoring between plant operators, analytic partners and chemicals manufacturers allowed to chemically and quantitatively characterize the formed scales during specific trials corrosion rate is measured with on-line sensor and in situ coupons.

The combined application of best-in-class corrosion inhibitors and scale inhibitors have sorted out in a synergistic way not only barium sulphate and corrosion mitigation but also significant mass reduction of the exotic metal-rich scales.

1. INTRODUCTION

Geothermal potential has been identified in the Upper Rhine Graben since decades with research on the Enhanced Geothermal System pilot plant at Soultz-sous-Forêts, at 50km to the North of Strasbourg, France. Geothermal fluid is naturally circulating at a temperature higher than 150°C in a fractured granite basement. Thanks to this high European research, geothermal projects have been developed from either side of the Rhine River in the URG in France and Germany, producing geothermal fluid for heat and electricity generation (Vidal et Genter, 2018).

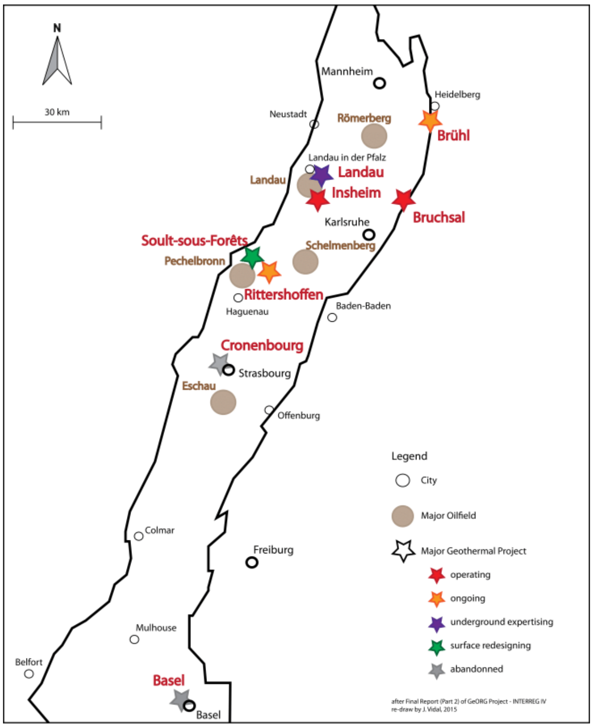
1.1 Soultz-sous-Forêts geothermal site

The Soultz-sous-Forêts geothermal project started in 1987, and is the cradle of the geothermal energy European research in granitic and fractured systems. After almost 30 years of research, the geothermal site is exploiting the fractured basement at 5 km depth, under industrial conditions, for the EEIG Heat Mining (Figure 1). The installed gross capacity of the plant is about 1.7 MW_e. The actual geothermal system is made up of three wells: one production well named GPK2 and two injection wells named GPK3 and GPK4. GPK1 is an old reinjection well, and EPS1 is an exploration well. The geothermal brine is coming at the wellhead at 150°C/23 bars, reaching the surface with a flow rate of 30 kg/s provided by a production Line Shaft Pump (Baujard et al., 2018). The geothermal brine is then flowing through a system of six consecutive tubular heat exchangers supplying heat to a secondary loop, i.e. Organic Ranking Cycle, in order to produce electricity. The geothermal brine is then fully reinjected at around 70°C, and the volume of reinjected brine is shared between two wells, one third in GPK4 and two third in GPK3 without reinjection pumps. The reinjection temperature is linked to the conversion process. The geothermal plant has been successfully producing electricity since September 2016 under industrial conditions (Genter et al., 2018).

Figure 1: Soultz-sous-Forêts geothermal site

1.2 Geothermal sites in the Upper Rhine Graben (URG)

Other geothermal project in the Upper Rhine Graben (URG) operate at very similar conditions with production temperatures up to 165°C and injection temperatures down to 60°C. In this area it is crucial to keep the brine pressurized in order to mitigate calcium carbonate scales. Therefore, production pressures above the Gas Breakout are applied.



after Final Report (Part 2) of GeORG Project - INTERREG IV
re-draw by J. Vidal, 2015

Figure 2: Geothermal Plants in the URG. Vidal et al., 2015

1.3 Geochemical Context

The salinity is about 100g/L, main components are Na-Ca-Cl (Figure 3). The brine has a very complex composition and contains heavy metals in the µg to mg range which participate at scale formation. The brines at other geothermal plants in the URG display very similar composition also the salt concentration varies from 97 to 125 g/L from the western to the eastern rim of the URG (Sanjuan et al. 2016).

The geothermal fluid is enriched in dissolved gases with a gas liquid ratio of 1consisting mainly of CO_2 with >90 Vol.%.

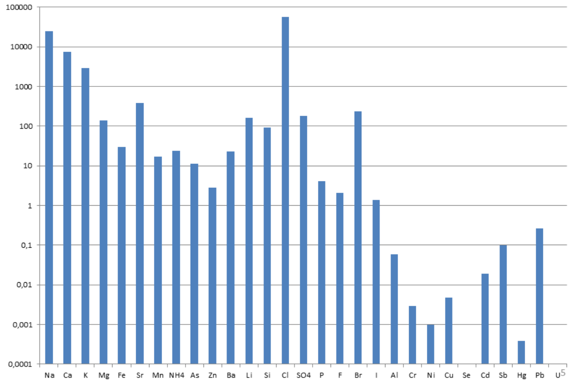


Figure 3: Chemical composition of the Soultz brine produced at GPK2 (September 2018)

Physical parameters of the brine are given in Table 1. Typical brines of the URG are slightly acidic with pH values close to 5, with a high conductivity due to the high salinity and naturally anoxic conditions with measured negative Eh values (Ag/AgCl).

Table 1: Physical parameters of the Soultz production brine from GPK2.

Parameters	Soultz
TDS (g/L)	99.6
GLR (Nm^3/m^3)	1.03
Gas (mass %)	0.17
pH	5.3
Electrical Conductivity (mS/cm)	110
REDOX potential (mV) (Ag/AgCl)	-43+/-5

1.4 Scale types and scale formation

In this geochemical context, barium/strontium sulphate is precipitating during the process of thermal transfer in the heat exchangers (Scheiber et al., 2012). Secondary precipitates are metal-rich minerals, where lead, arsenic and antimony are trapped. The metal-rich deposits In current operational conditions, the heat exchangers have to be cleaned minimum one time per year but in some cases once per trimester inducing high maintenance cost, loss of energy production and waste management issues. To manage these precipitations, plant operators of French and German geothermal sites have been in contact with water treatment companies in the framework of the French-German cooperation of power plant operators and in the framework of German research project SUBITO (FZK 0325790) to identify appropriate chemical treatment and strategy to reduce or inhibit these deposits for a sustainable energy production respectful of health and environment.

1.5 Corrosion

Piping and valves of the surface installations are mainly made of carbon steel whereas the tubular heat exchangers consist basically of stainless steel. Circulation of geothermal fluid, with a high chloride content and enriched in CO_2 induces generalized and localized corrosion. Researches on corrosion have highlighted a generalized corrosion rate of 0.15 - 0.22 mm/year at 80°C assessed by on-site trials during coupons exposure to the Soultz geothermal brine and by laboratory experiments with original Soultz brine and artificial brine (Baticci et al., 2010, Mundhenk et al., 2013).

Despite the fact that general corrosion is very low localized corrosion creates real issues for power plant operators. Localized corrosion occurs mainly at the return line and results in unscheduled shut-down times of the geothermal plants, therefore loss of revenues and additional costs for maintenance and disposal.

Based on the low general corrosion the application of a corrosion inhibitor was never considered in former times. The increasing incidents of localized corrosion and the observation that metal-rich scales are predominantly present in the areas of corrosion lead to the conclusion that corrosion and scale formation of metal-rich scales are interrelated. In conclusion corrosion inhibitors could have the potential to inhibit at least partwise the formation of scales which are rich in Pb, As and Sb.

2. CASE STUDY: SCALE AND CORROSION CONTROL PROGRAM AT SOULTZ-SOUS-FORÊTS

A combined scale and corrosion control program has been designed in cooperation with one service company to protect geothermal plants of the URG and to be able to evaluate efficiency of different applied chemical treatments. Scaling and corrosion inhibitors have been selected first on safety data sheets, at lab-scale and have been tested on-site. A monitoring campaign has been designed to follow action of inhibitors and response of surface and subsurface facilities at short and mid-terms.

2.1 Inhibitors selection and characteristics

The term scale inhibitor is widely used for chemistries which reduce scale deposition in equipment processing water streams, although the name antiscalant is more appropriate. Scale deposition reduction can be achieved with chemistries that truly inhibit the formation of the mineral crystal, properly named scale inhibitors; but also with chemistries that have the ability to disperse mineral crystals once formed, avoiding its deposition, hence called dispersants. Antiscalant chemistries can be inhibitors or dispersants, or mixtures of both. Each type of mineral scale may have a type of antiscalant which is more suitable for proper reduction / control. While scale inhibitors are very powerful to control barium sulphate scale, the metal sulphides are known to be better controlled with dispersants. In this particular case two types of antiscalant products were recommended. Antiscalant 1 is a mixture of inhibitor and dispersant, while Antiscalant 2 is purely a dispersant.

Injection of a filming corrosion inhibitor is recommended to reduce both, general and localized corrosion in the surface installations. Two different corrosion inhibitors have been recommended for two different plants at the URG: Filmer 1, a very powerful formulation widely used in European geothermal plants; and Filmer 2 which is an innovative formulation with better environmental profile.

In lab, compatibility test by dosing the product in the geothermal brine has been performed at 80°C. Changes in mineral precipitation/aggregation quantity and morphology reveal incompatibility issues (Figure 4).

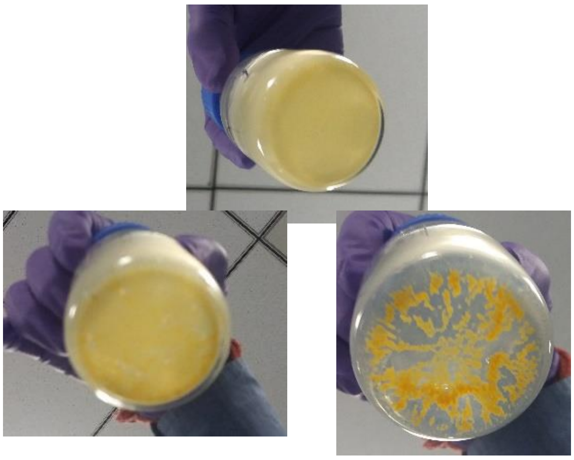


Figure 4: Brine Compatibility Test: 80C, 3h and 10ppm chemical dosage. Blank (top), compatible product (left) and non-compatible (right) products with GPK2 brine.

Different combinations have been tested and described in Table 2. It is recommended to inject products in the ppm range in the surface facilities using an injection quill and supplying product with a dosing pump.

Table 2: Inhibitors Trials at Soultz–sous-Forêts and another geothermal power plant in the URG.

Site	Antiscalant #1	Antiscalant #2	Filmer #1	Filmer #2
Soultz Test 1	X			
Soultz Test 2	X		X	
Soultz Test 3			X	
Soultz Test 4		X	X	
URG site Test 1				X

Filmer 2 was injected at another geothermal power plant in the URG in combination with a barium sulphate antiscalant which was already in use at this geothermal site.

2.2 Antiscalant efficiency assessment methodology – lab tests and on-site application

Before any application on-field, selected chemical treatment efficiency is assessed at lab scale. Few ppms of product are injected in an overdosed solution in barium sulphate. Any crystal growth is observed at different time slots, using a Scanning Electronic Microscope. Blank and treated solutions are then compared, in terms of amount of particles. Efficiency of chemical treatment can be assessed in percentage.

Once the chemical treatment is injected on-site, some indicators help plant operators and water treatment companies to detect good response of surface installations. Chemical treatment is injected right after the production wellhead, going through and protecting production line filters, heat exchangers, reinjection line and filters against scale deposition. All the facilities are notably equipped with pressure sensors, and detect any pressure changes (Mouchot et al., 2019). When needed, these facilities are then opened for cleaning. Scale sampling can be performed and chemical analysis as well. Main elements are analyzed 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. Structures of scale and chemical element distribution provide feedbacks on the efficiency of applied chemical treatments.

On the reinjection line, a by-pass system enables to monitor inhibitor efficiency on a carbon steel pipe without stopping production (Figure 5). Periodically, this monitoring pipe is opened for inspection and scale sampling. Indeed, mass samples are put in context to brine volume circulated between two dates. These ratios are then analysed in regard to applied chemical treatment.

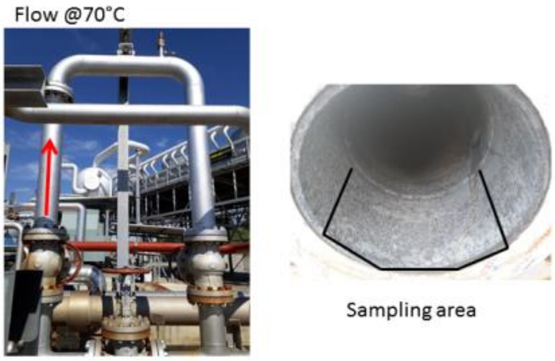


Figure 5: Monitoring Pipe, Soultz site.

For corrosion monitoring, the cooperating water treatment company proposes to install a device in by-pass at Soultz-sous-Forêts geothermal site (Figure 6**)**. Part of flow is deviated to the monitoring device, going through LPR sensor to measure on-line corrosion rate in mpy. To ensure that the fluid circulates at a speed that replicates the shear stress in the most critical location of the plant a circulation pump is used. The same equipment has coupons-holders and coupons are installed for a month at least. Corrosion rate is then measured by weight losses (ASTM standard). Geothermal fluid is reinjected in the main pipe. Two trials have been applied: a first one for three months on production line, and a second one for almost a year on the reinjection line.

Figure 6: Corrosion monitoring device, 3DTRASAR for Geothermal.

3. RESULTS

From July 2017 to November 2018, three tests have been applied at Soultz-sous-Forêts geothermal site, associating different antiscalants and a corrosion inhibitor. Scalings have been sampled along the monitoring pipe periodically and results are presented in terms of quantity and chemistry evolution of scale deposits under different treatments.

Additionally, the environmental friendly Filmer 2 has been injected for corrosion mitigation in association with a barium sulphate inhibitor from July to November 2018 at another power plant in the URG. The responsible mining and water authorities limited the testing time of the product to four months. The approval for continuous injection of scale and corrosion inhibitors at this plant, are expected to be granted after successful trial of the product combination.

3.1 Scaling control program results

From July 2017 to September 2017, Antiscalant 1 has been injected at Soultz-sous-Forêts geothermal site. Observation from the monitoring pipe in terms of quantity and structure of scaling are given in Figure 7 (up). Starting October 2017, corrosion inhibitor has been injected inducing a change in terms of quantity of deposit (Figure 7, down).

Figure 7: Monitoring pipe inspection, after Test 1 (up) and Test 2 (down) at Soultz -sous-Forêts plant.

During the injection of Filmer 2 in combination with the barium sulfate antiscalant very thin scales deposited at the piping wall. Total scale mass was significantly lower with ~ 60-70 mass % than during the application of barium sulphate without the filmer (Figure 8, Figure 9).

Figure 8: Scale deposition within the monitoring pipe the other geothermal site.

Chemical analyses of deposits collected in the monitoring pipe at Soultz are given in **Erreur ! Source du renvoi introuvable.**, following different tests mentioned in Table 2.

Results of Test 1, consisting in an antiscalant injection for barium sulphate inhibition highlight a high content in Pb, As, Fe, Sb and a low content in Ba, Sr (data from the 01/09/2017 -24/10/2017). These results are on line with a good efficiency of chemical treatment for barium sulphate inhibition, and an ongoing growth of metal-rich scales, with a ratio of 0.035mg/m^3 of scale formation in 56 days.

During Test 2, consisting in injection of both antiscalant and filming agents, two dosages have been tested. At the first period, a corrosion inhibitor has been injected during 34 days at the original dosage, producing scale formation of 0.015mg/m^3. Due to good efficiency in terms of scales mass reduction (57%), dosage has been reduced of 50%. In terms of mass reduction, half of the corrosion inhibitor dosage seems to be more efficient. Repeatability tests are required to better understand these first interesting results.

Figure 9 highlights notably the test 3 results, after 70 days of geothermal fluid circulation, very few scale deposit has been observed. The scales are enriched in Ba, Sr and Si. Pb, As, Fe and Sb contents are very low. These observations are confirming the action of corrosion inhibitor on metal-rich formation. Without antiscalant, an increase of (Ba, Sr)SO_4 is observed within a month.

A significant scale mass reduction (97%) has been observed after 92 days of exposure in the frame of Test 4 (antiscalant #2 and filmer, Table 2). With antiscalant injection, Ba content is low, but slightly higher than without corrosion inhibitor injection.

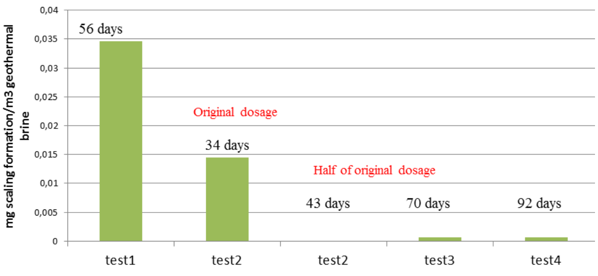


Figure 9: Monitoring pipe inspection, results of scales amount sampled after each test.

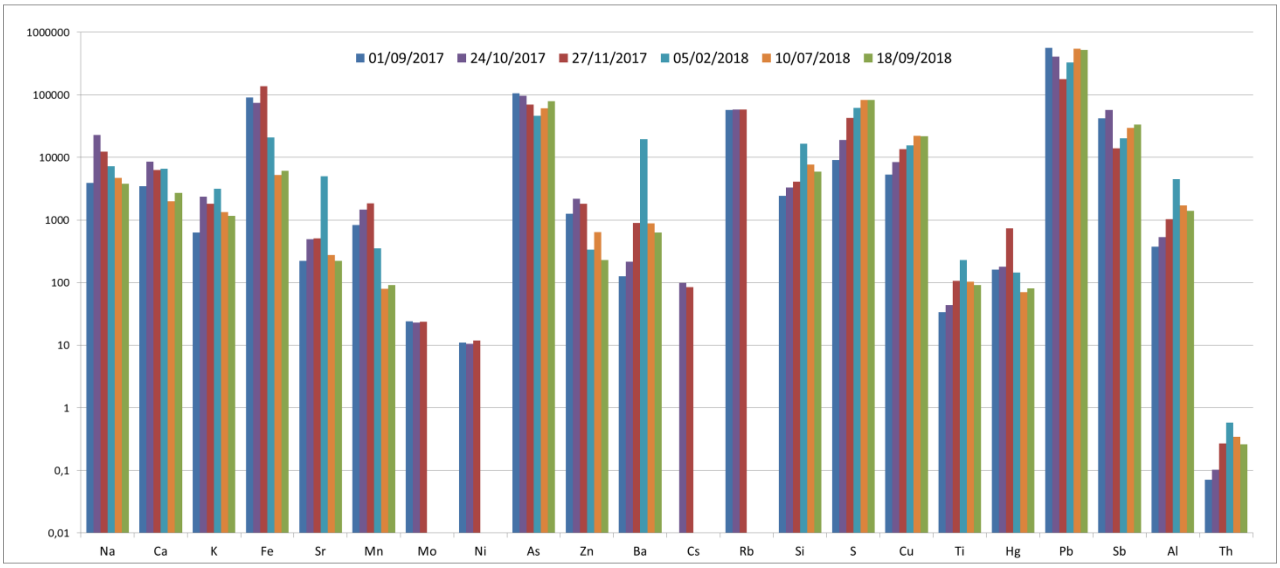


Figure 10: Chemical analyses of scale deposit samples from different inhibitor trials at Soultz-sous-Forêts plant.

After few weeks of Test 1 run at Soultz-sous-Forêts geothermal site, production filter has been unexpectedly clogged (Figure 11); deposit has been sampled for analyses. XRF and IR analyzes have been performed identifying high calcium and TOC concentration. This precipitate is resulting from interaction between a component of Antiscalant 1 and high calcium concentration of the GPK2 brine at high temperature.

Therefore, another Antiscalant agent has been selected for next the trial, named Test 4 (Table 2).

Figure 11: Production filter clogging: interaction between brine and scaling inhibitor at high temperature at Soultz-sous-Forêts plant.

3.2 Corrosion control program results

Since October 2017, corrosion inhibitor has been injected at Soultz-sous-Forêts geothermal plant. The 3DTrasar device has been installed few weeks before injection start to measure the corrosion rate as a baseline. A generalized corrosion rate of 5.5 mpy or 0.14mm/a has been measured with a LPR sensor before corrosion inhibitor injection start (Test 1). The corrosion rate fell in two hours when corrosion inhibitor started (Figure 12). Corrosion rate has been reduced of about 80%, and be quite stable after with an average of 0.58 mpy, equal to 0.014mm/a (Test 2).

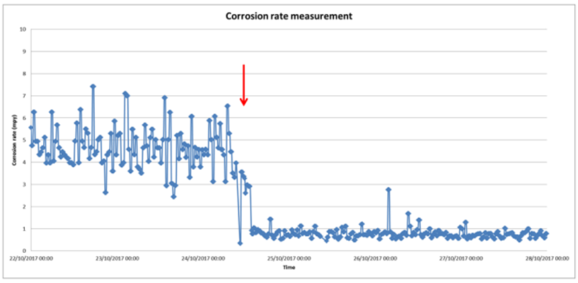


Figure 12: Corrosion rate decrease with corrosion inhibitor injection – Oct. 2017 Soultz site.

Then, corrosion rate has been measured on the reinjection line with a corrosion inhibitor injection only (Test 3). An average value of 0.21 mpy equals to 0.005 mm/a. During the injection of Antiscalant 2 and Filmer 1, an average corrosion rate of 0.37 mpy, equal to 0.009 mm/a, has been measured (Test 4). During each test, corrosion carbon steel coupons have been exposed to geothermal brine under operational conditions. Corrosion rate of carbon steel coupons are compared to LPR corrosion rate measurement per Trial in Table 3.

Table 3: Comparison between Corrosion rate assessment, by LPR sensor and carbon steel coupons.

Trials at Soultz	LPR Corrosion rate (mpy)	Coupons corrosion rate (ASTM - mpy)
TEST 1	5.57	2.3
TEST 2	0.58	0.7 -3
TEST 3	0.21	0.5
TEST 4	0.37	1.5

After 30 days minimum of exposition, corrosion coupons display generalized corrosion but also localized corrosion (Figure 13). This localized corrosion, not considered in the LPR sensor could explain the short variation.

After TEST 2

After TEST 4

Figure 13: Chemical analyses of mass samples from different inhibitor trials at Soultz-sous-Forêts plant

At the other URG plant the trial of the trial of the more environmental friendly corrosion inhibitor provided a dramatic reduction in the number of corrosion incidents that cause plant shutdown for maintenance as it can be seen in figure 14.

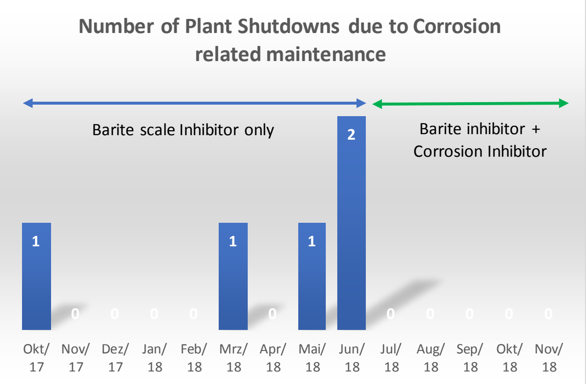


Figure 144: Reduction of corrosion related plant shutdowns during corrosion inhibitor trial at another URG geothermal plant.

4. CONCLUSIONS AND OUTLOOK

Geochemical context of brine exploited for heat and electricity production in the Upper Rhine Graben induces scaling and corrosion issues during operation. After few years of research on these processes, chemical treatments have been identified and tested on-site to protect surface facilities from corrosion and scaling issues, with the aims to (i) optimize the energy production, (ii) reduce operational maintenance period and (iii) manage waste from environment point of view. The on-site trials have provided many feedbacks on the scaling and corrosion control within these two years.

After chemical treatment selection at lab scale and under operational conditions to validate the high temperature compatibility between all products with the geothermal brine, products can be injected on the geothermal surface facilities. Thanks to monitoring methodology, good efficiency of products has been highlighted during these plural-monthly trials as listed after:

- Generalized corrosion rate decrease of 80% thanks to use of filmer agent acting as corrosion inhibitor on carbon steels;

- Significant – minimum of 60% scale mass reduction, with the combined use of antiscalant and filmer agent to prevent exotic scales formation.

The use of corrosion inhibitors on top of antiscalant in these plants located in the Upper Rhine Graben has clearly reduced the amount of scale deposition, and specially the deposition of metal-rich scales which confirms the theory of scale and corrosion interrelated processes being at least part-wise responsible for scale formation and deposition of Pb, As, and Sb rich scales. Once the filming corrosion inhibitor establishes a physical barrier for electrochemical reactions metal-scale formation is significantly retarded or even blocked.

On a second level of details, the combined use of antiscalant and corrosion inhibitor diversified the chemical spectrum with the precipitation at Soultz of copper, aluminium and silica.

At Soultz, the corrosion inhibitor injection decreases slightly the efficiency of the scaling inhibitor, and vice-versa, revealing some interactions between both technologies. The data suggests corrosion rate is increased slightly with the use of scaling inhibitor.

These questions are topic of research within the following months, to better understand the action of tested products and repeatability.

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