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Scale and Corrosion Mitigation: Economic Feasibility of Combined Mitigation Measures

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ABSTRACT

Today, five binary geothermal plants are operating in the Upper Rhine Graben (URG), a geothermal low enthalpy region at the German-French border. Several new projects are planned and two of them are close to realization. Typical scales in geothermal plants of the URG consist of barium/strontium sulfates and other deposits rich in lead, arsenic and antimony. Barium/strontium inhibition has already been realized successfully with an overall efficiency of >98% but it leaves the heavy metal deposits untouched.

Currently, additional product tests are conducted at three of the geothermal plants within the framework of the research project SUBITO, which is funded by the German Federal Ministry for Economic Affairs and Energy (BMWi). The project aims to reduce total scale mass of lead, antimony and arsenic deposits and to limit or eliminate the accumulation of toxic and radioactive elements by using chemical inhibitors. Additionally, corrosion phenomena like localized corrosion should be reduced to a minimum. All inhibitor tests are accompanied by investigating the economic feasibility by balancing inhibitor related investment and operational costs with cost savings through improved plant availability and efficiency as well as reduced follow-up costs.

The first goal of SUBITO was to target commercially available antiscalants which held the potential to inhibit barium sulfate and lead sulfide in one product. Results of lab and on-site tests showed some improvement related to scale mass reduction but the limited efficiency in combination with some compatibility issues were not satisfactory. Moreover, scale characterization highlighted the importance of electrochemical reactions like corrosion as a trigger for heavy metal scale formation. Therefore, the best results for scale inhibition of both types, sulfate scale and heavy metal scales, were obtained by combining scale and corrosion mitigation measures. After careful pre-selection, corrosion inhibitors were applied to all three geothermal plants in combination with the barium sulfate inhibitors. As a result, the total mass of deposits was significantly reduced as well as corrosion related to maintenance operations. Even considering the relatively high operational costs for continuous scale and corrosion inhibition, the positive effect of cost savings by improved availability and operational performance as well as significantly reduced follow-up costs lead to a decrease of the total average operational costs.

1. INTRODUCTION

1.1 Scaling and Corrosion in Binary Geothermal Power and Heat Plants from the Economic Point of View

The average total cost of geothermal power plant operation consists of operational costs, maintenance and repair and follow-up costs like cleaning and waste management. Reliable plant operation with maximum possible operating hours in combination with projectable, short and low expense maintenance operations are required to keep the total operational costs at a minimum.

Scaling and corrosion issues contradict these objectives due to the decrease of operational performance, unscheduled shut-down times, cleaning surveys, equipment impairment and its reduction of service-life. Especially the formation of toxic and radioactive scales like barium sulfate, lead sulfide, elemental lead, antimony and arsenic rich deposits require time and cost intensive safety-at-work measures as well as disproportional follow-up costs and time-consuming waste management.

Scale mitigation by chemical inhibition and usage of suitable materials lowers significantly the impact of scale and corrosion issues which are often interrelated; especially in the presence of high gas load and heavy metals. The additional costs of mitigation measures can be balanced by efficiency improvement of the geothermal plant through an improved plant availability and significant reduction of follow-up costs.

1.2 The Upper Rhine Graben: Challenges for Brine Treatment

The URG is a challenging environment for chemical brine treatment due to production temperatures of up to 170°C and highly mineralized brines with up to 105 g/L at the western rim of the URG and 125 g/L at the eastern rim (Scheiber et al. 2015, Sanjuan et al. 2016, Jähnichen et al. 2019). The brine contains 1.0-1.3 norm liter (NL) NCG per 1 L brine (~0.17 mass percent) and consists with more than 95% of CO_2. In comparison to geothermal high enthalpy fields which contain gas loads of up to 2.5-4.0 mass percent, the gas load of the URG seems low. In combination with high calcium concentration of up to 8000 mg/L, calcite scales are formed very fast in the production well and feed line if brine is not properly pressurized.

2. REVIEW: SCALE DEPOSITION IN GEOTHERMAL PLANTS OF THE UPPER RHINE GRABEN (URG)

2.1 Typical Scales in Geothermal Plants of the Upper Rhine Graben (URG)

Deposits in geothermal power and heat plants in the URG consist basically of five different types of scales: strontium rich barium sulfate, calcium carbonate, lead sulfide, elemental lead and "mixed"-scales which contain Pb, As, Sb in high concentrations (see Table 1 for details).

Calcium carbonate formation is the only one of the five scale types which can be efficiently mitigated by operational measures. All geothermal plants of the URG are using downhole pumps in order to increase flow rate but also to control the production pressure and avoid uncontrolled CO_2 degassing (Hettkamp et al., 2020; Mouchot et al., 2018; Ravier et al., 2015).

The remaining four scale types are present in all deposits but their mass fraction depends very much on the applied scale mitigation concept. Scales in the URG contain significant amounts of heavy metals and metalloids (Pb, As, Sb) but also radionuclides like Ra-226 and Pb-210. These radionuclides are strictly bound to the presence of specific scales. Barium sulfate incorporates very small quantities of Ra-226 by chemical substitution of Ba and all lead-containing scales incorporate Pb-210. The scales are classified as Naturally Occuring Radioactive Material (NORM) and toxic due to the presence of Pb, As, Sb.

Table 1: Typical scales of geothermal plants of the Upper Rhine Graben (URG): formation condition and related issues, area of deposition and mitigation strategy.

Scale Type	Formation	Deposition	Related Issues	Mitigation Strategy
barium sulfate $BaSO_4$ *present in fracture fillings of the reservoir*	T decrease	continuously • heat exchanger • pipe network mainly return line (cold side) • filters, valves of return line (cold side) • injection wells	• decrease of heat transfer efficiency in heat exchangers • increase of differential pressure in heat exchangers • cleaning operations required • classified as NORM due to chemical substitution of Ba by Ra-226 • difficult to dispose (contaminated equipment and scale residues) • safety at work • decrease of injectivity (long term – years)	antiscalants • retardation or blockage of crystal growth • high inhibitor efficiency of >98%
calcium carbonate $CaCO_3$ *present in fracture fillings of the reservoir*	p decrease	infrequently • separator, only when power plant is put in operation after shut-down periods	-	high p in surface installations • created by production pump
lead sulfide PbS *present in fracture fillings of the reservoir*	T decrease electrochemistry ?	continuously • heat exchanger • pipe network mainly return line (cold side) • filters, valves of return line (cold side) • injection well	• decrease of heat transfer efficiency in heat exchangers • increase of differential pressure in heat exchangers • cleaning operations required • classified as NORM due to by Pb-210 • toxic • difficult to dispose (contaminated equipment and scale residues) • safety at work • decrease of injectivity (long term – years) ?	antiscalants with dispersing properties • scale formation is too fast for threshold inhibition • functionalization of scale surfaces by dispersing agents
mixed scales Pb, As, Sb -rich amorphous or micro-crystalline NOT *present in fracture fillings of the reservoir*	T decrease **electrochemistry – corrosion related !**			**SUBITO result** corrosion inhibitors • protection of metal surfaces by formation of a protective layer (filming)
lead Pb(0) NOT *present in fracture fillings of the reservoir*				

2.2 Similarity of Reservoir Fracture Fillings Mineralogy and Scale Formation in Surface Installations

Interestingly, scale mineralogy in surface installations of power and heat plants of the Upper Rhine Graben (URG) is very similar to fracture fillings in the reservoir with some important exceptions. Fracture fillings of the sandstone which covers the crystalline basement of Soultz-sous-Forêts consist mainly of quartz, barium sulfate and calcium carbonate but contain also traces of lead sulfide as shown in Figure 1. Fracture fillings of the granitic basement are dominated by clay minerals and quartz but also contain barium sulfate, calcium carbonate and traces of lead and iron sulfides (Genter et al., 1989).

Basically, calcium carbonate, barium sulfide and lead sulfide formation in surface installations only mimic the mineralogy of fracture fillings in the Upper Rhine Graben (URG), however, elemental lead and "mixed"-Pb, As, Sb scales are absent in fracture fillings of the reservoir.

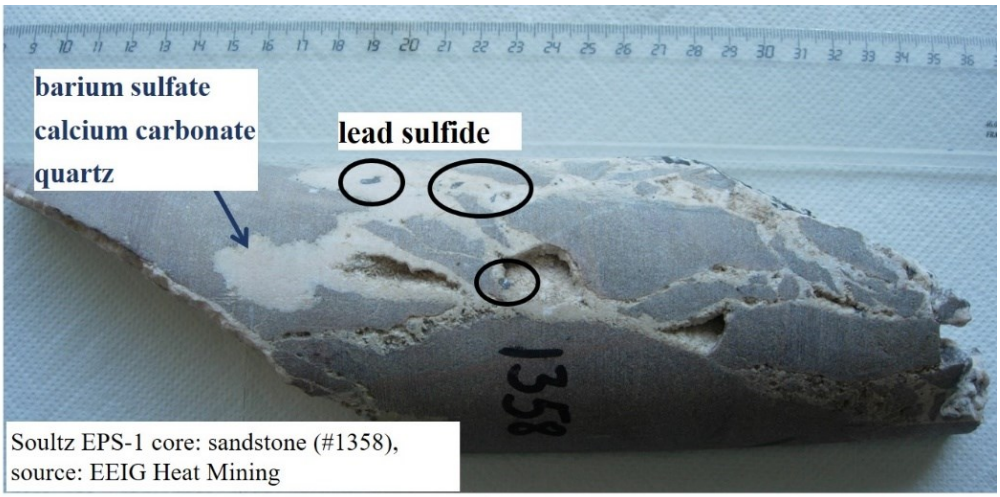


Figure 1: Piece of a sandstone core of the Soultz EPS-1 well which contains typical fracture fillings of barium sulfate, calcium carbonate, quartz and traces of lead sulfide.

2.3 Scale Formation, Scale Deposition and Related Issues

Barium sulfate ($BaSO_4$) is less soluble at lower temperatures than at high temperatures and its formation in surface installations results from the temperature decrease in the heat exchangers. A similar concept could be applied to the lead sulfide (PbS) formation except for the facts that aquatic S^{2-} was never detected in brines of the URG and H_2S was not detected in the gas phase of non-condensable-gases (NCG) in the URG (Sanjuan et al., 2016; Scheiber et al., 2015). The origin of S^{2-} as counterion to Pb^{2+} is still under evaluation and will be discussed later in this paper. The formation of elemental lead and amorphous "mixed"-Pb, As, Sb scales cannot be explained by simple decrease of solubility; more complex reactions linked to electrochemistry are to be considered.

Binary power plants of the URG operate the geothermal loop as a closed system which means that non-condensable-gases (NCG) are not released to the environment but are kept pressurized in the brine and are re-injected into the reservoir. Surface pressures in the geothermal plants ranges from 19-25 bars and production temperatures ranges from 150-170°C (Hettkamp et al., 2020; Mouchot et al., 2018).

Scale formation and deposition starts in the heat exchangers and is observed in every equipment of the return line (cold side / injection side) and even inside the injection well (Scheiber et al., 2012). Scaling related issues are therefore not limited to surface installations but also potentially concern injectivity and reservoir performance.

Despite the fact that scales in the URG grow relatively slow with some mm per year and do not have the tendency for pipe or heat exchanger blocking the scale related issues do affect reliable plant operation severely. The heat exchanger performance is limited by decrease of the heat transfer and the differential pressure increases with increasing scale thickness. Frequent cleaning operations are required which is time and cost intensive and high disposal costs must be added to costs of the cleaning operation and significant loss of revenues. Scales must be treated as NORM and as toxic waste in both Germany and France; therefore, all contaminated equipment and scale residues must be handled with care following specific regulations for safety-at-work and disposal. Especially all costs related to disposal such as scale conditioning for immobilization of Pb, As and Sb in Germany and the associated administrative workload build up high follow-up costs.

2.4 Scale Composition Without Chemical Brine Treatment

Without brine treatment strontium rich barium sulfate dominates the scale matrix, lead sulfide, elemental lead and "mixed"-Pb, As, Sb scales are only present in minor amounts as shown in Figure 2 (Scheiber et al., 2012; Nitschke et al., 2014). The scale forms thin, brittle and plate like deposits which cover all surfaces in the heat exchanger and in the return line which are in contact with brine. Due to the incorporation of Ra-226 radiation protection measures are required on-site and for disposal of scale residues and scale contaminated equipment (Cuenot et al., 2013).

Scale adherence to metal surfaces is very strong especially on rough and/or mild steel surfaces and abrasive cleaning methods are required. In high alloyed tubular heat exchangers scale adherence is not as strong but cleaning operations are quite difficult and time intensive due to the fact that metal surfaces are not allowed to be affected by cleaning and the production of larger amounts of contaminated water should be avoided.

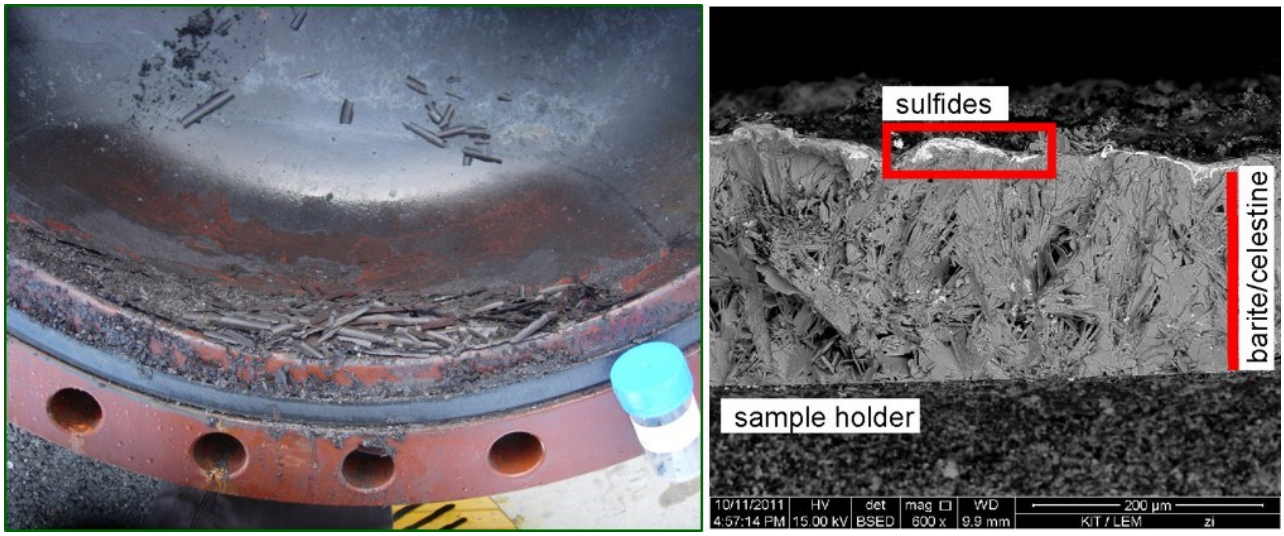


Figure 2: Left) Plate like and brittle barium sulfate scales are found in the water boxes of the heat exchanger. Right) Cross section of the barium sulfate scale from the water box: Large barium sulfate crystals dominate the scale matrix and lead sulfide covers the surface. (both pictures after Scheiber et al., 2012)

2.5 Application of a Barium Sulfate Antiscalant

The application of barium sulfate antiscalants changes the mass fraction of scale types present in the deposits significantly. Barium sulfate inhibitor efficiency with phosphonic acid is >98% and barium sulfate is present at trace amounts below 0,5 mass %. Instead lead sulfide and "mixed"-Pb, As, Sb scale dominate the matrix with 40-45 mass % respectively and elemental lead is present with several mass % (Haas-Nüesch et al., 2018; Jähnichen et al., 2020).

The scale matrix is made up by very thin but long dendrites which, interestingly, do not touch each other and scale thickness grows within 4 months up to 4 mm at the Insheim geothermal power plant as shown in Figure 3. During the next 25 months the scale thickness varies between 5-8 mm but does not increase further. The adherence to metal surfaces is only limited and the scale is very easy to be removed. However, cleaning frequency of heat exchangers remains unexpectedly similar and cleaned surfaces are covered with scale deposits of several mm within very few weeks to months.

Haas-Nüesch et al., (2018) investigated the redox state of lead in the amorphous phase of the deposits and which turned out to be Pb(0). Further investigations proved that also arsenic and antimony do not exist in their cationic state within the mixed scales but probably in their elemental form As(0) and Sb(0) (Jähnichen et al., 2020). These results highlight the importance of electrochemical reactions on scale formation in the URG which is in contradiction to very low uniform corrosion rates of mild steel which is known to be very low with 0.15 mm/y. Pitting and crevice corrosion occurs at low temperatures of the return line (Battici et al., 2010; Mundhenk et al., 2013).

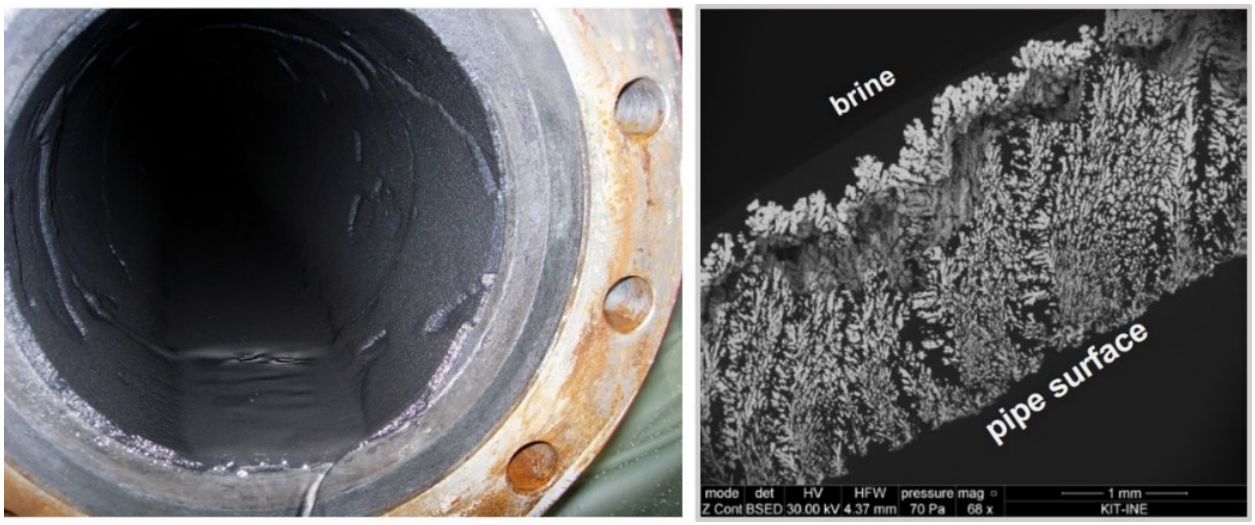


Figure 3: Left) Scale deposits of 5-8 mm thickness cover the complete 360° of the piping walls at the Insheim power plant. Right) Electron microscopy exposure of a scale cross section: scale matrix is made of thin but long dendrites which do not touch each. (After Haas-Nüesch et al., 2018)

3. SCALE MITIGATION OF LEAD SULFIDE AND LEAD, ARSENIC AND ANTIMONY RICH SCALES

3.1 Research Project SUBITO - Sulfide Inhibition and Disposal

The research project *Sulfide Inhibition and Disposal* (SUBITO (FKZ 0325790A)) was created out of the difficulty to establish efficient brine treatment in the URG which tackles both mineral types, sulfates and sulfides. At that time, it was assumed based on elemental analysis that As and Sb also form sulfide deposits.

The aim of the research project is to reduce total scale mass and to eliminate or at least to limit the accumulation of toxic and radioactive elements by using products with specific abilities like antiscalants, filming and dispersing properties. One of the most crucial tasks for the project was the requirement to keep up the continuous successful barium sulfate inhibition at any time during product tests. As a side effect of barium sulfate formation, the radionuclide Ra-226 gets trapped in the crystal lattice by chemical substitution of barium and the sulfate scales must be considered as low-level radioactive waste (Scheiber et al., 2012; Cuenot et al., 2013). During the first phase of the project antiscalants which were selected specifically for sulfide mineral mitigation were tested followed by the combined application of antiscalants with corrosion inhibitors in the second phase:

- Phase 1 – antiscalant + dispersant.
- Phase 2 -antiscalants + dispersion agent + corrosion inhibitor.

Product tests were performed with permission of power plant owners and cooperation of the operators at two geothermal sites of the URG: the geothermal power plants of Insheim (Germany) and Soultz-sous-Forêts (France). Both geothermal power plants, Insheim and Soultz, started directly after commissioning with barium sulfate mitigation by continuous injection of at both sites.

3.2 Product Selection and Number of Products Tested On-site

Product selection and dosage adjustment is a question of plant location and its geochemical conditions, but if brine chemistry does not vary too much, specific product groups can be applied in a larger geological region. Exotic scales like lead sulfide are very difficult to mitigate by standard chemical measures like antiscalants or dispersants and are therefore rarely included in the standard portfolio of service companies for water treatment. High production temperature and salinity of the brine complicates proper product selection.

In total, seven service companies for water treatment were contacted or project partners themselves were contacted for product recommendations. Six out of the seven companies recommended one or several products for testing antiscalants or corrosion inhibition or both. All in all, 19 products were tested in the lab and 9 products applied in the field as shown in Table 2. Lab test evaluated brine/product compatibility at injection conditions which are different from dose rates per liter brine. Directly at the injection point the product enters the brine as a concentrate and must therefore be tested for its calcium tolerance. During SUBITO Phase I, products were injected instead of the standard product of the geothermal power plants for a few months. Barium sulfate inhibitor efficiency had to be investigated before field application. During SUBITO Phase II, corrosion inhibitors were injected additionally to antiscalants and it is known that cationic and anionic substances can negatively interact with each other and reduce product efficiency. Therefore, it was also tested that corrosion inhibitors do not limit barium sulfate mitigation.

Table 2: SUBITO product selection during project Phase I and Phase II.

SUBITO	Mineral Type	Product Type	Number of Inj. Products	Lab Tests	Field Tests
Phase I 2015/03 – 2018/02	barium sulfate	antiscalant + dispersant	**1**	**12**	**6**
	lead sulfide				
	mix – Pb, As, Sb				
Phase II 2018/02 – 2019/08	barium sulfate	antiscalant	**2**	**7**	**3**
	lead sulfide	dispersant			
	Pb(0), As(0), Sb(0)	corrosion inhibitor			

3.3 Monitoring Concept

Brine, particulate matter in the brine and scales were sampled and analyzed quantitatively. Results of this monitoring are presented by Jähnichen et al. (2020). Fluid and particulate matter were sampled close to production wellhead before inhibitor injection and after the heat exchanger before the filters as shown in Figure 4.

Scale monitoring of the different product tests was realized by sampling scales from heat exchangers as a function of the temperature profile. The heat exchanger at the Insheim geothermal plant is cleaned one time per year and scale deposition and composition depends on all products tested during the elapsed time period since the last cleaning. In order to monitor the scale mitigation efficiency of products and product combinations a specific “SUBITO-pipe” was integrated into the surface installations. For the research project SUBITO the power plant operator of Insheim and Soultz agreed to install bypass systems which allowed to operate the monitoring pipes in the framework of the normal surface installations. “SUBITO-pipe” diameter and material were chosen to be the same as the ones of the surface installations and therefore similar flow regime and temperature and pressure conditions were established (see Figure 5).

Each product was tested for several months. Before starting field trials, either a new pipe was installed or the pipe was cleaned rigorously by water jetting. Scale sampling was realized after pipe deinstallation and scale adherence to the surface, its morphology, color and thickness was documented every time.

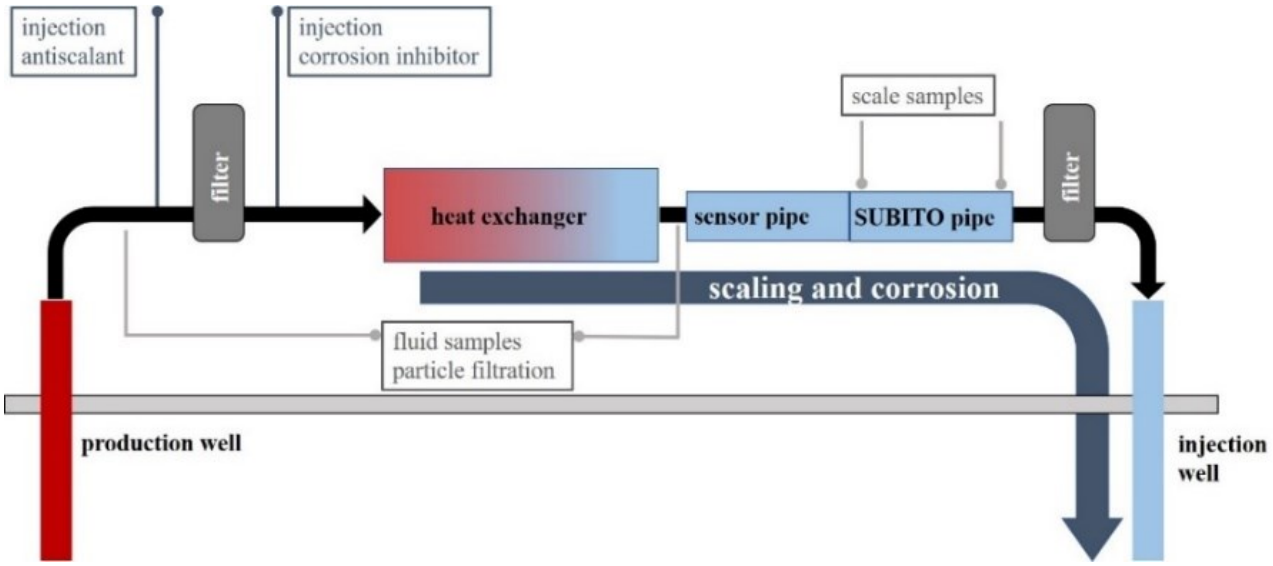


Figure 4: Schema of the monitoring program for sampling of fluid and scales within the SUBITO project. Scaling and corrosion are observed in the heat exchangers downstream from the injection well.



Figure 5: "SUBITO-Pipes" of the return line for scale monitoring at the geothermal site of Insheim.

4. SUBITO RESULTS

4.1 Brine / Product Compatibility

Three of the tested products were highly incompatible with brine of the URG at high temperature (feed line – production side). Two of the products were applied at Soultz (Inhibitor 10 and Inhibitor 11) and the other one at Insheim (Inhibitor 1). Inhibitor 1 was tested successfully at Soultz @150°C and proved its ability for significant mass reduction of the scale deposits. Therefore, it was also recommended for the field test at Insheim. Production temperature of Insheim is higher than the one at Soultz with a difference of 16K. At Soultz, any indicator of incompatibility has been detected but at Insheim the Δp of the production filters increased within the first ten days of injection and the test of this product had to be aborted immediately due to severe incompatibility issues. The inhibitor blocked the complete production filter with a brittle and sticky yellow deposit which contained 23 mass % of Total Organic Carbon (TOC) as shown in Figure 6 left. This type of deposit can be assumed also to be present in all surface installations upstream to the heat exchanger and even inside the heat exchanger to the point where the brine cools down below 150°C. The formation of the deposits indicates a strong incompatibility of at least one or even more components of Inhibitor 1 at temperatures of 164°C. The inhibitor blocked not only the filter but also the inhibitor injection-coil and as a result the power plant had to be shut down for two hours in order to clean the coil as shown in Figure 6 right. The incompatibility of three different products from three different service companies showed the urgency for compatibility tests at production temperature before field application even if the retention time at this temperature is below 50 s as it is the case for Insheim.



Figure 6: Incompability of brine/antiscalants at high temperatures and high calcium concentration at the geothermal power plant Insheim. Left) Incompatible inhibitor residues block production filter. Right) Incompatible inhibitor residues block the injection-coil.

4.2 Scale Monitoring and Scale Mass

Scale sampling from the "SUBITO-pipe" was realized after pipe deinstallation. The attachment of the scale to the surface, the scale morphology, its color and thickness was monitored for every tested product or product combination. The results of the Soultz scale-monitoring are part wise summarized by Mouchot et al. (2019). One parameter of efficiency evaluation was the mass balance of scale formation as a function of the deposited mass per 150 cm^2 surface area per accumulated brine volume during the time of exposure and dose rate of the products as shown in Figure 7.

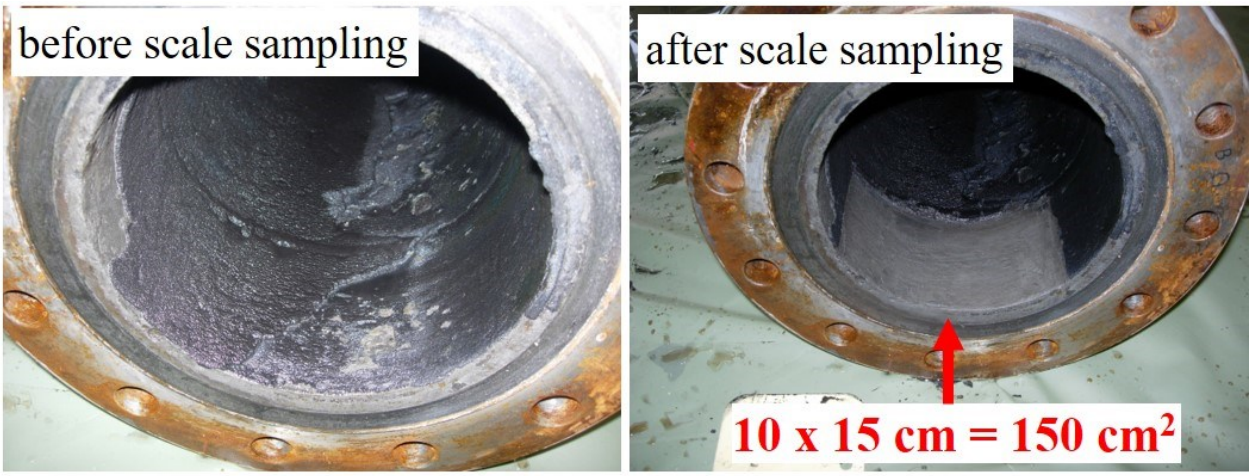


Figure 7: Left) Scale deposition inside the monitoring pipe with barium sulfate inhibitor. Right) Scale sampling from 10x15 cm surface for mass quantification.

At Insheim, the injection of the reference inhibitor (barium sulfate antiscalant based on phosphonic acid) lasted for twenty-nine months during the project duration of SUBITO and was considered as long-term monitoring. Within the first 4 months, dark grey and soft scales were deposited with a total thickness of nearly 4 mm as shown in Figure 8 left. The scales were easy to be removed. Over the period of the next twenty-five months scale thickness increased only slightly to about 5-8 mm. Scale composition did not change significantly over time and consisted mainly of PbS and mixed scales with Pb, As and Sb. The combined application of the antiscalant Reference 1 in combination with the corrosion inhibitor Additive 3 showed excellent results in scale mass reduction to nearly 60-70%. Scale thickness after 4 months was <1 mm as shown in Figure 8 right. Morphology of the scale was very different in comparison to the injection of solely Reference 1. The scale was also easy to remove but very brittle and paper like.

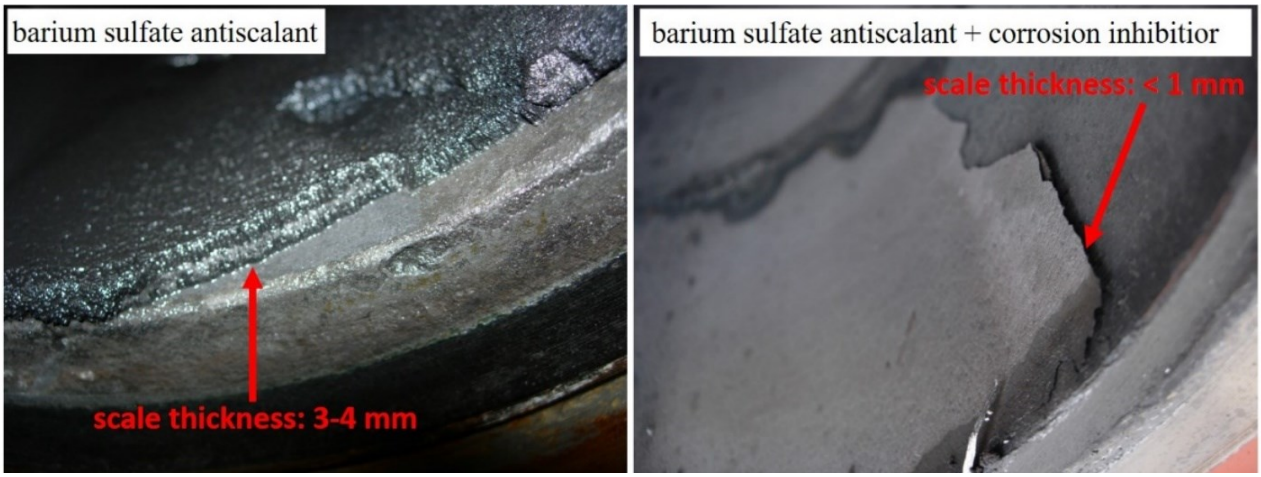


Figure 8: Left) Scale deposit inside the monitoring pipe with injection of the barium sulfate antiscalant (Reference Inhibitor) after 4 months exposure. Left) Scale deposit inside the monitoring pipe with injection of the barium sulfate antiscalant (Reference Inhibitor) in combination with the corrosion inhibitor (Additive 3) after 4 months exposure.

Since scale mass reduction is one of the most important objectives of the SUBITO research project, the results from both geothermal sites are summarized in Figure 9.

Antiscalants which focus on barium sulfate mitigation produce the highest scale masses, see Ref. 1 and Ref. 2. Antiscalants which combined properties for barium sulfate and lead sulfide mitigation in one single product decreased total scale mass except for Inhibitor 8, see Inhibitor 1, Inhibitor 10 and Inhibitor 11. Inhibitor 8 was a specific product because laboratory tests indicated that it combined antiscalant and corrosion inhibitor properties in one product. Unfortunately, it did not show these properties in the field and scale deposition was even more intense in comparison to the barium sulfate antiscalant Reference 1. Different results of Additiv 4 can be explained by different test durations which also have an influence on scale deposition (Mouchot et al., 2019).

Best results were obtained by injecting two products, barium sulfate antiscalant and corrosion inhibitor. Here, the application of Reference 1 in combination with Additive 3 decreased the total scale mass to nearly 65% in comparison to the application of only Reference 1 at the geothermal power plant at Insheim.

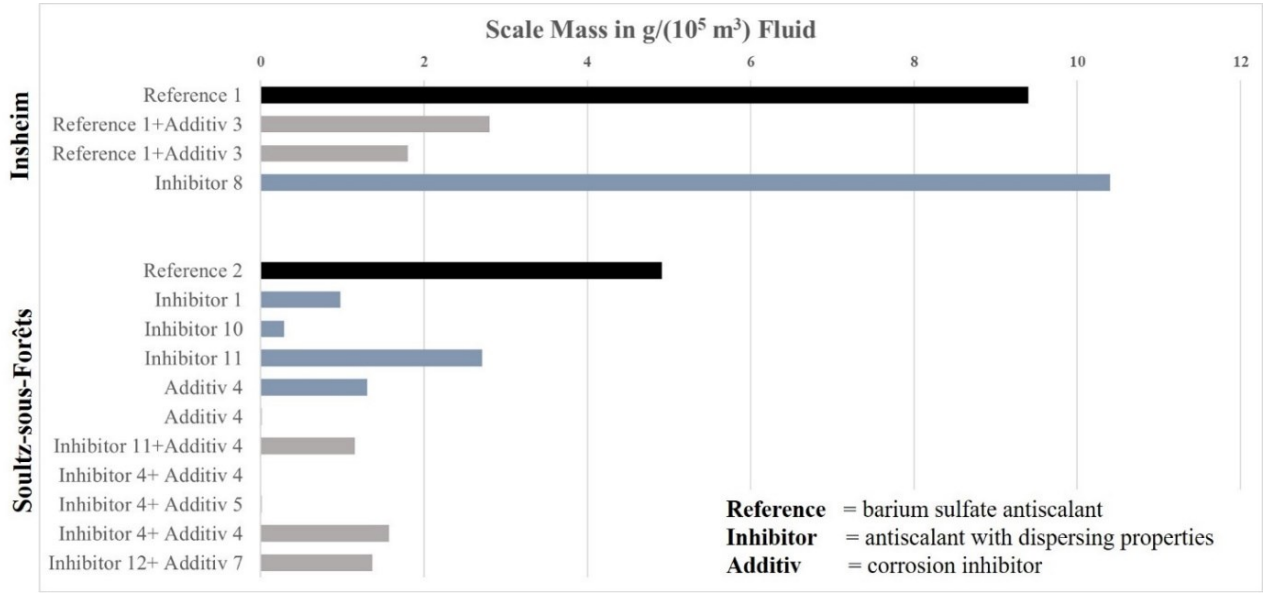


Figure 9: Evaluation of scale formation as a function of accumulated brine volume and deposited scale mass, updated after Scheiber et al., 2019.

It was observed that barium sulfate formation increased slightly during combined injection of Inhibitor 11 with Additive 4 which indicates negative interactions between the antiscalant and the corrosion Inhibitor. The test result of Inhibitor 4 + Additive 5 can be neglected due to the short testing duration of two weeks.

4.3 Corrosion Mitigation

Surface equipment of geothermal plants in the URG does not suffer from uniform corrosion but mainly from localized corrosion which appears to be random and very difficult to forecast. All types of geometries are affected, straight pipes elbows, low and high parts. Leakages occur mainly at the bottom or sides but usually not at the top.

In 2017 and 2018, corrosion related maintenance operations were frequently required due to localized corrosion and small-scale leakages at one of the geothermal sites of the URG as shown in Figure 10 left. After starting of the corrosion inhibitor injection in July 2018, no corrosion maintenance was required during the following 12 months and no leakage was recorded as shown in Figure 10 right. In May and June 2018, parts of the surface installations had to be replaced by new pipes, but other pre-damaged pipes remained. It is difficult to state whether or not the corrosion inhibitor injection is responsible for the long maintenance-free operation period at Insheim because of the installation of some new equipment directly before starting the corrosion inhibitor field test. It can be stated however, that lots of the "old" and pre-damaged pipes remained in the surface installations and no new leakages occurred. The possibly positive effect of the corrosion inhibitor on the mitigation of localized corrosion cannot be neglected.



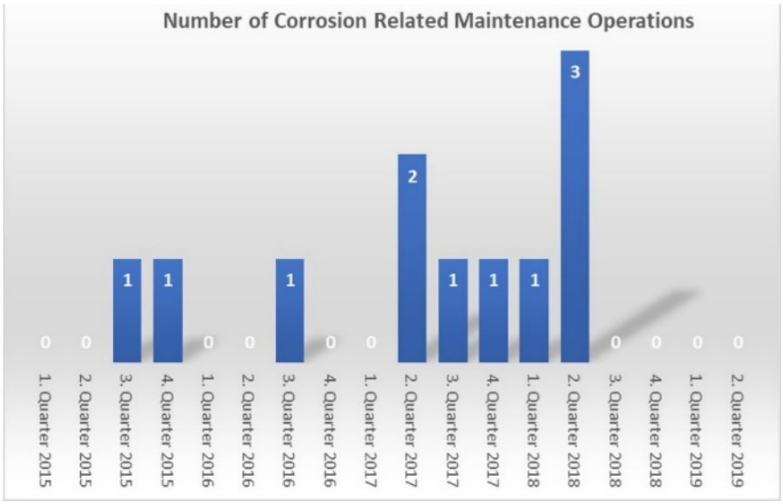


Figure 10: Left) Brine leakage due to localized corrosion. Right) Evaluation of scale formation as a function of accumulated brine volume and deposited scale mass, after Scheiber et al. 2019.

4.4 Economic Feasibility of Combined Mitigation Measures

Taking intense scale and corrosion mitigation measures can be financially worthwhile as soon as the benefits are higher than the losses caused by scaling and corrosion which are very often interrelated processes. For example, corrosion can trigger the formation of heavy metal deposition on one hand and on the other hand scale deposition potentially triggers under-deposit or galvanic corrosion (in case of metal deposition on metallic surfaces). Typical mitigation strategies focus on preventative measures in order to minimize required actions of damage control before the actual impairment or damage is created. In consequence, mitigation concepts, financial investment and workload needs to be applied before impairment, performance decrease or damages are measurable or visible. This creates a psychologically difficult situation for power plant owners and operators when measures for scale and corrosion mitigation are taken when actually no scaling or corrosion related issues are affecting plant performance yet.

The earlier preventative measures are applied the better the potential savings. In the best case, a comprehensive mitigation strategy is launched simultaneously with plant commissioning but in reality, mitigation concepts are developed during operation as soon as the first problems start to appear. If the treatment starts too late, actions for both damage control and damage mitigation have to be taken at the same time which increases the total costs of scale and corrosion related issues. Measures of scale and corrosion mitigation in binary geothermal plants of the URG are operational, chemical or based on material selection.

Calcium carbonate scaling is mitigated simply by pressurizing the brine at production above the GBO which is an operational mitigation strategy. Barium sulfate scaling can't be mitigated by operational measures nor by material selection, it is driven by temperature decrease. Therefore, chemical brine treatment is up to now the only successful mitigation strategy. Lead sulfide and mixed scales (Pb, As, Sb -rich) can be mitigated chemically by the injection of corrosion inhibitors and probably to some extend by material selection by reducing electrochemical reactions.

Cost for chemical brine treatment include the investment for the injection system, its maintenance and operation and total product costs as a function of dose rate. In order to estimate the economic impact of a continuous chemical brine treatment, all costs related to corrosion and scaling were listed in Table 3 and divided in:

- fixed costs per year which can't be lowered by successful scale and corrosion mitigation.
- "variable" costs per year which can be lowered by the application of successful scale and corrosion mitigation strategies.

Table 3: Fixed and "Variable" costs related to corrosion and scaling.

Issue	Fixed Costs per year	"Variable" Costs per year
Direct Costs	• HEX inspection • inhibitor product costs • inhibitor injection system: investment, maintenance and operation • operational minimum measures: safety-at-work (chemotoxicity and radiation protection), re-organization piping	• HEX cleaning • HEX reduced heat transfer: loss of revenues • loss of revenues due to unscheduled shut-down periods • operational extended measures: maintenance costs (material and service companies, administrative workload)
Follow-up Costs	• administrative workload related to chemical brine treatment	• scale handling and disposal – scale treatment (Germany: immobilization) – scale disposal – personal protective equipment – PPE – safety-at-work: chemotoxicity and radiation protection: enhanced concept for the certain presence of scales • administrative workload regarding scale disposal and equipment, contaminated by scales (combustible and metallic)

Based on the results of the combined application of antiscalant and corrosion inhibitor, we can easily assume a total reduction of the yearly variable costs by minimum 50%. For example, the heat exchanger at the Insheim power plant hasn't had to be cleaned after ten months of corrosion inhibitor injection and the overall performance of the HEX kept very constant over this time. As a consequence, no scale treatment and disposal had to be scheduled which also decreased the administrative workload significantly. Corrosion related maintenance was not necessary within a full year of operation.

For normalization, all Fixed costs were added together and set to 100% as shown in Figure 11. The costs of the corrosion inhibitor and all of the variable costs were normalized based on the total amount of the fixed costs. The product costs of the barium sulfate inhibitor are included in the fixed costs but the corrosion inhibitor is listed separately since it was the objective to investigate its economic benefit. The costs of the corrosion inhibitor of Insheim equals 45% of the fixed costs which is quite high and had to be compensated by a significant reduction of the flexible costs. With barium sulfate inhibition and without the positive effect of the corrosion inhibitor the variable costs add up to 168% of the fixed costs (see Figure 11). These "variable" costs of 168% were reduced by successful application of the corrosion inhibitor to approximately 84% due to successful corrosion mitigation and reduction of corrosion related Me-scales.

168% (variable costs without corrosion inhibitor injection)
– 84% (variable costs with corrosion inhibitor injection)
– 45% (product cost corrosion inhibitor)
= **39% savings** (relatively to fixed costs).

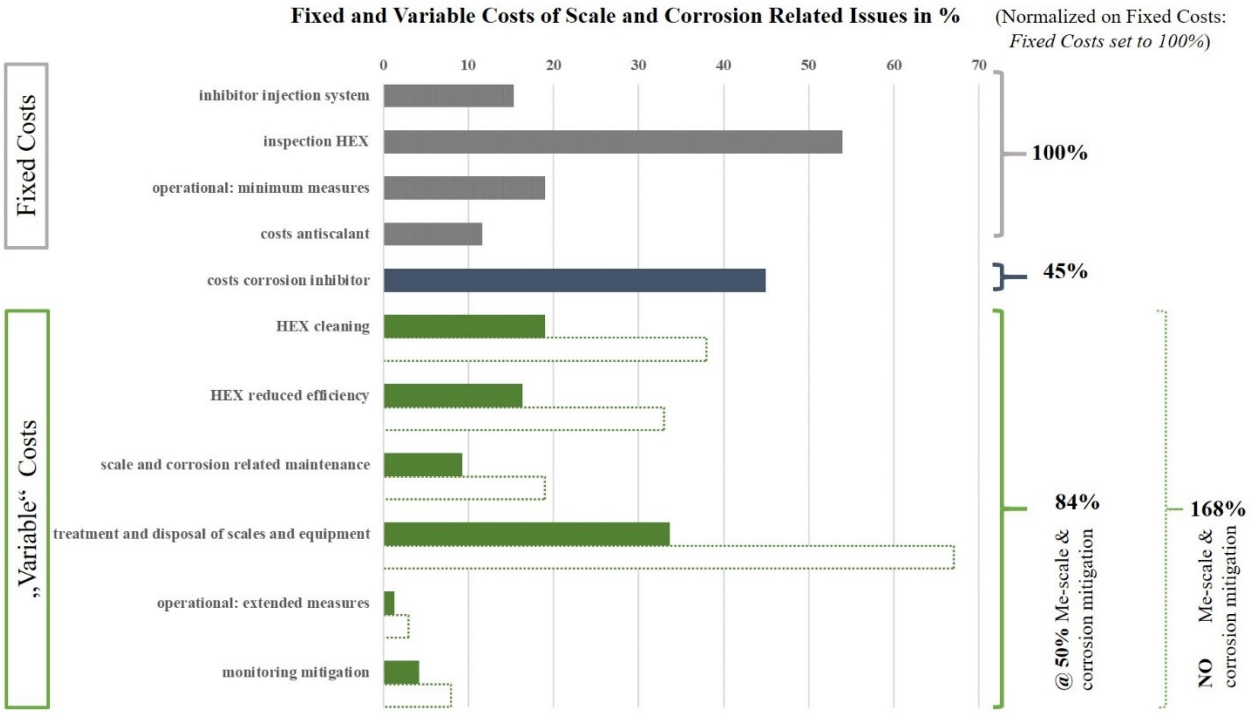


Figure 11: Yearly Fixed and "Variable" costs of scale and corrosion related issues. The "Variable" costs can be reduced by successful scale and corrosion mitigation but the saving needs to compensate the high product costs of the corrosion inhibitor.

5. DISCUSSION

5.1 Difficult Development of a Successful Brine Treatment Concept

5.1.1 Product Selection of Antiscalants and Corrosion Inhibitors

The SUBITO project aimed to test 4 different antiscalants which combined the ability to mitigate barium sulfate and lead sulfide deposition in one product. The project ended up to having to test 19 commercially available products, 12 antiscalants with dispersing properties and 7 corrosion inhibitors. The total number of laboratory and on-site tests reflects the difficulty and somehow also the desperation to identify fast and efficient scale mitigation strategies in the challenging geochemical environment of geothermal power and heat plants in the Upper Rhine Graben. High salinities of 100-110 g/L Total Dissolved Solids (TDS) in combination with high calcium concentrations of up to 8000 mg/L at production temperatures of 150-170°C are very harsh conditions for efficient chemical brine treatment. Water treatment companies were mostly very helpful and cooperative and put in a lot of effort and working time in the development of treatment strategies.

5.1.2 Identification of Scale Types and their Formation Conditions

Product selection was not only difficult because of complex brine chemistry and production temperature but also because the formation conditions of all scale types present in the scales were not completely known when the project started in 2015. At the time, it was assumed that Pb, As and Sb form different types of sulfide minerals and service companies were approached to provide lead sulfide antiscalants which also have the ability of barium sulfate inhibition. Thanks to the intensive studies performed within the research project SUBITO, it is now known that more than 50 mass % of the deposits, formed during barium sulfate inhibition, consist of elemental deposits (Pb(0), As(0), Sb(0)) and originate therefore from electrochemical reactions (Haas-Nüesch, 2018). Very low uniform corrosion rates of mild steel in surface installations never lead to the conclusion that corrosion inhibitors could be required. Plants of the URG suffer mainly from localized corrosion which becomes more and more severe over time like a self-sustaining snowball system.

5.1.3 Origin of S^{2-} for PbS formation

Lead Sulfide (PbS) constitutes 40-45 mass % of the scales and is formed during barium sulfate mitigation. Since Galena (PbS) is naturally present in fracture fillings of the URG reservoirs it is possible that lead sulfide is formed simply as a result of the decreasing the solubility of lead sulfide with decreasing temperature in the heat exchangers. This theory was never officially confirmed, mainly because aqueous S^{2-} was usually not detected in the production brine except for one event. S^{2-} concentration below the detection limit would be sufficient to explain the scale formation of the total lead sulfide mass in the geothermal power plants simply based on the total accumulated brine volume produced within a year. However, other sources of S^{2-} are also discussed such as sulfate reduction by corrosion processes or Sulfate Reducing Bacteria (SRB). Both processes are very hard to prove and would take place at the micro-scale level directly on metal surfaces. It remains a fact that aqueous S^{2-} cannot be detected with state-of-the-art methods in brines of the URG.

5.2 Combined Application of Antiscalants and Corrosion Inhibitors

The formation of metal-rich deposits can be retarded by antiscalants which inhibit barium sulfate and lead sulfide in one product. However, the best results were obtained by using two very different products at the same time. One powerful antiscalant for barium sulfate mitigation and a corrosion inhibitor. One of these products should possess good dispersing properties for lead sulfide mitigation. The presence of elemental lead indicated the influence of electrochemical reactions on scale formation in the URG and the scale mass reduction of probably more than 65% due to the application of a corrosion inhibitor proved this theory.

5.3 Negative Interaction of Antiscalant and Corrosion Inhibitor

Chemicals for scale and corrosion mitigation can interact with each other when more than one product is applied. In the best but very rare case, the efficiency of one or both products increase as it was observed during one of the laboratory tests. Unfortunately, it happens more often that the antiscalant efficiency is reduced by simultaneous injection of a corrosion inhibitor. Lab tests proved this phenomenon for two of the product combinations (Scheiber at al., 2019). This phenomenon was also observed during one of the field trials.

The mitigation of exotic scales which contains elements like Pb, As and Sb as main components requires a much better understanding of the mode of operation of the different products and their various constituents within the geothermal brine but also with other products when applied in product combinations.

5.4 Product Incompatibility at High Temperatures

Brine/Inhibitor compatibility needs to be confirmed for high temperature and low temperature conditions even if retention time in the feed line (hot side / production side) is very short with less than 60s like at Insheim geothermal site. High mineralized brines with calcium concentration up to 8000 mg/L at production temperatures up to 170°C are extremely challenging for antiscalants and corrosion inhibitors which are mainly based on organic compounds.

5.5 Influence of Geothermal Plant Operation on Inhibitor Efficiency

Most corrosion inhibitors are filming agents and their efficiency rely on the fact that the inhibitor needs to get in contact with metal surfaces. All geothermal brines in the URG contain a considerable gas fraction dominated by CO_2. Except for one of the five geothermal sites in the URG, the brine is produced at production pressures above Gas Breakout (GBO) pressure which corresponds to single-phase flow conditions. At single-phase flow, corrosion inhibitors come in contact with all surfaces and the protective film can be formed. However, most geothermal power and heat plants of the URG operate very close to the GBO which can result in micro-degassing in areas of turbulent flow. The full protection provided by the inhibitor filming cannot be guaranteed under these conditions. In some cases, it was observed that two-phase flow conditions were present in the return line (cold side / injection side)

for several weeks of operation. Two-phase flow is a mixture of fluid and free gas. At linear flow conditions the gas covers the liquid phase but at turbulent flow conditions both phases are rapidly mixed. Corrosion inhibitors in the URG are soluble in the fluid but not in the gas/steam phase. This means that they will not protect gas dominated areas as it was already observed at the Insheim geothermal power plant.

5.6 Material Selection as Scale Mitigation Measure

As already discussed more than 50 mass % of the scales, formed during barium sulfate mitigation, result from corrosion processes. Therefore, material selection which is less prone to corrosion processes could be another suitable option to decrease total scale mass in geothermal power plants of the URG. Due to the high brine mineralization high alloyed steels need to be selected carefully because of their tendency for pitting corrosion at high chloride concentrations but coatings or glass-fiber reinforced polymer pipes could be an option for further scale and corrosion mitigation.

5.7 Economic Feasibility of Combined Mitigation Measures

Corrosion inhibitors are one of the most expensive product types which can be used for chemical brine treatment in geothermal. The economic benefit which results not only from significant reduction of corrosion related maintenance operations but also from a significant mass reduction of heavy metal scales containing lead, arsenic and antimony are higher than the additional costs for the product and the injection system. After ten months of corrosion inhibitor injection the yearly costs of issues related to scaling and corrosion were significantly reduced.

6. CONCLUSIONS AN OUTLOOK

The SUBITO project showed clearly how difficult it is today for geothermal power plant operators of binary plants in the Upper Rhine Graben (France and Germany) to select an appropriate inhibitor or better inhibitor combinations that could possibly lead to an efficient and feasible brine treatment for scale and corrosion mitigation. The best results for scale inhibition of both types, barium sulfate scale and heavy metal scales, were obtained by combining scale and corrosion mitigation measures. This is because more than 50% of scale deposits consist of metalloids and metals like arsenic, antimony and lead in their elemental form As(0), Sb(0) and Pb(0). After careful pre-selection, corrosion inhibitors were applied at both geothermal plants in combination with the barium sulfate antiscalant. As a result, the total mass of deposits was significantly reduced as well as the number of corrosion related maintenance operations. In consequence, no cleaning of the heat exchangers was required after ten months of corrosion inhibitor injection and thereby also no scale treatment and disposal. Despite the high product cost of corrosion inhibitors, the successful mitigation strategy at the geothermal power plant of Insheim, Germany, decreased the total average operational costs which are related to scale and corrosion issues.

Further improvement of scale and corrosion mitigation could be achieved by adjusting the material that is used downstream of the heat exchangers in a way that the electrochemical interaction of brine and material is reduced to a minimum. The application of coatings or glass fiber reinforced polymer pipes could be a solution or the selection of more noble alloys.

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