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Development of a novel NORMs inhibitor for Rittershoffen geothermal plant in the Upper Rhine Graben

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ABSTRACT

Scale and corrosion inhibition is critical in operating effectively geothermal plants for power generation and heat production in the Upper Rhine Graben (URG). Indeed, these phenomena are often responsible for loss of system efficiency and premature equipment failure or replacement. In this study, we focus on finding a new scales inhibitor compatible with the URG geothermal brine, but also with corrosion inhibitors.

The URG is a rifting formation part of the European Cenozoic rift system, which extent for 300 km of length from Basel (Switzerland) to Mainz (Germany). Geothermal fluids produced in the URG have a Total Dissolved Solid content of ~100 g/L and is considered as Na–Ca–Cl type with minor and traces elements like lithium, lead, arsenic or antimony and a pH comprised between 5.00 and 5.77. Additionally, main dissolved gases in these fluids are CO_2 (90%), N_2 (8%) and CH_4 (2%) with a Gas Liquid Ratio in a range of 1.0 to 1.3. Consequently, the combination of low pH and high content of chlorine contributes to enhanced geothermal fluids natural corrosive effect on most steel grades. Moreover, during the heat transfer in geothermal plants, liquid-solid equilibrium is changing, leading to barium sulphate precipitation and metal-rich (Pb, Fe, As, Sb) sulfides. They can co-precipitate together with radioactive isotopes, creating Naturally occurring Radioactive Materials (or NORMs). These by-products enriched with radioactive elements leads to health hazards for operators, and environmental damages in case of discharge. All of these reasons, clearly highlight why geothermal plants in the URG require an effective control of scaling and corrosion.

The work described in this paper is related to the development of a new solution for the Rittershoffen geothermal plant, located in the URG. Although, the facility is currently using two separate technics for controlling sulphate / sulfide deposition and corrosion issues, a manual hazardous (mostly due to the presence of NORMS) cleaning of the heat exchangers is required once a year. Scales have a significant impact on plant efficiency and power generation; therefore, it is necessary to develop a scale inhibitor with higher performance. Furthermore, this anti-scaling technology needs to be compatible with the current anti-corrosion agent. Therefore, both products would be injected close together before the heat exchanger where main scaling and corrosion issues are typically observed.

To produce this new technical solution, an extensive work in the lab has been done. Due to high amount of calcium in the solution, ensuring compatibility with the geothermal brine was a critical point. Several compatibility tests with geothermal brine and the current corrosion inhibitor, in addition to performance against barite and lead sulfide, have been assessed. All these experiments were achieved by applying conditions close to geothermal brine operation.

As a result of this work, a new technology having significantly better performance has been developed and industrialized to be used onsite during several months. This period of trial allows to check under real field conditions the efficiency of new NORMs inhibitor and to confirm all the results obtained in the lab.

INTRODUCTION

Geothermal potential was identified in the URG for decades thanks to the research on the Enhanced Geothermal System (EGS) pilot plant at Soultz-sous-Forêts, 50 km in the North of Strasbourg, France (Genter et al., 2018). The URG is a rifting formation, oriented NNE, part of the European Cenozoic rift system. It spreads over a length of 300 km, from Basel (Switzerland) to the South to Mainz (Germany) in the north. Important thermal anomalies were identified in this area owing to a rich geological exploration. These anomalies delineate thermal gradient locally over 100°C/km in the first km of sediments and are controlled with normal faults parallel to the graben direction. On the French side of the URG, two plants were commissioned in 2016, producing heat (Rittershoffen) and electricity (Soultz-sous-Forêts) under industrial conditions.

1.1 Rittershoffen geothermal site

The Rittershoffen geothermal project was developed to supply heat for industrial processes in a starch plant operated by Roquette Frères Company. The geothermal heat plant, with an installed capacity of 24 MWth, is providing the whole of its heat production to this company via an isolated heating transport loop of 15 km length (Ravier et al., 2017). The geothermal brine is produced at a temperature of 170°C from a production well, GRT-2 at 2700 m depth that penetrated into Triassic sedimentary layers and the top crystalline fractured basement interface (Baujard et al., 2015, Baujard et al., 2017). Furthermore, the produced brine is flowing through a system of twelve consecutive tubular heat exchangers (Ravier et al., 2016), and it is fully reinjected without additional pumps at 80°C into one injection well, GRT-1, at 2500 m depth. This geothermal plant successfully produced heat since June 2016 under commercial conditions.

1.2 Corrosion and scaling issue in the URG

Geothermal fluids at Rittershoffen is a Na-Ca-K-Cl dominated brine with a pH about 5 at 50°C (Bosia et al., 2021). The major elements constituting the brine composition and Non-Condensable Gases (NCG) content are given in Table 1. Minor species (< 0.5 g/L) are also present in the fluid such as Ba^{2+}, Li^{+}, Mg^{2+} Sr^{2+}, and SO_4^{2-}, together with trace elements (< 0.05 g/L) like Pb, As, Sb and B.

Table 1: Minimum and maximum values of Rittershoffen brine composition in (major species and NCG concentrations)

Major species in fluid in g/L	Minimum	Maximum
Cl^-	57.4	67.3
Na^+	26.0	29.0
Ca^{2+}	7.4	8.9
K^+	3.4	3.9
Gases content in %	**Minimum**	**Maximum**
CO_2	88.1	92.9
N_2	5.2	9.7
CH_4	1.8	2.4

Thermodynamic equilibrium variation occurs in heat exchangers due to the brine temperature decrease, which leads to scale formation (Mouchot et al., 2018). In the URG fluids, most common mineral precipitations are sulfates (barite, celestite), sulfides (galena, pyrite), nanocrystalline intermetallic mixed compounds (such as Sb, As), elemental metals (Pb, As, Sb), oxides metals and carbonates (Haas et al., 2018). Those scales can trap, in their crystalline lattices, radionuclides such as ^{226}Ra and ^{210}Pb that come from the decay of uranium and thorium naturally present in the granite mineral at high depth. However, the use of sulfate inhibitors can greatly reduce the precipitation of barium sulfate in surface equipment and limit the formation of multi-metallic sulfides. (Mouchot et al., 2019). These scale inhibitors work by forming water-soluble complexes to slow down crystal growth. Their combination with an anti-corrosion inhibitor with "filming" properties also reduce the formation of sulfides minerals (Scheiber et al., 2019). The general corrosion of mild steel is expected to be below 0.2 mm/year in the URG (Mundhenk et al., 2013).

The schematic representation of the process and the areas prone to corrosion and scaling problems in geothermal plants are depicted in Figure 1. Geothermal fluids of Rittershoffen are corrosive which can cause low-alloy steel tubing, casing, and other components to fail as a result of corrosion. Severe localized corrosion of steels, and scaling lead to shut down of the plant for maintenance operations (reducing production efficiency). Although the use of selected inhibitors was shown to reduce the frequency of such incidents (Scheiber et al., 2019), corrosion and scaling remain ongoing concerns and can result in materials and equipment failures, as well as environmental problems. Thus, Total Cost Ownership, including capital expenditure (CAPEX) and operational expenditure (OPEX) are affected by corrosion and scaling. Consequently, economic viability and durability of geothermal projects in the URG are dependent of the management of those problematics.

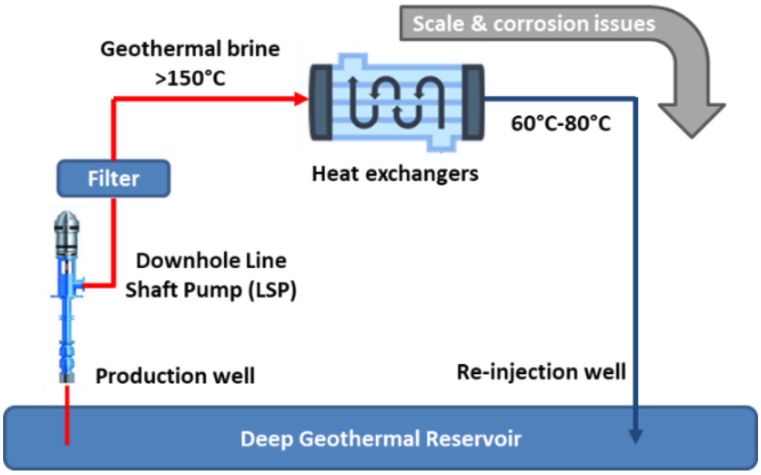

Figure 1: Corrosion and scale issues at the Rittershoffen geothermal plant

Methodology

Three different experiments were conducted to check the efficiency of the new products developed.

a) Brine compatibility

Compatibility of the scale inhibitor with the geothermal brine was performed using 60ml glass vials (AceGlass) equipped with PTFE caps and a Binder M series oven. Synthetic Rittershoffen geothermal brine (Table 2) was freshly prepared before every test with a pH of ~5 (CO_2 injection). Scaling anions were removed to avoid the precipitation of inorganic scales. Inhibitors were dosed at 1% (e.g., 1 mL of the inhibitor + 99 mL of brine) in the synthetic brine and stored for 1 hour at 170°C. Visual aspect and pH of the solution was recorded immediately after the addition of the inhibitor and at the end of the test. For instance, presence of precipitate, phase separation or high turbidity indicates an incompatibility between the inhibitor and the brine.

Table 2: Brine chemical composition used for compatibility test, barium sulfate static test, and lead sulfide dispersion test. *pH is unitless.

	Brine composition (mg/L)		
Ions	Compatibility test	Barium sulfate static test	Lead sulfide dispersion test
Na^+	27957	20550	25000
K^+	3893	385	-
Mg^{2+}	111	900	-
Ca^{2+}	7450	1756	6400
Sr^{2+}	492	330	-
Ba^{2+}	19,3	125	-
Cl^-	65027	37193	90000
SO_4^{2-}		1240	1000
HCO_3^-		67,5	-
pH*	5-5,5	5,5	6

b) Barium sulfate static test

This test was performed to assessed inhibitor performance against barium sulfate, one of the scale types that affect Rittershoffen plant. As the concentration of barium in the real brine is too low for getting reliable and reproducible results in this type of test, it was decided to use a standard brine (Table 2) and more severe conditions compared to the field.

Barium sulfate inhibition properties of the scale inhibitor were evaluated following the NACE TM0197-2010 protocol. Test temperature was set at 90°C and residual barium in solution was analysed by ICP-OES after 10 minutes, which is the expected residence time of the geothermal brine in Rittershoffen plant. Testing dosage of the scale inhibitor was 20 ppm, higher than what is currently dosed in the field. The reason is that, for this test, the Saturation Index for Barite calculated using a software (Scale Soft Pitzer from Rice University) is 2.39 while the theoretical deposit rate is 212mg/L and both values are higher than what is calculated for Rittershoffen plant (0.16 and 9mg/L respectively).

The same test was then repeated adding 27.7 ppm of the corrosion inhibitor currently used in the plant. This dosage was selected to maintain the current scale inhibitor / corrosion inhibitor field ratio.

c) Lead sulfide dispersion test

Dispersion/inhibition test of lead sulfide (PbS) was performed at room temperature in 250 mL glass jars (Matheis et al., 2019). Brine considered for the test (Table 2) was adapted from a real geothermal water source (Bruchsal plant). Lead sulfide was produced in the testing jars by adding aqueous solutions of lead acetate and sodium sulfide subsequently to the brine in stoichiometric ratio.

In total, 200 mL of the synthetic brine were produced in the testing jars and the magnetic stirring was set at 200 rpm. The required amount of scale inhibitor, lead and sulfide were added to the brine in this specific order to avoid any early precipitations. The jar without the addition of scale inhibitor was considered as a blank.

Testing solutions stirred for 3 minutes leading to a reasonable PbS particles growth in the blank. After 3 minutes of stirring the agitation was stopped and the turbidity of the solutions was continuously monitored for 6 hours using a portable HACH 2100Q IS turbidimeter.

RESULTS AND DISCUSSION

a) Brine compatibility

Chemistries identified as potential candidates were screened considering their compatibility with the synthetic brine (Figure 2).

	Scale inhibitor A		Scale inhibitor B		Scale inhibitor C		Scale inhibitor D		SPE2122 A		SPE2122 B		SPE2122 C	
Dosage (ppm)	t=0	t=1h	t=0	t=1h	t=0	t=1h	t=0	t=1h	t=0	t=1h	t=1	t=1h	t=2	t=1h
0.01%		ppt		sl. Turbid		sl. Turbid		sl. Turbid						
0.1%	turbid	ppt		turbid		sl. turbid		ppt						
1%	ppt	ppt	sl. Turbid	ppt	sl. Turbid	ppt	sl. Turbid	ppt						
2%	ppt	ppt	turbid	ppt	sl. Turbid	ppt	turbid	ppt						

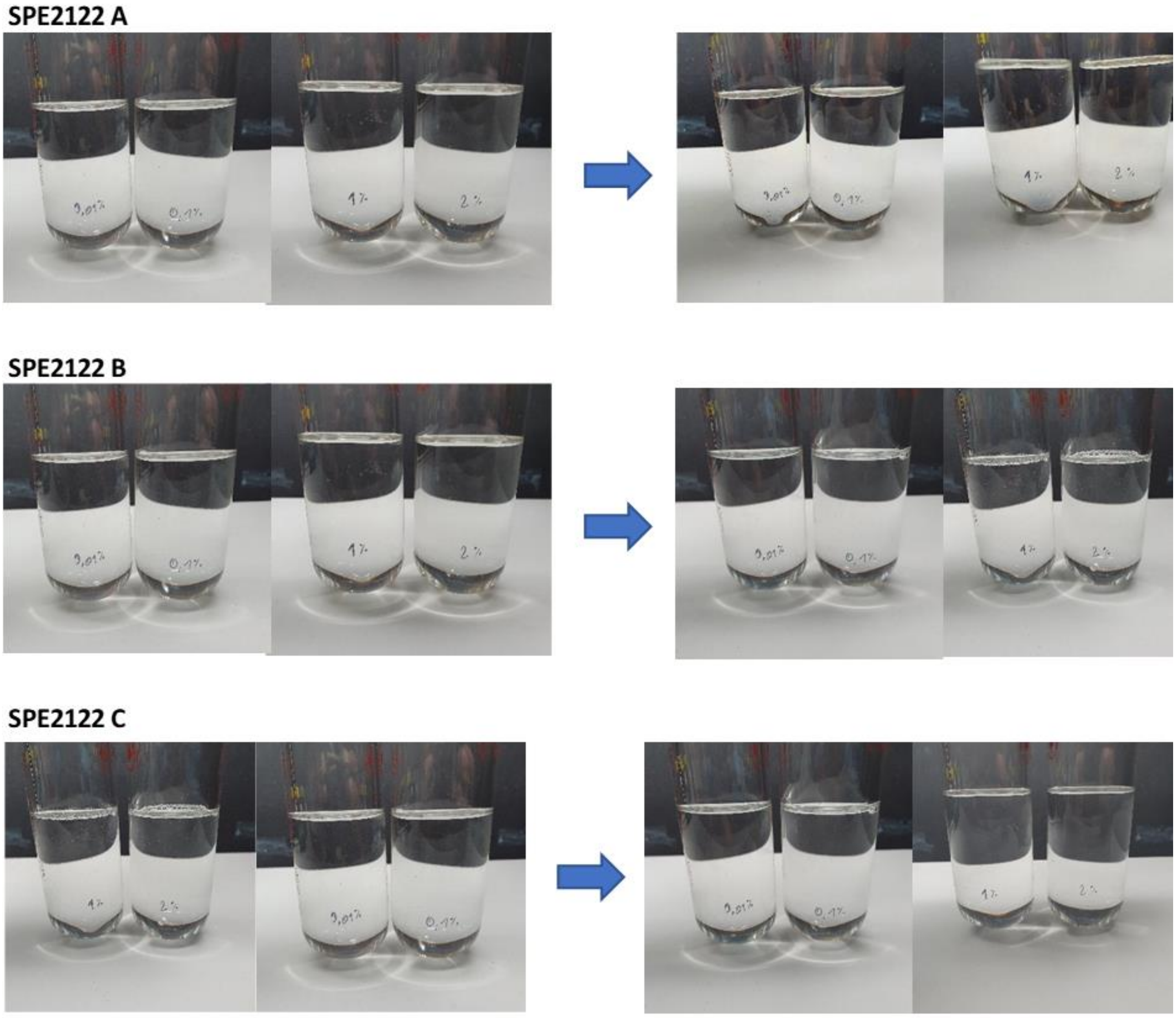

Figure 2: Compatibility of different scale inhibitor with synthetic Rittershoffen brine. Green color highlights the compatibility of the product with brine at a time and concentration given. Orange color indicates an increase of the turbidity and red color (ppt) indicates that precipitation occurred during the experiments. In the pictures, on the left compatibility (0.01%, 0.1%, 1% and 2% respectively) at t=0, on the right compatibility after 24h.

Due to the high calcium content and salinity, most of the technologies tested failed this test, leading to precipitation after about 1h at high temperature. Only few solutions (named as SPE2122 A, SPE2122 B and SPE2122 C) showed a compatibility with the brine and therefore, they were included in the performance tests.

b) Barium sulfate static test

Barium sulfate static tests were performed on the SPE2122 A, SPE2122 B and SPE2122 C products that successfully passed the compatibility test. The objective is to check if the products can reduce the growth of barium sulfate in the solution (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

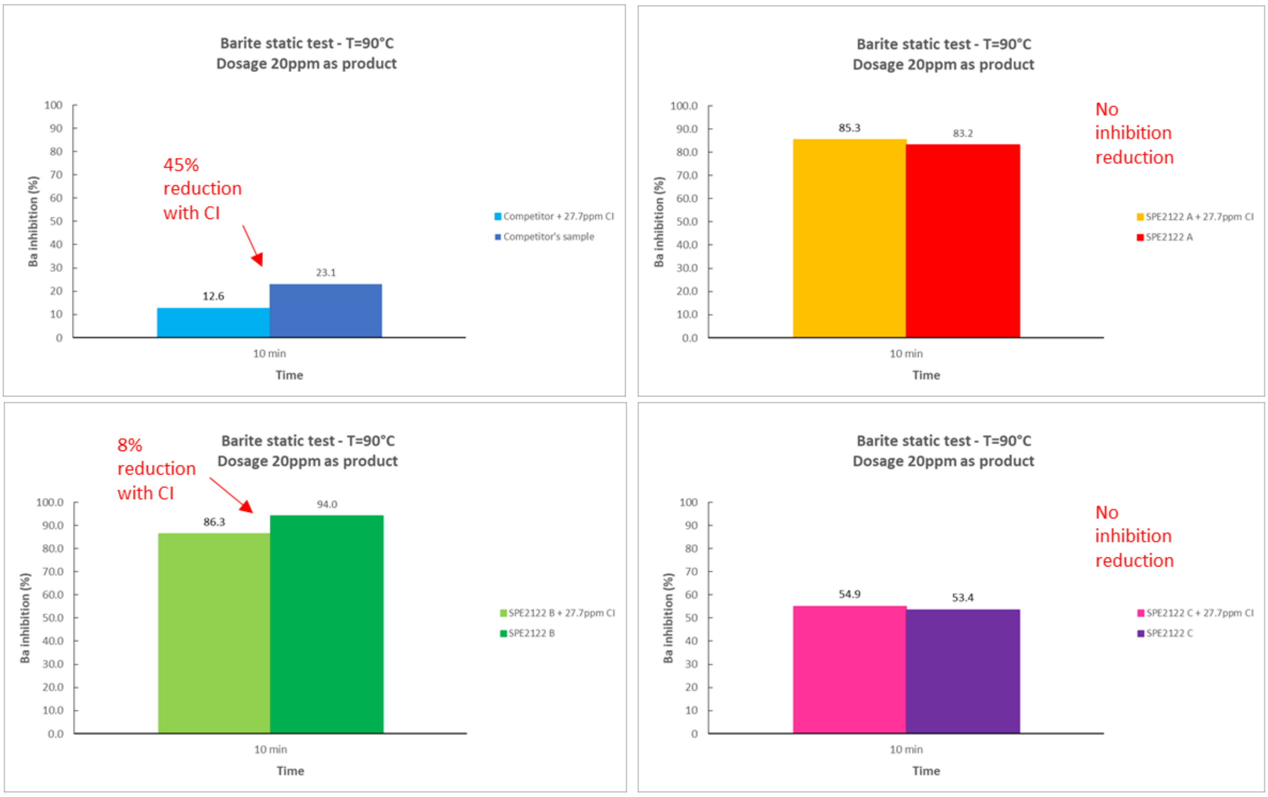

Figure 3: Barite static test results. Differences of the products efficiency with and without a corrosion inhibitor are highlighted in red.

Both SPE2122 A and B provided excellent performance, with an inhibition higher than 80%. SPE2122 C gave a slightly lower result while competitor's sample inhibition was only slightly higher than 20%.

Interesting to note that, in the presence of corrosion inhibitor, the inhibition decreased for both competitor's sample (45 % reduction) and SPE2122 B (8 % reduction), while for SPE2122 A and SPE2122 C performance variations are within the experimental error. Inhibition reduction could be related to an interaction between anionic scale inhibitors and (partially) cationic corrosion inhibitor.

c) Lead sulfide dispersion test

The second performance test was made to reduce the lead sulfide scale formation, another scale type that are formed in Rittershoffen plant. This scale has a very low solubility constant (2.6 $\times 10^{-11}$ kg/kg) which makes it difficult to be inhibited. Instead of relying on a threshold inhibitor, a dispersant is often a more effective approach. The objective of this test was to assess the dispersion properties of the different products under consideration. To have a measurable turbidity in the testing vessel, the amount of Pb used was significantly higher than what can be detected in the geothermal brine, leading to harsh conditions that necessitated a high amount of inhibitor (50 ppm as product) to observe any effect (Figure 4).

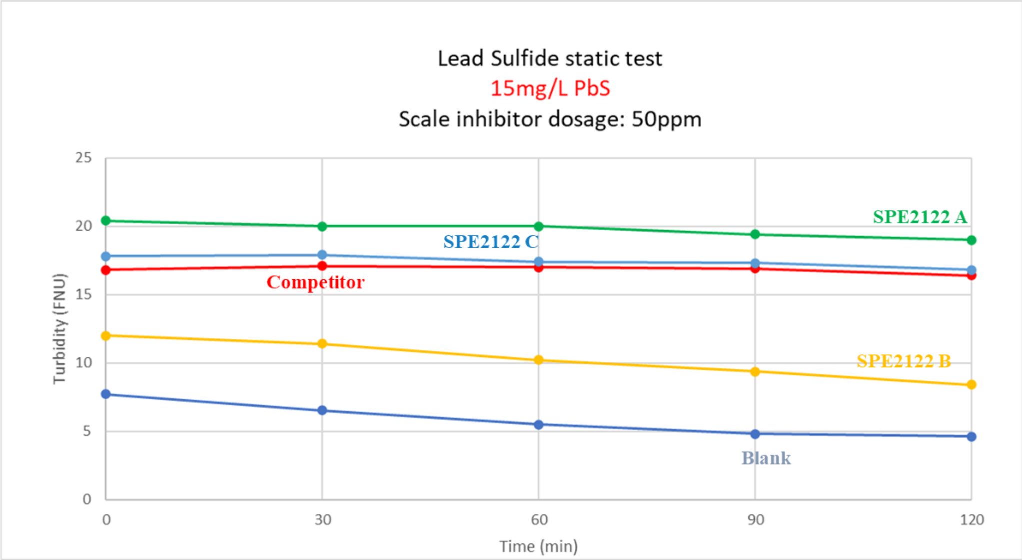

Figure 4: Results of PbS dispersion test (above).
In the pictures (t=0 and t=2h respectively), from left to right: Blank, Competitor, SPE2122 A, SPE2122 B, SPE2122 C

Competitor's sample, SPE2122 A and SPE2122 C provided best performance, keeping turbidity stable over the two hours of test which means that most of PbS particles remained well dispersed in solution. On the other hand, for blank and SPE2122 B a significant decreasing of turbidity over the time was observed. In these two vials, after 2 hours, a severe deposition was observed while for the other products tested, the visual aspect of the solution didn't change significantly and Lead sulfide particles remained well dispersed.

Furthermore, the higher starting turbidity observed for competitor's sample, SPE2122 A and SPE2122 C seems to be related to the dimension of PbS particles. In particular, the higher the turbidity, the smaller and more stable are particles of Lead sulfide (Matheis et al., 2019).

This test was also repeated adding the corrosion inhibitor but compared to barium sulfate static test, no significant effect on performance was observed for all the tested inhibitors. It appears that the presence of a corrosion inhibitor slightly slows down the formation of lead sulfide particles in the test, though further investigation is required to confirm this effect.

CONCLUSION

NORMs scale formation occurs at Rittershoffen geothermal power plant can lead to health hazards or losses of efficiency. The high temperature and high dissolved solids of the fluids create challenging conditions that require a specially designed inhibitor solution to reduce the occurrence of NORMs. Furthermore, presence of corrosion inhibitor needs to be considered as it can interact with the scale inhibitor, decreasing the efficiency of both inhibitors and could lead to unexpected issues in the field.

Results described in this paper confirmed that a scale inhibitor, SPE2122 A, is a promising candidate to be used on the Rittershoffen geothermal plant. Indeed, the product is compatible with the brine at high temperature, effective against barium sulfate formation (> 80% inhibition) and lead sulfide (no significant deposition after 2 hours) scales. No negative interaction or decrease in the performances were observed with the incumbent corrosion inhibitor, making it a great candidate for a field trial.

Tests performed with synthetic brine are essential to evaluate the effectiveness of various scale inhibitors, particularly in high-salinity fluid environments like the URG. The results of these tests will provide a basis for conducting a field trial, which will aim to validate and corroborate the laboratory findings using a fresh geothermal brine.

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