

A Novel Approach for Selecting and Evaluating BaSO₄-scale Inhibitors under in-situ Conditions

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Abstract

During the operation of geothermal plants in the Upper Rhine Graben, secondary mineral formation and precipitation—primarily barium and strontium sulfates, along with metal sulfides—are frequently observed as a result of pressure and temperature fluctuations. A promising strategy to mitigate these issues is the application of scale and corrosion inhibitors.

Within the framework of the EIKE project (Development and testing of inhibitor combinations for the efficient use of hydrothermal reservoirs, grant number: 03EE4022), funded by the German Federal Ministry for Economic Affairs and Climate Action, inhibitors from various substance classes were selected and tested in combination for potential practical use. (Heberling et al., 2024). This process involved a series of preliminary investigations, progressing systematically from compatibility screening tests to turbidity measurements, to assess the efficiency of scale inhibitors both with and without the presence of corrosion inhibitors.

These investigations led to the identification of a combined inhibitor product suitable for application in the Upper Rhine Graben. The research aimed to prevent the problem of solids formation and deposition with just one chemical application to simultaneously inhibit barium sulfate formation and prevent corrosion.

The study presented here is intended to demonstrate how a safe inhibitor combination and its minimum application concentration can be systematically developed. A particular innovation here is that compatibility can be tested not only in the laboratory but also via a tube-blocking test facility developed by KIT-ITES, which can be directly integrated into the geothermal plant's thermal water cycle.

1. Selection of starting materials

Since phosphonates successfully prevent barium sulfate formation, the commercially available inhibitors were tested according to the following aspects:

1. Good availability of substances (deliverability, diversification of producers)
2. The respective active component should be a defined compound
3. The active components should be identifiable based on the data sheets, or at least the substance classes should be recognizable
4. Exclusion of aquatically toxic substances to ensure that the water hazard is classified as WGK 1 (Wassergefährdungsklasse = Water Hazard Class according to German water law) in the formulation
5. Good solubility in water or a solubilizer should enable dispersion in water

The selection of substances to be procured was based on the molecular structure, i.e., the type of functional groups, the molecular size, and the associated surfactant chemical properties.

2. Investigation program

The following sequence was established to assess the suitability of individual substances for the formulation process:

1. Compatibility of individual substances with the geothermal brine:

The substances should not cause turbidity or precipitations when added to the model or original brine at 60°C. To evaluate this, they were tested at different application concentrations (2.5%, 1%, 0.25%, 0.1%), significantly higher than the actual concentration used in the geothermal power plant.

2. Stable formulation (combination):
During the formulation process, various concentration ratios of active components were prepared with the addition of solvents, and the pH was adjusted. Only mixtures of scale and corrosion inhibitors that did not exhibit phase or solid formation even after thermal treatment were classified as stable.
3. Compatibility of the inhibitor combination with geothermal brine, following the procedure described in point 2.
4. Good efficiency of the combination against BaSO_4 precipitation comparable to the pure scale inhibitor. (Assessment of the influence of the corrosion inhibitor on the effectiveness of the scale inhibitor.)
5. Verification of anticorrosive properties by determining the corrosion rate of the formulation through long-term immersion tests, electrochemical polarization tests (including mechanism analysis), and corrosion tests in the bypass corrosion test stand (CORA-Loop at KIT-ITES).
6. No negative effects on the reservoir rock's capacity to absorb reinjected fluid containing the inhibitor.

3. Efficiency tests

3.1 Turbidity measurements

Turbidity measurements have proven effectiveness in determining the reaction progress of barium sulfate precipitation over time. A measure of light scattering by undissolved particles in a turbid solution is the resulting reduction in transmission. The aim of the investigations was to assess the extent to which the efficiency of scale inhibitors is impaired by corrosion inhibitors.

Experiments were conducted with phosphonates in combination with corrosion inhibitors. Previous studies have shown that the simultaneous use of a corrosion inhibitor can negatively affect the performance of the scale inhibitor (Scheiber et al., 2019).

The following solutions were produced for the laboratory experiments:

1. Primary salt solution: Model brine (1.393 mol/L NaCl, 0.206 mol/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 5.09 mmol/L $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, filtered via 0.45 μm cellulose acetate filter)
2. Secondary solutions: Na_2SO_4 and BaCl_2
3. Test products: Phosphonate 1, Phosphonate 2, Phosphonate 2 in combination with commercially available corrosion inhibitor A and corrosion inhibitor B

In a tightly sealed glass vial, 50 mL of the Na-Ca-Sr-Cl model salt solution was heated to 60°C for at least 24 hours. Then, 0.5 mL of a diluted inhibitor solution was pipetted in to achieve an inhibitor concentration of 10 mg/L. Subsequently, a diluted Na_2SO_4 solution and a BaCl_2 solution were added in sequence. After briefly shaking the solution, this moment was defined as the reaction start $t = 0$. To subject the inhibitor combination to a stress test, barium and sulfate were added at four times the concentration of the original fluid (Concentration factor $\text{CF} = 4$).

Transmission was measured using a Photometer SQ 118 (Merck) at 405 nm, and the resulting absorbance values were analyzed over time. The samples were kept in an incubator (Certomat H, Braun) at a temperature of $60^\circ\text{C} \pm 0.5^\circ\text{C}$ under dynamic conditions ($n = 125$ rpm, Certomat S) for a maximum of 50 hours. Each measurement was based on at least three parallel experiments.

3.1.1 Results

Figure 1 shows the absorbance development over time. Visually, no solids were recognizable in all four test series. Only a very slight increase in absorbance can be seen in the combinations of scale and corrosion inhibitor. This observation is confirmed by the analytical results of the residual Ba ion concentrations determined at regular intervals in filtered samples (Figure 2).

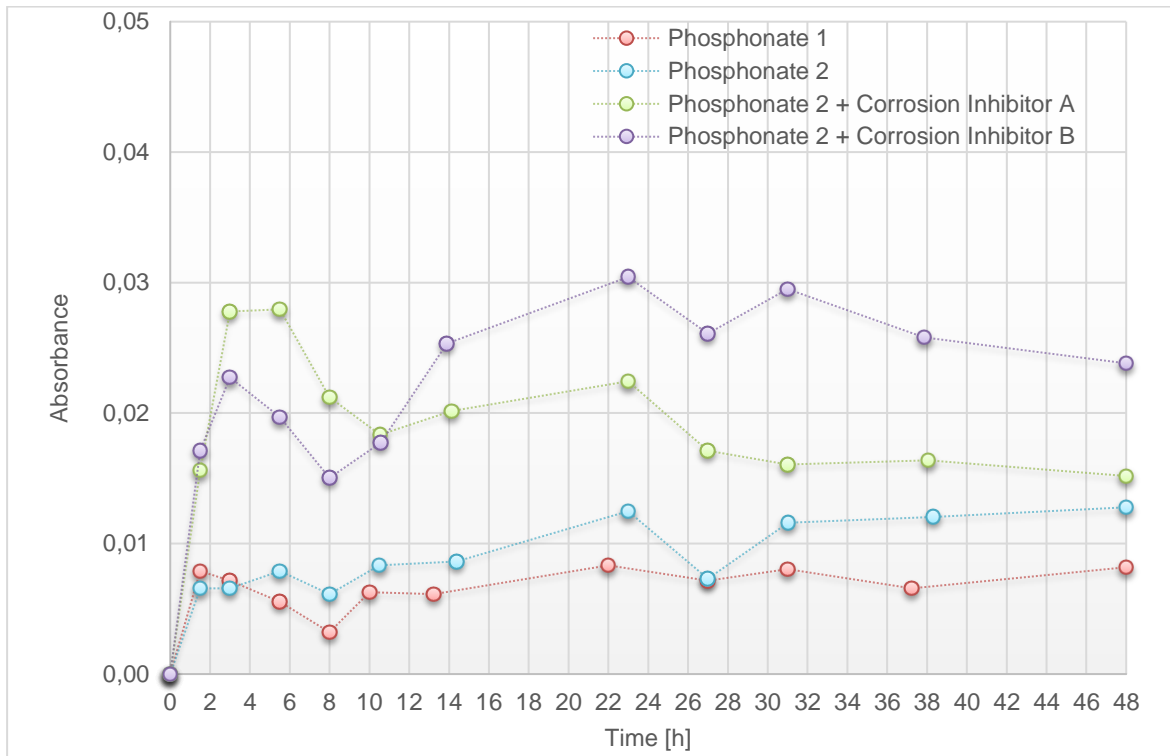


Figure 1: Absorbance versus reaction time, CF= 4, Ba baseline concentration=152 mg/L, T= 60 °C (± 0.5 °C), n=145 rpm, inhibitor concentration each c=10 mg/L

In the first six hours of reaction time, the Ba values fluctuate considerably so that no clear tendencies are recognizable. In general, the inhibitor efficiency (remaining proportion of the initial Ba content in the solution) remains above 80 % during the entire observation period in all experiments. The barium sulfate inhibition with the phosphonate remains largely unaffected by both corrosion inhibitors used under the selected test conditions.

Both the results of the turbidity measurements and the evaluation of the residual ion concentrations of barium in the solutions, which are determined at regular intervals, show that corrosion inhibitor A and corrosion inhibitor B reduced the efficiency of the scale inhibitor phosphonate 2 almost equally to a small extent.

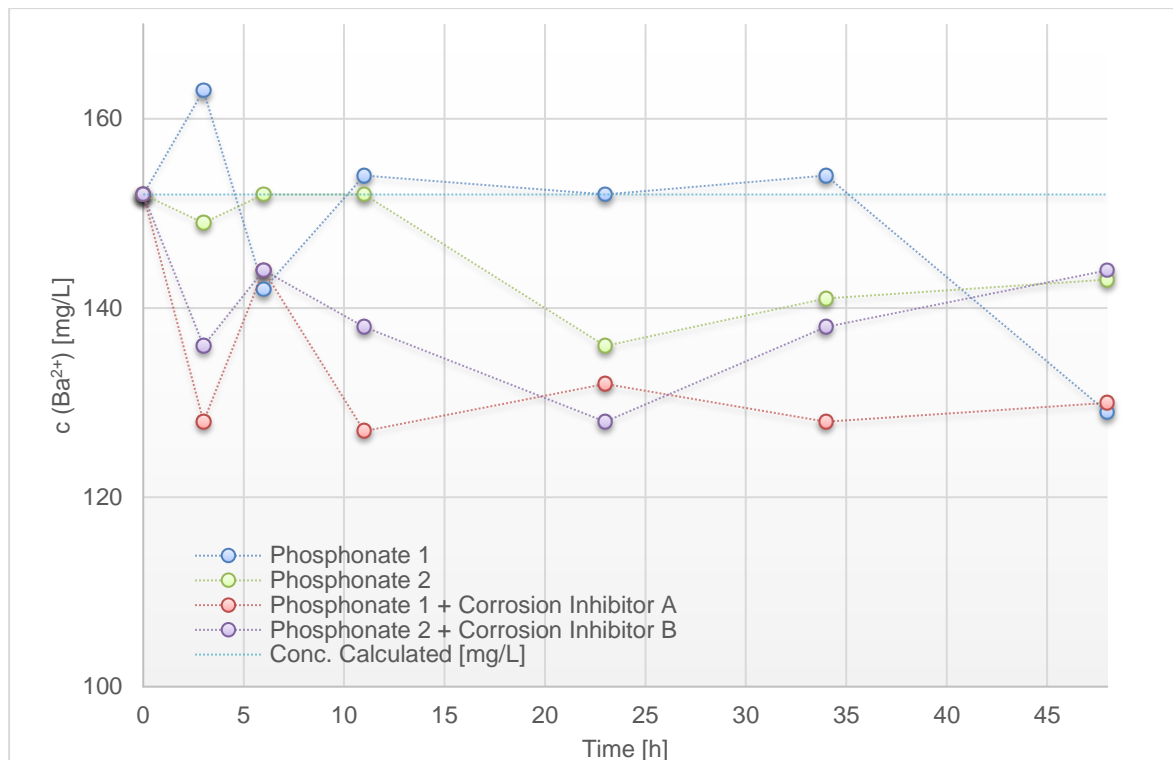


Figure 2: Residual barium ion concentrations versus reaction time; CF4, T= 60 °C (± 0.5 °C) and a shaking speed of n=145 rpm; Inhibitor concentration c=10 mg/L

3.2 Bypass system for determining the minimum application concentration of scale inhibitor

The minimum effective concentration of the scale inhibitor is typically determined using dynamic Tube Blocking Tests (TBT) (Kelland, 2014). While such tests are typically conducted in laboratories with synthetic thermal water, a key innovation in this study was the development of an open bypass system by KIT-ITES, which can be directly integrated into the geothermal plant's thermal water cycle (Figure 3).

In this setup, barium chloride and sodium sulfate solutions—with or without inhibitors—are introduced into the original fluid stream. The resulting barium sulfate-supersaturated fluid flows through a capillary, where precipitated solids adhere to the walls. This gradually reduces the flow rate as the capillary becomes progressively blocked, enabling a dynamic evaluation of scaling behavior. This is intended to create an opportunity to carry out tests with real thermal water directly at the power plant on the open bypass. After the construction of the plant, it was first tested and optimized in the laboratory with model water.

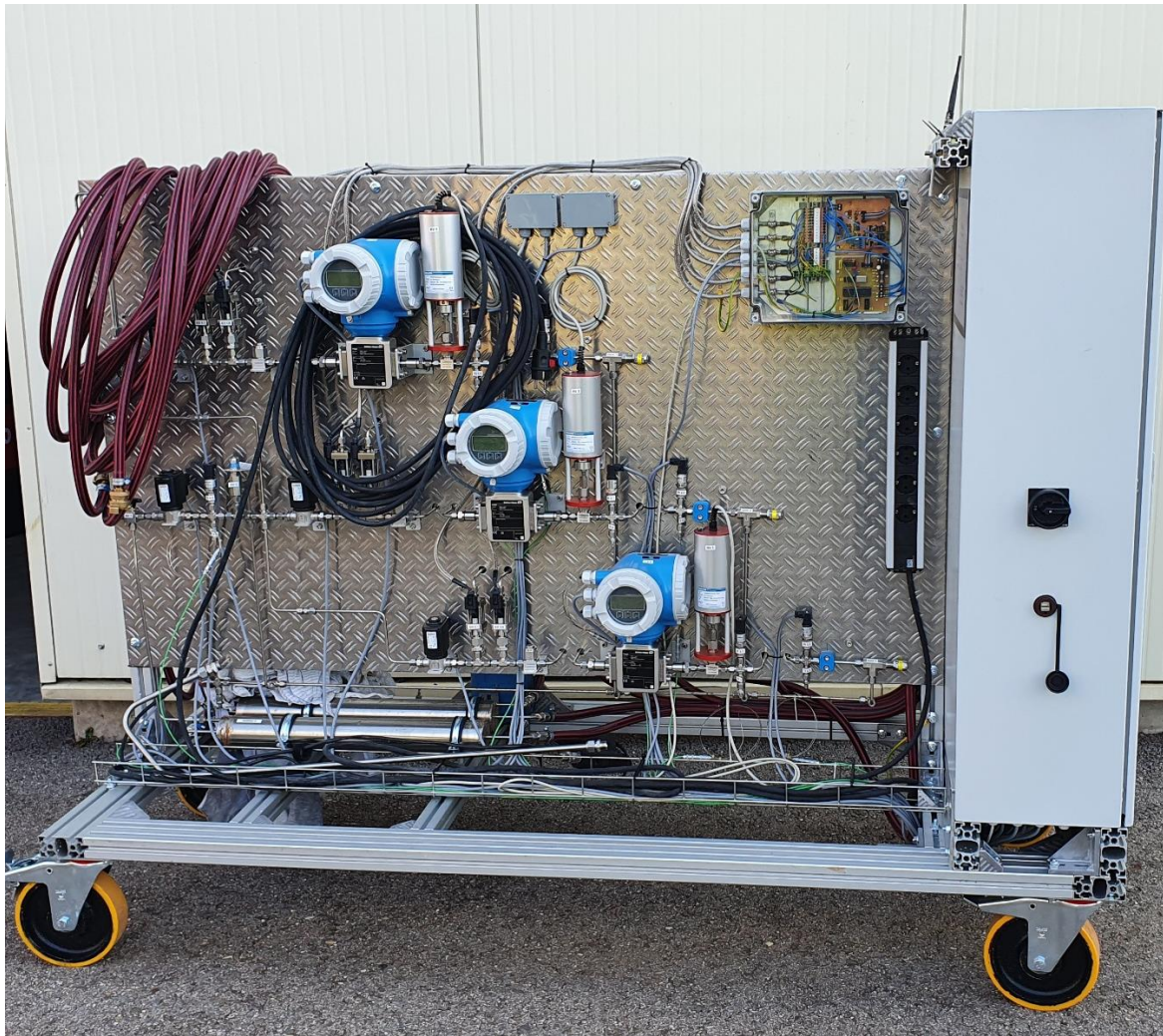


Figure 3: Field tube blocking test facility

In the laboratory tests, a pump was used to transport the model water (primary salt solution) with a predefined flow rate via a heating hose into the plant, where the fluid is then separated into two streams. During the on-site tests, the thermal water was directly extracted from the production well via a bypass without cooling, flowing into the plant and splitted into two streams.

The further process steps are identical, regardless of whether laboratory or power plant tests are carried out. The secondary salt solution containing barium chloride was injected into one stream via an injection nozzle. The secondary salt solution containing sodium sulfate (possibly mixed with inhibitor) was injected into the other steam. There is a mixing chamber after each of the two injectors so that these secondary salt solutions mix homogeneously with the primary salt solution. The solutions from the two streams are then combined and mixed. The resulting experimental solution flows through a capillary tube (1 m long, 1 mm diameter) and then into a collection vessel.

The addition of the secondary salt solutions to the primary salt solution in separated fluid streams and the subsequent combination have proven to be necessary to achieve optimal mixing, which was a prerequisite for reproducible results. The increasing formation and deposition of barium sulfate in the capillary tube causes a continuous reduction in the flow velocity until it drops to 0 L/h. Effective inhibitors prevent an increase in pressure in the capillary or a reduction in the flow velocity within a predefined measurement time. The suitable operating conditions were determined in a series of preliminary tests in the laboratory.

The aim was to set the parameters so that in experiments without an inhibitor, the blocking takes place in less than 15 minutes. In addition, there should be a significant difference in the blocking time compared to the inhibitor trials. In addition, the concentration of barium sulfate should be as small as possible so that the difference to the real conditions when using an inhibitor in the power plant (concentration factor = 1) is not too great. Table 1 shows the resulting operating conditions.

Table 1: Operating Conditions in Tube Blocking Tests

Operation Conditions	Laboratory tests	Field tests
Pressure before outlet [bar]	5.4	20.5
Setpoint inlet temperature [°C]	60	60
Concentration factor barium	4.5	4.5
Sulfate concentration factor	4.5	4.5
Primary saline solution flow rate (inlet) [L/h]	2.45	---
Total flow rate (outlet), calculated [L/h]	2.60	---
Thermal water flow rate (inlet) [L/h]	---	2.45
Total flow rate (outlet), calculated [L/h]	---	2.60

3.2.1 Results of laboratory tests

Before the actual dose-optimization experiments, it was necessary to test which concentration factor of barium and sulfate ions had to be selected at a given flow velocity in order to provoke significant precipitations without the use of an inhibitor within a workable time (possibly at different test temperatures). Furthermore, reproducibility tests were necessary, i.e., repeatability of the scaling formation through multiple measurements without inhibitor and to optimize the preliminary tests (temperature drop, flow velocity, test duration). A measure of the reproducibility of the results is the time to block, which should be almost the same for at least 3 attempts, thus representing an average time for the blank value.

Figure 4 compares the flow rates of the tests without inhibitor (V10) and with inhibitor (V13) over the test time until termination, demonstrating the effectiveness of previously mentioned phosphonate 2.

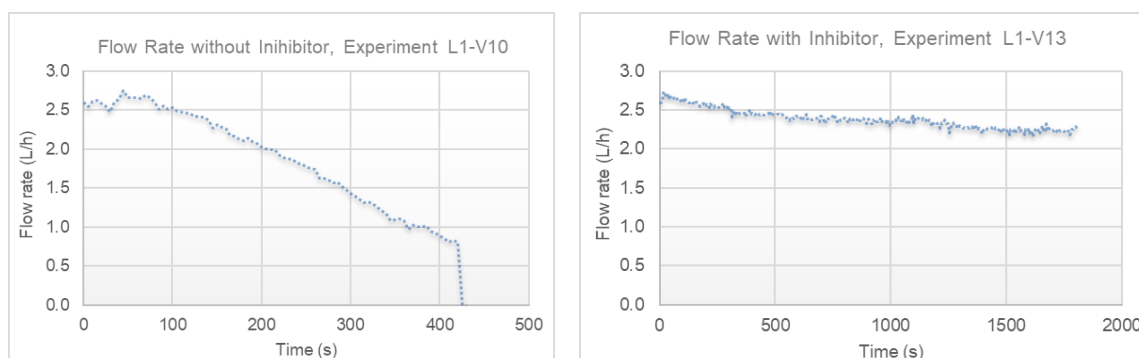
Figure 4: Flow rate in L/h vs. time, left V10 without inhibitor; right V13 with phosphonate 2 ($C_{\text{product}} = 20 \text{ mg/L}$)

Table 2 shows the results of the laboratory experiments depending on the inhibitor concentration used at $T = 50.9 \text{ }^{\circ}\text{C} \pm 0.5 \text{ }^{\circ}\text{C}$, at an initial flow rate of 2.45 L/h and a concentration factor of 4.5.

The result is clear with the addition of 2 mg/L phosphonate 2, where the flow rate fell to 0 L/h after only 8 min (n=3). From an inhibitor concentration of 10 mg/L, the experiments were terminated after 30 minutes. However, the final speed here fluctuated between 1.43 and 2.36 L/h.

Table 2: Results of laboratory tests, $v = 2.45$ L/h, $CF = 4.5$

Number (n) of evaluated trials	3	3	6	4 / 3	3	6
Inhibitor mass concentration in test solution [mg/L]	20.0	15.0	10.0	5.0	2.0	0.0
Corresponding real inhibitor mass concentration [mg/L]	4.4	3.3	2.2	1.1	0.4	0.0
Time until blocking [min]	30	30	30	6.8 / 30	8	6.8

3.2.2 Field experiments

In order to prove the reproducibility of the tests on the one hand and to further specify the minimum application concentrations on the other, several tests were carried out in the field. A selection of results from field measurement campaigns is presented in Table 3.

Table 3: Averaged results of the tests in the field measurement campaign, $v = 2.45$ l/h, $CF = 4.5$

Number (n) of tests evaluated	2	3	3
Concentration Factor of barium sulfate	4.5	4.5	4.5
Inhibitor mass concentration in test solution [mg/L]	0.0	6.75	9.00
Corresponding real inhibitor mass concentration [mg/L]	0.0	1.5	2.0
Time until blocking [min]	13	19	> 30

With the application of a concentration factor of barium sulfate of 4.5 without inhibitor, a complete blocking of the capillary was achieved after about 13 min in two experiments. Under the same operating conditions, there were also tests in which no blockage occurred within 30 minutes. In the evaluation of the subsequent tests, the blockade at 13 min was assessed as realistic. The reason why the capillary was not blocked within a specified test time of 30 minutes in the other experiments may possibly be due to the fact that contamination in the fluid (oil from pump lubrication) prevented the deposition of the formed solids in the capillary.

The curves of the tests with 6.75 g/L inhibitor (n=3) are shown in Figure 5 on the left. The time until the capillary was blocked ($v = 0$ L/h) was an average of 19 min, which was only about 6 min higher than the comparable results of the experiments carried out without an inhibitor. The results of the experiments with 9.0 mg/L inhibitor are documented in Figure 5 on the right. Here, there was no blockage of the capillary within the test time of 30 minutes.

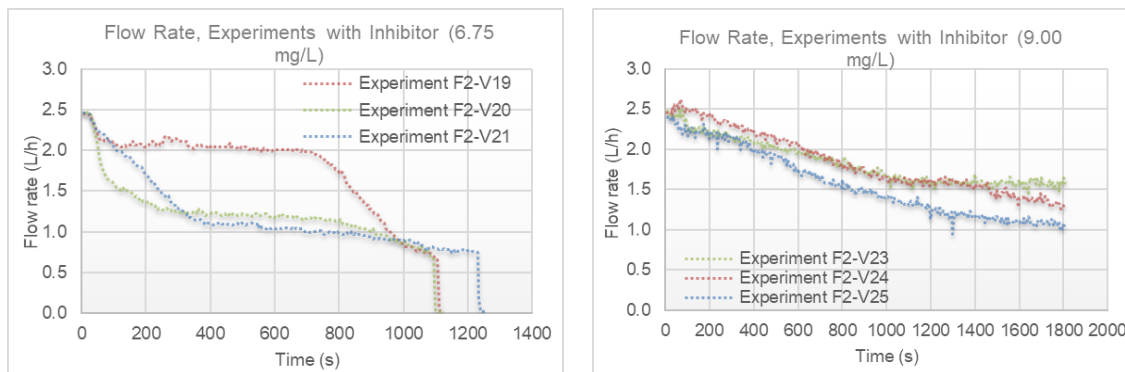


Figure 5: Comparison of flow in L/h vs. time, CF = 4.5. Left: Experiments F2-V19 to F2-V21 with 6.75 mg/L phosphonate 2. Right: Tests F2-V23 to F2-V25 with 9.00 mg/L phosphonate 2.

4 Conclusions

As part of the EIKE project, a systematic procedure for the selection of inhibitors for geothermal plants was developed. In a first step, inhibitor combinations will be fundamentally characterized in the laboratory using turbidity measurements. Thus, a basic functionality with reservoir-analog artificial fluids can be cost-effectively tested for a wide range of combinations.

For a realistic test of the inhibitor combinations as well as for the determination of the minimum application concentration, a bypass system was also developed, which, in addition to the conventional tube blocking tests, allows inhibitors to be tested on site with original fluid. The bypass system was designed in such a way that fluid can be taken directly from the thermal water circuit on site and barium chloride and sodium sulfate solutions with or without inhibitor are added to this fluid flow in order to deliberately provoke solids formation. The fluid, which is supersaturated with barium sulfate ions, flows through a capillary, where the solids adhere and thus reduce the flow velocity due to the increasing closure. The tube blocking test (TBT) has been shown to provide information about the mechanisms that act on the process and is used to determine the efficiency of inhibitors. Since barium sulfate precipitation depends on several factors, consistent experimental conditions are a prerequisite for achieving reliable and reproducible results.

After extensive preliminary tests in the laboratory with model fluid, the system could be configured in such a way that the efficiency of phosphonate 2 could be determined using this method as a function of the inhibitor concentration used. These results gave a first indication of the minimum inhibitor concentration to be used in practice.

Based on the findings in the laboratory, the blank value (tests without inhibitor) was determined before each series of experiments with inhibitor. Here, it was shown that other factors influence barium sulfate precipitation and that many experiments were necessary to set constant conditions. These depended not only on the weather conditions, i.e., the outside temperature had a significant influence on the temperature control, but also on the wear and tear of system components such as nozzles (formation of scales). In principle, however, proof of the functionality of this plant could be provided on-site. Further optimizations to be carried out on the system, such as the shortening of the flow paths, not only contribute to improving the reproducibility of the measurement results but are also an essential factor in reducing the time required.

Following extensive laboratory testing with model fluids, the system was configured to determine the efficiency of selected scale inhibitors based on the applied inhibitor concentration. Although this TBT method, specifically designed for on-site applications, remains time-consuming and cost-intensive, it provides a practical means of selecting inhibitors tailored to specific geothermal fluids. Furthermore, it enables the determination of the minimum inhibitor concentration required, depending on the cooling temperature.

This novel approach marks a significant advancement in optimizing scale and corrosion control in geothermal systems. It offers practical benefits for improving operational efficiency and ensuring sustainable resource utilization.

5 Acknowledgement

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6 Literature

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