

The inhibition of lead sulfide scale in geothermal plants

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Keywords: geothermal, scaling, lead sulfide, inhibitor, dispersing, test method.

ABSTRACT

Geothermal energy is a rapidly growing market in the sector of renewable energy. Due to the chemistry of geothermal brines plant operators face challenges by corrosion and scaling of very different composition. A less commonly occurring type of scale is lead sulfide, which frequently occurs in combination with other scale types such as silicate or barite.

Lead sulfide or galena is characterized by an extremely low solubility. Lab testing of anti-scalants faces special challenges due to the limited analytical detection limit of sulfide and the toxicity of lead sulfide. For the ease of handling the tests were carried out with simulated geothermal brine using very high supersaturation factors.

Unless the concentration ratio of scale-inhibitor to lead sulfide was high, an almost spontaneous precipitation of lead sulfide normally occurred. The most simple and still reliable method found was determining the minimum inhibitor concentration needed to completely prevent precipitations. Alternatively, if precipitations take place, a number of methods are available to differentiate the efficacy of anti-scalants respectively their ability to delay particle growth: particle size distribution, turbidity measurement, visual evaluation and chemical analysis after filtration. As for dispersing, a simple visual evaluation method was found sufficient.

Tests carried out with varying anti-scalant chemistry and concentration and lead sulfide concentration showed that the best efficiency could be obtained with a combination of anti-scalants which differ in the mode of action, i. e. both a threshold active substance and a dispersant.

1. INTRODUCTION

Sustaining efficiency and low maintenance efforts in a geothermal plant depend a great deal on a smooth circulation of the geothermal water from the underground through the heat exchangers and back. Changes of e.g. water temperature, pH-value and pressure frequently lead to reduced solubilities of salts dissolved in the water, often causing precipitations in heat exchangers and pipes with subsequent heat transfer

losses and increased maintenance costs for e.g. pipe cleaning and subsequent stand-stills.

For applications like cooling water treatment, standard methods to test anti-scalants have already been established. While their basic procedures can be in principle transferred to geothermal conditions, modifications are needed to take into account at least the differing chemical compositions and pH of the water tested. Differences of physical parameters like higher temperatures and pressures as they occur in geothermal plants were not simulated so far.

The focus of this work was put on lead sulfide (galena, PbS), a representative of inorganic salts of very low solubility that can be found in a number of geothermal waters.

Table 1 shows an example of a scale composition from a geothermal plant (Andritsos and Karabelas, 1991). This was determined by X-ray fluorescence-spectroscopy and showed mainly iron and lead. The authors state that a significant amount of sulfides was deposited despite the low concentration of heavy metals (particularly of lead) and limited availability of sulfide species in the brine.

Table 1: Example of composition of lead sulfide scale.

Element	Wt%	Element	Wt%
Na	0.3	Cu	0.3
K	0.1	Ni	0.1
Mg	0.1	Ag	0.5
Ca	0.1	Si	2.9
Mn	0.1	Cl	0.5
Pb	40.7	SO ₄ ²⁻	0.3
Fe	15.4	Na	0.3
Zn	0.8		

Figure 1 shows an example of a galenit formation.



Figure 1: Galenit (side lengths ~5 cm), with some little cubes of light purple fluorite on it. (Attribution: Rob Lavinsky, iRocks.com)

2. EXPERIMENTAL

2.1 Test water

All trials were made with one water quality only; data were adapted from the water analysis of a geothermal source where lead sulfide precipitations regularly occur (Scheiber et al, 2013). The test water was produced by dissolving the particular salts in de-ionised water.

Table 2: Composition of test water

Parameter	Unit	Value
Ca ²⁺	mmol/L	160
Mg ²⁺	mmol/L	0
Na ⁺	mg/L	25.000
Cl ⁻	mg/L	90.000
SO ₄ ²⁻	mg/L	1.000
pH		6
Temperature	°C	25

2.2 Test substance

Lead sulfide was produced by adding aqueous solutions of lead acetate and sodium sulfide subsequently to the test water maintaining a stoichiometric ratio of 1 : 1.

2.3 Inhibitors

A range of scale inhibitors commonly applied like phosphonic acids and polycarboxylates (Hater et al, 2013) respectively combinations of the latter with different co-polymers was tested.

2.4 Test procedure

For scale inhibition, test water was added into a 1 liter glass beaker, together with the inhibitor. The two test substances were added under stirring (300 rpm). If precipitations took place they were characterized by different methods.

Chen et al (2010) used a similar approach to test lead sulfide inhibition under oil producing conditions.

For dispersing, the inhibitor was added after a time of stirring to first allow for particles to form before measuring dispersion respectively their settlement speed.

2.5 Evaluation procedures

Four methods were used, listed in the order of increasing efforts required.

2.5.1 Visual evaluation

The relative turbidity of the test solutions was judged by eye and fotos taken.

2.5.2 Turbidity

The turbidity of the test solutions was measured with an immersion probe VisoTurb 900-P from WTW, at a wavelength of 860 nm.

2.5.3 Particle size distribution

The size of the precipitated particles was evaluated using a LUMiSizer, an analytical centrifuge that measures the extinction of the transmitted light across the entire length of a sample. This allows for analysing particle velocity distributions for sedimentation phenomena and performing particle sizing (ISO 13318 - 2).

2.5.4 Analytical

The lead content was measured by means of plasma mass spectrometry (ICP-MS) after acidification of samples with nitric acid p.a.

3. RESULTS AND DISCUSSION

3.1 Observations

The water solubility of lead sulfide is very low; Linke (1965) quotes 2.6×10^{-11} kg/kg. This value can also be approximately obtained by calculating with the solubility product ($K_L = 8.80 \cdot 10^{-29}$ mol²/l and dissociation constants of the H₂S/HS⁻/S₂⁻ system ($K_{s1} = 3.16 \cdot 10^{-8}$; $K_{s2} = 1.10 \cdot 10^{-12}$, CRC Handbook of Chemistry, 66th edition).

Consequently, to keep experiments evaluable by standard means, working with highly oversaturated solutions had to be accepted.

In blank trials lead sulfide particles of blackish colour form instantly after mixing sodium sulfide into the lead acetate solution. If stirring is stopped immediately, particles remain very small taking > 10 h to settle down. If stirring is being continued, particles constantly become bigger thus settling faster, i.e. within 15 minutes under continuous stirring. A stirring time of 3 minutes was found suitable to obtain particle sizes settling within a reasonable time span of some hours.

Figure 2 shows test waters after 3 min of stirring with lead sulfide concentrations ranging from 10 mg/L (= 10^{-5} kg/kg) to 1 mg/L (oversaturation ranges from about 1 million- to 100.000-fold). While a concentration of 10

mg/L lead sulfide shows clearly visible precipitations of a black-brown colour, this becomes less pronounced at concentrations of 1 mg/L.



Figure 2: Blank tests with lead sulphide concentrations of 10, 5, 4, 3, 2, 1 mg/L (from left) after 3 min of stirring plus 20 min of settling.

3.2 Key parameters

Since different evaluation methods were explored, certain parameters were adapted for optimization of the performance window. Table 3 below shows an overview of key parameters and methods used.

Table 3: Composition of test water

Approach	Lead sulfide (mg/L)	Product conc. (mg/L)	Evaluation
Delay of growth of particles created in situ	15	50	Visual, Particle size distribution, Turbidity
Prevention of precipitation	3	100 – 500	Visual
Prevention of precipitation	1	10 – 500	Analysis of Pb

3.3 Stabilizing

3.3.1 Delay of particle growth – evaluation visually and by particle size measurement

Following the observations as described above, lead sulfide particles were produced under stirring for 3 minutes in presence of the inhibitor (dosed at start). An effective inhibitor would reduce particles growth and thus settling of particles would be more slowly according to Stokes' law), resulting in a longer lasting turbidity.

Figure 3 shows beakers with a lead sulfide concentration of 15 mg/L, 6 hours after the stirring was stopped. The turbidity can be linked to the respective particle sizes (2 samples per beaker) measured at the end of the stirring time.

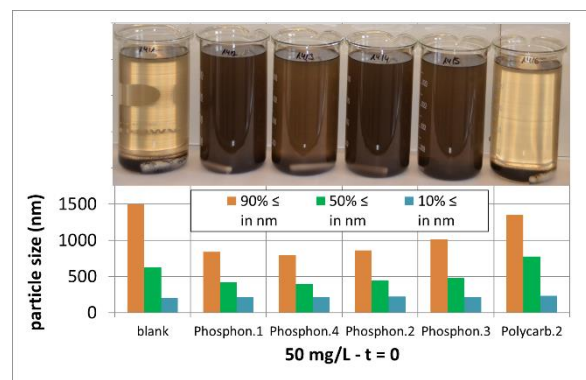


Figure 3: Performance of inhibitors evaluated visually (6 hours settling time) and by particle size measurement directly after preparation.

3.3.2 Delay of particle growth – evaluation by turbidity

The observation that particles grow with stirring time led to an alternative evaluation method using a turbidity meter. With this approach, the stirring is continued over the entire trial time (1 h) and the resulting turbidity recorded.

Figure 4 shows a typical initial phase where particles are best dispersed as long as they are small, followed by a phase of settlement caused by an increasing particle size (despite presence of inhibitor), arriving at a plateau that is maintained by rotation speed.

Both, the higher turbidity at start and the higher plateau after one hour can be attributed to smaller particle sizes respectively a good inhibitor performance.

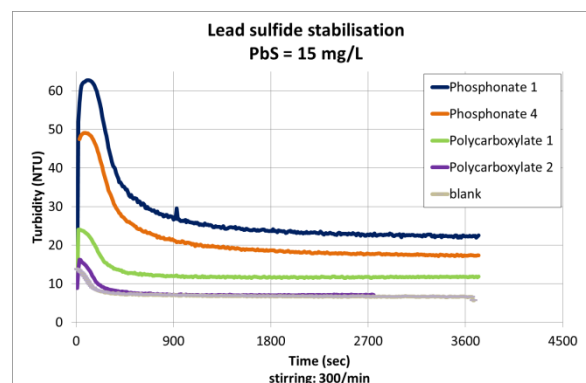


Figure 4: Turbidity of lead sulfide suspension over time while stirring in dependence of different inhibitors dosed at 50 mg/L.

3.3.3 Prevention of precipitation – visual evaluation

With 15 mg/L lead sulfide in the test water, inhibitor concentrations of 50 mg/L were only able to delay precipitations; for complete prevention it was found that concentrations > 1000 mg/L were necessary. In order to transfer this approach to lower thus more practical ranges, a lead sulfide concentration of 3 mg/l was set as the lowest possible limit for visual evaluation (see also Figure 2).

By determining if a test solution stays clear (3), slightly turbid (2) or showed precipitation (1), a relative quick and easy distinction could be made regarding the inhibitor's capacities (figure 5).

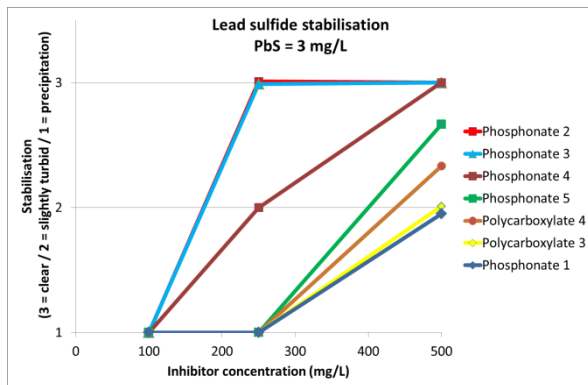


Figure 5: prevention of lead sulfide scaling in dependence of inhibitors and concentrations. The evaluation was made after 60 minutes. Evaluation categories of stabilisation (ordinate) are mean values of 3 measurements.

3.3.4 Prevention of precipitation – evaluation by analysis

A lead sulfide concentration of 1 mg/L does no longer allow for a visual evaluation by eye. In order to substantiate the results as shown with the quick method (figure 5), the lead sulfide solution (1 mg/L) was filtered (0.45 µm) after stirring of 3 min and the lead content in the filtrate analysed by ICP. This content divided by the calculated theoretical lead concentration of 867 µg/L yielded the relative stabilisation (in percent).

Figure 6 shows, on the basis of 3 representative inhibitors, that the ranking obtained matches the one found with the quick methods: phosphonate 2 > phosphonate 1 >> polycarboxylate 1 (the latter does not appear in figure 5 since it did not show any effect even at a concentration of 500 mg/L).

While further testing at even lower lead sulfide concentrations than 1 mg/L would be desirable, the accuracy of this method would be increasingly compromised e.g. by adhesion effects (beaker, filter). However, Scheiber et al (2013) showed that some geothermal brines contain lead concentrations of e.g. 96 µg/L, which is only a ten-point lower.

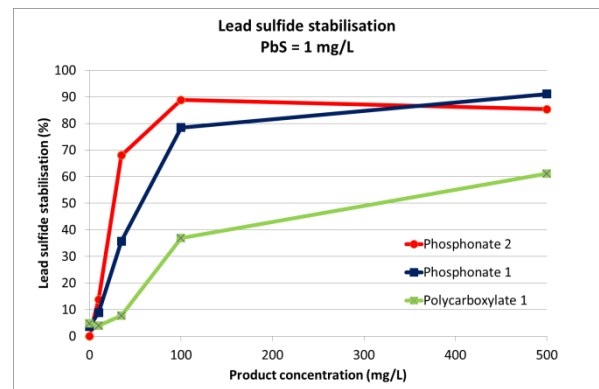


Figure 6: Relative lead sulfide stabilisation of different scale-inhibitors as function of inhibitor concentration.

3.4 Dispersing

Visual evaluation

Similar to measuring stabilizing effects, the dispersing capability of inhibitors was tested. The key difference between stabilizing and dispersing experiments was the time when the additive was added: for the anti-scalant tests the inhibitor to be evaluated was dosed at the beginning, for dispersing tests after 3 minutes of stirring when the scale precipitation had been practically finished.

The best differentiation between the inhibitors respectively dispersants was eventually achieved under the following conditions (see also table 4):

- limiting particle growth during the first 3 minutes with a good stabilizer: Phosphonate 1 was dosed at a concentration of 50 mg/L.
- promoting particle agglomeration by another 12 minutes of stirring after dosing of dispersant (making use of the observations as described under § 3.1 and in figure 4).
- evaluation of the suspension after 75 minutes of settling time.

Table 4: key steps taken for the evaluation of dispersants for lead sulphide

Time (min)	Step
0	Start stirring Dosage of Phosphonate 1 (50 mg/L) Dosage of lead acetate and sodium sulfide
3	Dosage of inhibitor to be tested (50 mg/L)
15	Stop stirring
75	Evaluation

Figure 7 shows that polycarboxylates perform better than phosphonates.



Figure 7: Efficiency of lead sulphide dispersing of different inhibitors after 60 min of settling time (from left to right: blank, polycarboxylate 2, phosphonate 5, polycarboxylate 1, phosphonate 1, polycarboxylate 5). The inhibitor concentration was 50 mg/L.

4. CONCLUSIONS

Test methods presented showed that suitable inhibitors can prevent or delay the formation respectively settlement of lead sulfide particles.

In general, working with lead sulfide concentrations that are to some extent higher than typically found in practice allows for easier evaluation methods. Inhibitor performances respectively rankings obtained this way could be exemplary confirmed however, when working at lower and more practical concentrations of lead sulfide.

The different methods showed enough accordance to allow for using the most rapid and simple approach for product screening. Results made with the turbidity meter (figure 4) suggest that Phosphonate 1 performs best when precipitation has already started, but is less effective with regards to complete prevention of precipitations.

Results obtained so far indicate that scale prevention is rather achieved by substances based on phosphonates while dispersing is the domain of polycarboxylates. This reflects findings typically made for calcite inhibition in the field of cooling water treatment. Most likely this calls for combining these two chemical groups to obtain a suitable balance of preventing and dispersing properties for a respective application.

Transferring these results into practice still has to take into account parameters that were not varied during these investigations. Since especially temperatures > 100°C often occur in geothermal waters, the thermal stability of a product will also influence its performance.

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