New chemistry development to address stibnite scale inhibition in geothermal plants

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ABSTRACT

Among all the inorganic scale species that affect geothermal applications, stibnite is one of the most difficult to treat due to its extremely low solubility constant. Stibnite typically occurs in binary systems and is more commonly found in geothermal fields in countries such as Italy, Turkey, and the USA. Its precipitation in the heat exchangers of geothermal plants often reduces heat exchange efficiency, leading to a decrease in power output and increased operational costs.

Various methods, such as offline mechanical cleaning, offline chemical cleaning with acid or caustic, and the continuous application of scale inhibitors and dispersants, have been applied to prevent or eliminate stibnite precipitation. However, these approaches can be expensive when plant downtime is considered and may pose safety risks due to the formation of H_2S.

While chemical treatment can offer a more cost-effective and safer solution, only a few technologies are currently available on the market, and many of them fail to provide complete inhibition, particularly under severe conditions.

This paper introduces a new stibnite inhibitor, providing a detailed description of its development, with a focus on the challenges and testing conditions designed to mimic real-world scenarios. An analysis of the mechanism of action of this innovative technology is also discussed. Preliminary results indicate that the new inhibitor outperforms standard solutions, functioning effectively under more severe conditions and achieving a reduction in the Minimum Inhibitor Concentration (MIC) by 2x to 3x. It has demonstrated the ability to control stibnite in brine containing approximately 10 ppm of antimony—around twice the maximum antimony level found in geothermal brines.

Ongoing field trials in Europe and North America are validating the lab results, showing a significant improvement in mitigating stibnite scaling compared to previously adopted solutions. The technology's ability to reduce environmental risks, such as H_2S formation, and its potential to save up to 30-50% in operational costs, make it a promising solution for broader industrial applications beyond stibnite control.

1. INTRODUCTION

Metal sulfides are a relevant issue in geothermal facilities. Among all the different metals and semi metals that can combine with sulfide anions and precipitate, antimony is one of the most important. Antimony sulfide is also called stibnite and exists in two different forms:

- Crystalline (grey-black)
- Amorphous - Metastibnite (red)

It typically precipitates in the colder areas of binary plants, creating issues especially in heat exchangers where it can cause a loss of heat transfer and can eventually block the heat exchanger tubes creating a very porous layer that can trap brine or favor silica polymerization.

It is typically a regional issue, mainly occurring in countries like, for example, Turkey and Italy. Solubility constant is very low, meaning that even ppb or ppm of antimony can precipitate in the presence of sulfide. Solubility decreases with temperature, and it is affected by pH, with a minimum solubility level around pH 5.0 – 6.0.

Different ways of preventing stibnite deposition are typically used:

- Avoiding supersaturated conditions
- Caustic dosing
- Acid dosing
- Mechanical removal
- Chemical inhibition

Working above the saturation temperature at which stibnite starts precipitation leads to a loss of power that can be generated by the plant. Dosing of caustic is effective but can increase the risk of calcite and metal silicate deposition while acid dosing isn't always effective and can create health risks for operators due to the formation of toxic H_2S. The same risk can occur during the mechanical cleaning of pipelines and heat exchanger. Furthermore, this approach is quite expensive and require a shut-down of the plant that has a significant impact on the cost of this treatment. Chemical inhibitor treatment is another mitigation strategy currently adopted by operators. Only few inhibitors present on the market confirmed to be effective under field conditions and research is actually very active with the aim to develop more cost-effective technologies. One of the main challenges of this research work is related to testing methodologies to be used to evaluate performance. Most of the protocols involved low temperature static tests which aren't very representative of what happened in the field. Furthermore, they typically required high amount of antimony while in geothermal brines the content of this element is typically 1ppm or lower.

For this reason, the development of a new cost-effective technology able to eliminate or at least mitigate the formation of stibnite in binary plant must start from the development of a proper testing methodology which allow to better mimic geothermal plants and to run performance screening test under conditions which are aligned to those typically found in the field.

2. EXPERIMENTAL

The brine used for the tests is a modified geothermal brine (Table 1). NaCl (ACS reagent, Sigma Aldrich), $CaCl_2*2H_2O$ (ACS reagent, Sigma Aldrich), $MgCl_2*6H_2O$ (ACS reagent, Sigma Aldrich), $SbCl_3$ (ACS reagent, Sigma Aldrich), $NaHCO_3*2H_2O$ (ACS reagent, Sigma Aldrich), $Na_2SO_4*10H_2O$ (ACS reagent, Sigma Aldrich) and Na_2S*9H_2O (ACS reagent, Sigma Aldrich) were used for the preparation of the synthetic brine. Testing brine is fleshly prepared before every test, with sulfide added at the beginning of the test.

Test is performed under dynamic conditions, under below conditions:

- Temperature = 60°C
- Time = 1 hour
- Dosage = 25ppm as active content

Brine composition (ppm)	
Na^{+}	8404
Sb^{3+}	9.6
Mg^{2+}	10
Ca^{2+}	300
Cl^{-}	5600
S^{2-}	5
SO_4^{2-}	5000
HCO_3^{-}	300
pH	5.5

Table 1: Testing brine composition.

The stibnite formation in the dynamic system was monitored using a laser, any variation of the laser intensity is related to the precipitation and/or deposition of the insoluble particles.

Thermal stability is another key property for a chemistry applied in geothermal fields, for this reason the selected product was placed in the oven at 150°C for 4h and tested again to confirm the same inhibition properties.

3. RESULTS

3.1 Blank test

The test ran with untreated brine is labelled as blank (Fig. 1). As soon as the sodium sulfide is added to the brine, the stibnite precipitation occurred. The precipitation led to an increasing of the turbidity of the solution and a lower laser intensity detection. After a few minutes the suspended particles started to agglomerate and deposit on the tubing and the laser intensity slowly recover to the initial value. This suggests that a good stibnite inhibitor must be able to avoid or at least delay the intensity drop observed at the beginning of the test and/or avoid agglomeration or particle deposition, resulting in a stable intensity once it reaches the minimum value.

3.2 Performance test

Several chemistries based on poly carboxylic technologies were tested in dynamic conditions and Geogard SB2 resulted to be the best performing product. In Fig. 2 Geogard SB2 is compared to the benchmark Geogard SB (first generation stibnite inhibitor). Initially, Geogard SB curve follows the same trend of blank curve but, once the intensity reached the minimum, we didn't observed a significant increasing, meaning that particles don't agglomerate or precipitate our of the solution, with Geogard SB acting more like a dispersant than a scale inhibitor. On the other side, Geogard SB2 behaves in a different way being able to significantly delaying the intensity drop, which is by the way also lower compared to the benchmark and the blank. This indicates a potential inhibition of the stibnite particles formation. In the second part of the curve a minimal intensity recovery is observed, confirming the product has also improved dispersant properties.

3.3 Thermal aging

After the thermal aging Geogard SB2, no significant changes in the product aspect were observed and, when the performance test was repeated, no loss in performance was observed (Fig. 3), with Geogard SB2 showing the same combination of inhibition and dispersion properties observed with the unaged sample.

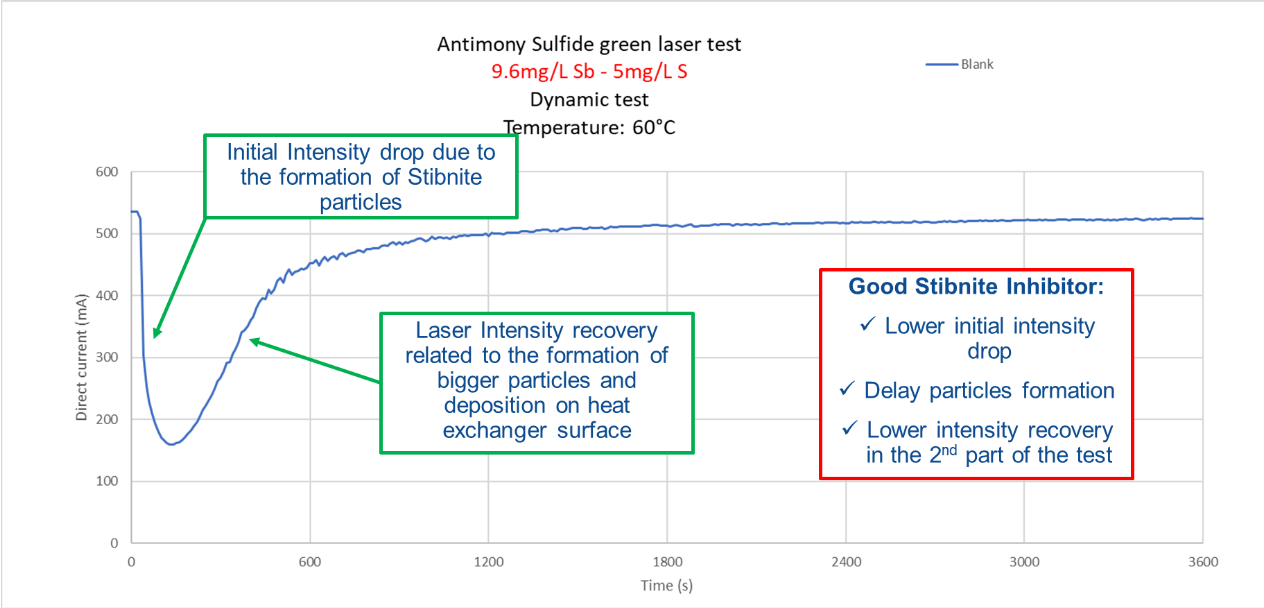

Figure 1: Blank test.

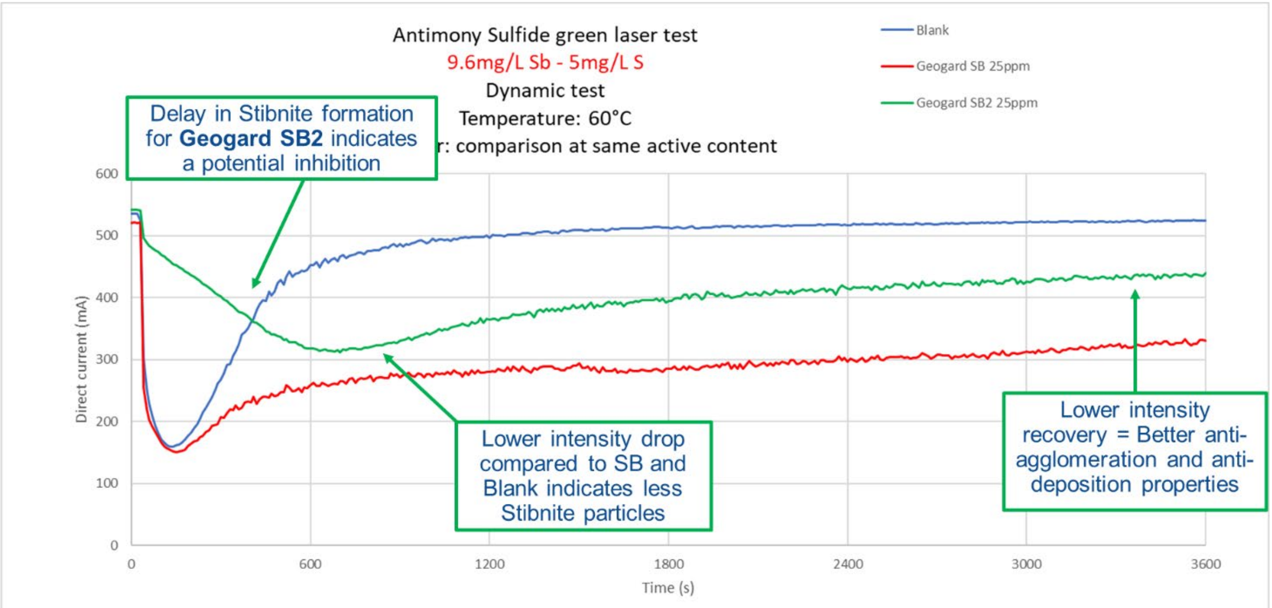

Figure 2: Geogard SB2 performance test.

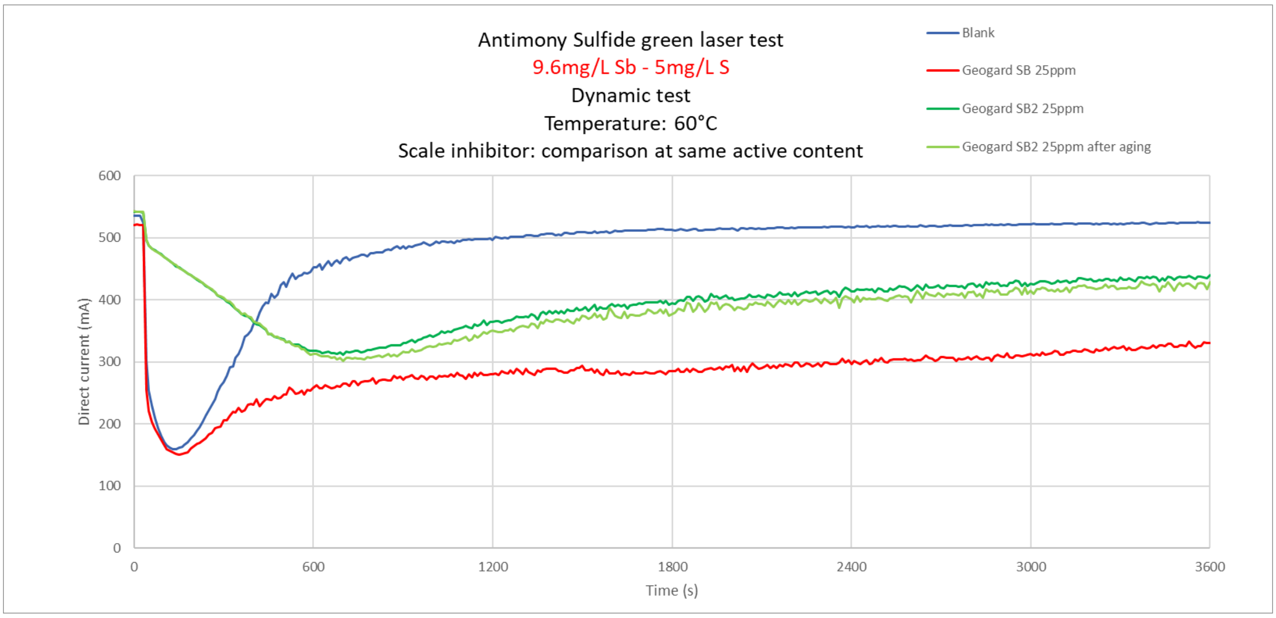

Figure 3: Aged Geogard SB2 performance test.

4. FIELD TRIAL

With the aim to confirm promising lab results, several field trials have been scheduled, with most of them started over the last six months and still ongoing.

For example, Geogard SB2 was evaluated to mitigate stibnite scale in a geothermal binary plant having a an inlet temperature of about 150°C, while reinjection temperature is lower than 100°C. Despite antimony concentration in the brine is lower than 1ppm, it was observed to be enough to create serious scale issues in the heat exchanger, causing periodically plant shut down for mechanical cleaning, with a significant loss of profit for the operator.

It has been agreed to start from a dose rate of 2.5ppm, keeping monitored scaling build-up on metal coupons and plant pressure to evaluate product performance. As shown in Fig. 4, plant pressure remained completely stable during the first phase of the trial while a preliminary observation on metal coupons seems to confirm a significant lower deposition.

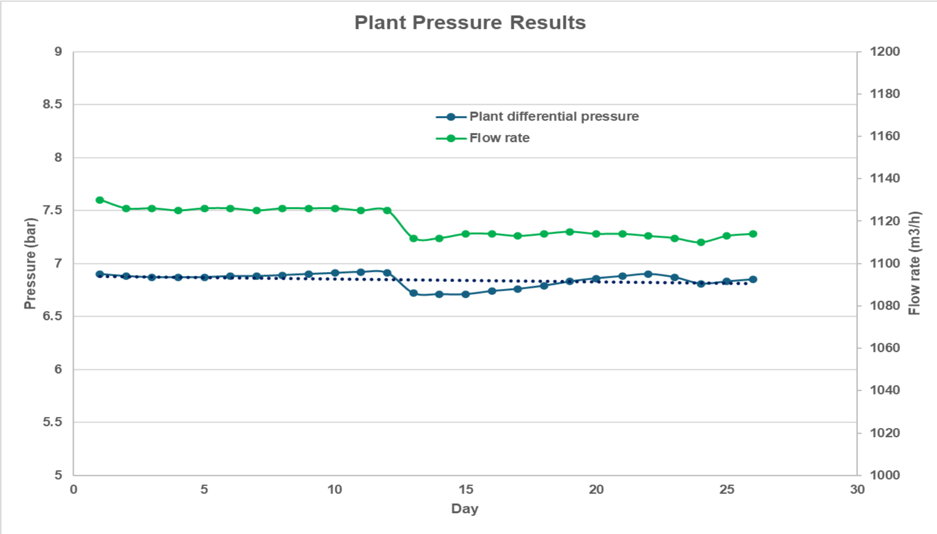

Figure 4: Field trial plant pressure

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5. CONCLUSION

Stibnite is one of the major issues that geothermal operators have to face while running their plant. Due to its extremely low solubility, it is very difficult to be inhibited and even small amount of antimony (often < 1.0ppm) can lead to the formation of a significant amount of deposit.

This work showed the results of a new technology, specifically selected after an extensive lab work which also involve the development of a dedicated testing methodology which allow to run tests under more representative conditions (lower amount of antimony vs standard jar tests, dynamic conditions). This new product, called Geogard SB2, shows both inhibition and dispersion properties against stibnite and it outperforms the first generation of stibnite inhibitors.

Multiple field trials are currently ongoing with the aim to confirm lab results, with first results showing a positive and promising impact of Geogard SB2 in minimizing issues related to stibnite formation. As next step, we will continue to monitor field test and collect more data to explore and confirm product capabilities.

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