Development of a novel HT calcite scale inhibitor for Geothermal applications

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ABSTRACT

Chemical treatment for preventing scale formation and deposition is now widely used in the geothermal industry. The high temperatures involved in the geothermal processes constitute one of the major challenges for most of the standard chemistries currently applied for scale inhibition. The chemical product may undergo a thermal degradation which cancel their scale inhibition effect and, in some cases, may generate additional scale due to by-product formation.

In this paper, the development of a novel, highly stable, chemical product is presented. Extensive lab work has been done with results and protocols described in detail. Compared to standard technologies, this new product has shown an exceptional thermal stability and excellent performance against calcite, which is one of the most common types of scale generally present in geothermal plants.

Following the good results obtained in the laboratory, an industrial trial was done in a 30MW plant in Turkey having high temperature reservoir (> 200°C) and severe silicate and calcite scaling issues. In the same plant, several different chemical products were applied with very bad results. The new product was applied for two months, and the performance were assessed by checking the amount of scale formed on scale coupons and by monitoring the geothermal brine composition in order to identify any variation in ions content that could be linked to scale precipitation.
At the end of the trial, the results confirmed the lab observation, by showing excellent performance in scale inhibition at such high temperature conditions.
Results presented in this paper represents a step forward in the development of new chemical product which can offer a more effective technology to geothermal operators aiming to improve their plants efficiency.

1. Introduction

Calcite scaling in production wellbores is one of the major operational problems encountered by many geothermal field operators. This process normally occurs just above the flash point inside the wellbore. CO_2 loss at flash point pushes the equilibrium (Equation 1) towards the formation of Calcite. Furthermore, it increases pH causing bicarbonate to be transformed into carbonates, leading to oversaturated conditions and making possible the nucleation and deposition process (Arnórsson et al, 1989):

$$Ca^{2+} + 2HCO_3^{-} \rightleftharpoons CaCO_3\downarrow + H_2O + CO_2\uparrow$$

Equation 1: Calcite formation mechanism

The above process is believed to be the dominant calcite deposition mechanism in geothermal production wells (Quinao et al). The highest potential for scaling is usually within the flash temperature range of 240-280°C but it decreases below 220°C due to the retrograde solubility of calcite with temperature (Arnórsson et al, 1982).

Calcite management can be typically done by mechanical clean-out or acidizing or preventing calcite formation adding scale inhibitor the geothermal brine.

Mechanical clean-out and acidizing are common approaches used to recover loss in production from a well affected by calcite deposition. However, these options are expensive to implement, in addition to the cost of business interruption with wells needing to be taken off-line from the power plant. Clean-out costs can be in the range of $0.5 to $2.0M for a major operation, with a clean-out often required at least every one/two year (Siega et al). Temporary mechanical broaching (running of different specially designed gauge tools) may be considered in the short-term but, as calcite scale can harden over time, this approach can lose effectiveness over the time, needing a full mechanical and/or chemical clean-out becomes necessary to restore well performance. In some cases, it may help try to move the flash point location away from feed zone and into a more accessible cased sections of the well, so that cleaning process results to be easier.

Calcite inhibitors can proactively avoid the deposition of scale in the production wells, representing a cost-effective solution in the long term as they can avoid costly shutdowns needed for mechanical treatment. However, a rigorous selection process is needed to make sure that the inhibitor is able to provide the desired performance in the well without being affected by high temperature that could degrade the inhibitor molecule leading to loss of performance or formation of pseudo-scale resulting from the interaction between degradation by-products and cations present in the geothermal brine. To ensure a proper mixing, inhibitor has to be injected in the brine prior to flashing. Cost related for a stand-alone injection system in a well can vary between NZ$300-500K, but they can increase in case a centralized mixing system is required or if there are other wells to be treated. Annual chemical costs depend on the amount of fluid to be treated and the required dosage rate to effectively control scaling. Hence, the need of new stable inhibitor able to protect wells working at lower dose rates in order to reduce the overall cost of the treatment.

2. Lab tests

To develop a proper thermally stable and cost-effective calcite inhibitor, Dynamic Scale Loop (DSL) tests have been performed working at 250°C to stress as much as possible tested products. Brine chemistry, DSL set up and software simulations carry out with ScaleSoftPitzer software from Rice University are reported in Table 1 and Table 2:

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Water Chemistry (mg/l)	
Na^{+}	1,714
Mg^{2+}	0.29
Ca^{2+}	75.40
Cl^{-}	1,775
HCO_3^{-}	1,000
TDS	5,000
pH	8.5

Table 1. Brine composition used for DSL tests

DSL Test Conditions	
Parameter	**Condition**
Temperature	250 °C
Pressure	2500 psi
Flow Rate	4 ml/min
Coil	Stainless Steel 1m Length 0.5 mm I.D.

Scaling Indices & Theoretical Deposit (mg/l)	
Scale	**SI / Deposit**
Calcite	3.87 / 188 mg/l

Table 2: DSL set up and software simulation

Despite the moderate theoretical deposit rate predicted for this case, Saturation Index (SI) is very high, indicating a strong thermodynamic precipitation tendency.

DSL tests have been carried out testing many different chemistries, including standard phosphonates and polymers typically used to handle calcite in O&G or water treatment application. All of them failed, quickly reaching the target differential pressure set for this test. Most likely, inhibitor degrade at high temperature and/or conditions are too severe for common technologies. One of the few products passing this test, and the only one providing a Minimum Inhibitor Concentration of 10-15ppm as product, was Geogard®HCA, an innovative solution based on a brand-new and patented technology.

Figure 1 reports result for Geogard®HCA in comparison with two selected benchmarks. While these products failed, the new inhibitor provided a quite flat line at the same dose rate, passing the test with an differential pressure increasing of about 1.5psi.

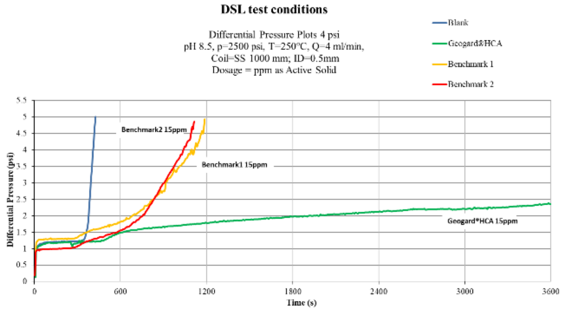

Figure 1: DSL calcite test at 250°C

DSL results indicates that Geogard®HCA has good thermally stability but, knowing how important this parameter is, a dedicated and more accurate test was performed. A sample of this product was aged at 180°C (maximum temperature achievable in our lab) for 18h, a residence time much higher compared to what is expected in a geothermal facility. Stability was evaluated checking the visual aspect of the sample after thermal aging (Figure 2) and repeating DSL test at 250°C (Figure 3).

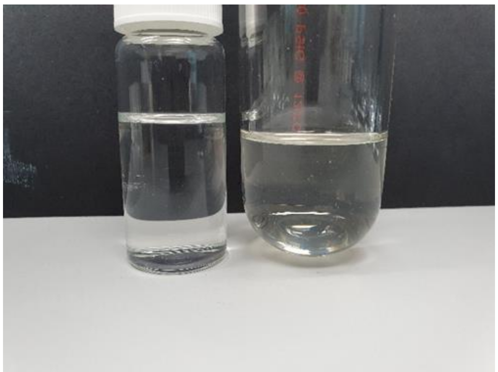

Figure 2: Geogard®HCA sample before aging (left) and after 18h at 180°C (right)

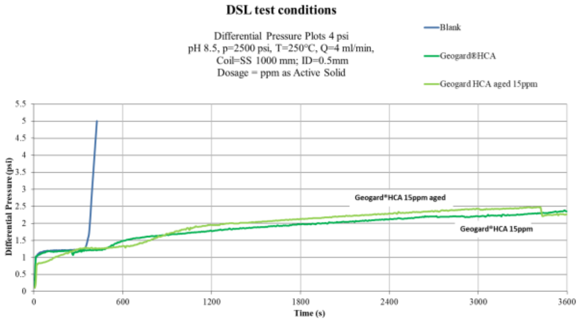

Figure 3: DSL test performance of Geogard®HCA after thermal aging

After aging test, no significant change in the sample aspect was detected. Also, performance remain unchanged, with the curve obtained for the aged sample being perfectly in line with the one of unaged sample. These results and observations confirmed the superior stability and performance at high temperature of this product compared to standard technologies, making it a perfect candidate for those plants suffering from severe calcite deposition or simply looking for improving the cost-efficiency of their chemical treatment.

3. FIELD TRIAL

Results obtained in lab, especially for a new technology, have to be validated in the field running one or more field trials.
For Geogard®HCA trial was performed at 60MW binary plant in EMEA region, having 10 production wells with a downhole temperature close or higher than 250°C.
Geothermal brine is characterized by a low amount of Magnesium and Calcium (<20ppm), pH (7.8–9.0) and high level of bicarbonate (1500ppm). However, even if calcium level is low, high temperature and bicarbonate level lead to supersaturated conditions and production wells need to be protected from calcite deposition.
Due to high injection temperature (>250°C), standard calcite inhibitors failed providing in some cases poor performance or creating deposit close to the injection point.
Trial was carried out for about 3 months and the KPIs considered were:

- Scaling on metal coupons located in different areas of the pipeline
- Monitoring of brine analysis
- Monitoring of pressure variations in heat exchangers

At the end of the trial, Geogard®HCA was approved and its use in the plant was confirmed. Trial results showed no significant variation in the heat exchanger pressure while the composition of the brine remained constant and no drop in calcium or bicarbonates levels were observed.
Scale on metal coupons was always minimal, confirming the good ability of this product in preventing calcite in high temperature environments. As an example, Figure 4 and 5 show the aspect of metal coupons after 1 week and 3 weeks respectively.

Figure 4: Metal coupons after 1 week of trial

Figure 5: metal coupons after 3 weeks of trial

4. CONCLUSION

Calcite is one of the most common scales that affect geothermal plants. Chemical inhibitors are widely used to prevent the deposition of this inorganic salt and avoid pipeline plugging. However, standard chemistries are typically affected by the high temperature that they could experience in production wells, requiring an higher dose rate to work well or leading to potential issue linked to the formation of degradation by-products that might not be fully compatible with the geothermal brine, especially downhole.

For this reason, a new cost-effective calcite inhibitor has been developed and lab tests proved that Geogard®HCA outperforms standard technologies in DSL test carried out at 250°C and confirmed it has a superior stability even was aged for long time at high temperature.

Results from the lab were confirmed during a 3 months trial performed in an EMEA plant characterized by high downhole temperature (>250°C) and affected by severe calcite deposition. Geogard®HCA provided good protection where most of the other product tested before failed.

As next steps, Geogard®HCA will be dosed and tested in other geothermal plants having slightly different conditions and brine compositions, to further confirmed its performance and extend its applicability range.

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