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New Inhibitors for Silica and Calcium Carbonate Control In Geothermal

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ABSTRACT

Scale and corrosion control are big challenges in utilizing geothermal energy. In the production wells, during or after flashing, brineresults in higher pH, which can happen deep inside the well.Higher pH in combination with high temperature causes calcium carbonate precipitation. Silica/Silicate precipitation becomes a problem when the brine gets cold in the surface equipment and the rejection well. The paper discusses in addition to basics of scale control, new inhibitors for both silica/silicate and calcium carbonate control.

1. INTRODUCTION

Global increase in population and improvement in living standard has stressed the current energy supplies. Alternate sources of energy must be found, especially those, which are environmentally sustainable and more acceptable. Geothermal energy has a minimal effect on the environment depending on how the geothermal energy is produced. Direct use of geothermal resources for supplying heat and hot water to the buildings has almost no negative impact on the environment. Geothermal plants those use either dry-steam, flash steam, or binary systems release about 1-3% of the carbon dioxide compared to fossil fuel plants. Hydrogen sulfide, often found with geothermal brine can be abated using scrubbers or other chemical means. The major issue in power production using geothermal resources is the scale formation in production wells, surface equipment and the injection wells. Geothermal brines due to high total dissolved solids and high temperature create very harsh environment. Wells plugged due to scaling require large sums of capital for reworking or digging new wells. While there are several other minerals such as barium sulfate, calcium fluoride, antimony sulfide, etc., which are specific to some of the sites that can cause fouling, but calcium carbonate and silica scales are more universal. In this paper we have focused on developing inhibitors to prevent calcium carbonate and silica/silicate scales.

2. SCALES

2.1 Mechanism of scale formation

There are two main routes of fouling of heat exchangers and wells. One is through water-borne (Gill, 1996)and the second one is the water-born (Gibbs, 1928). Water-borne is referred to the suspended material such as silt, clay or corrosion products existing as such in water. Water-born is referred to the formation of precipitation in situ either in the bulk brine or directly on the surfaces. Water-borne material can also greatly influence the water-born precipitation by providing as seed or substrate on the surface to facilitate adherent of the precipitated material on the surface. There are several steps for water-born precipitant to form scale. These steps are

1. Achievement of supersaturation with respect to a particular material which results from scale forming ions, pH changes or temperature changes.
2. Formation of a cluster from scale forming ions and ultimately providing nuclei for further crystal growth.
3. Growth of the nuclei to form precipitation.
4. Transportation of bulk precipitation to the surfaces to cause fouling, however, sometimes there is a direct precipitation on the surfaces as well.

All of these steps are equally important to both fouling and its mitigation. Achievement of supersaturation for both calcium carbonate and silica can be altered for example by changing the pH of the brine. Inhibitors can be used in modifying steps 2 through 4. Some of the inhibitors can prevent nucleation and crystal growth while others prevent the growth of the nuclei; yet another class of inhibitors can interfere in step 4 by modifying the morphology, size or charge of the precipitated material.Inhibitors discussed in this paper interfere in steps 2 through 4.

Inhibitor consumption is very minimum when precipitation is completely inhibited (Gill, et.al, 1983). However, incomplete inhibition can result in significant inhibitor consumption. Other modes of fouling mitigation such as crystal modification, non-adherent, and dispersency require inhibitor to be consumed as a result of surface adsorption of inhibitor on the precipitating material

2.2 Calcium carbonate

Calcium carbonate precipitation in the production wells isone of the majorobstacles that limit the use of geothermal brines for power generation. Geothermal brines ascending to the earth's surface undergo changes, loosing or gaining chemical constituents, as a result of physical and chemical processes these brines endure during their ascend to the surface. Precipitation of calcium carbonate is caused by the increase of brine pH during and after flashing of the brine, resulting in escape of carbon dioxide. High temperature in combination with high pH in production well is an ideal place for calcium carbonate precipitation. Fouling occurs in the production well or in the surface equipment. Even a small amount (<5 PPM) of calcium in brine is responsible for precipitating enough calcium carbonate to scale-up the geothermal production wells and the pumps.

Calcium analysis at the well head or at the high pressure (HP) separator can be misleading, especially if there is calcium carbonate precipitation is occurring in the production well. Thus the sampling of the brine from the production well is very critical and any number of geothermometers can also be used to predict the temperature and the ionic concentration well below the surface. The dose of the scale inhibitor should be based on the brine chemistry prior to flashing rather than the surface brine chemistry. The scale inhibitor must also be delivered below the flash point and the pump to protect all the assets.

2.3 Silica

Silica is another very critical limiting factor in harvesting thermal energy and water reuse. Silica scale is extremely tenacious, highly insulating, and very difficult to remove. Silica deposit is caused as a result of its polymerization, co-precipitation with other minerals, precipitation with other multivalent ions, and monomeric silica deposition on the surface of the heat exchangers. Several of these processes may take place concurrently, making it difficult to predict equilibrium solubility. To prevent silica-based deposit, it is essential to control all these paths, simultaneously (Gill, 1993).

The terms silica and silicates are often used interchangeably. In fact, silica and silicate represent two distinct families of compounds. These terms should not be used interchangeably. Silica generally refers to SiO_2. Silica dissolves in water to form a very weakly ionized species, silicic acid, which may be represented by the formula H_4SiO_4. Silica, in the solid phase as silicon dioxide, is identified in its crystalline form as quartz or in its non-crystalline form as amorphous silica. Amorphous refers to the lack of an ordered or crystalline structure determined by X-ray diffraction. The compound cannot be identified by its characteristic crystallanity since the particle size is so minute.

Silicate refers to the compounds of silicic acid, which are formed by reacting ionized silica with metals such as Ca, Mg, Al, Fe, Zn, etc. Clays, such as kaolinite and illite are examples of silicates found in brine and cooling water as water-borne silica deposits.

Some of the confusion in terminology is a result of underestimating the complexity of silicon chemistry. The classical approach to reporting chemical analyses also serves to over simplify the broad range of silica species, which could be present. Results of both water and deposit (elemental only) analyses are reported as SiO_2 regardless of whether the compound present are silica or silicate. When reporting water analyses, SiO_2 is the preferred means of expressing data, since the silica measured is considered to be present as a non-ionized species and is not considered in the sum of anionic and cationic components of the water.

The use of SiO_2 in expressing elements, identified in a deposit sample, whether silica and/or silicate are present, assumes that an oxygenated form of silicon (Si) is present. This facilitates the summation of elements present to make certain that 100% of the deposit is accounted by the analysis. Proper interpretation of water and deposit analyses along with an understanding of the variables contributing to silica or silicate deposition is critical for assessing and correcting operating conditions, which result in deposition.

3. EXPERIMENTAL

3.1 Hydrothermal stability of the scale inhibitors

Hydrothermal stability of the inhibitor was evaluated using Differential Scanning Calorimeter (DSC). We performed DSC analysis of the silica Inhibitor. The sample (~50 mg) was placed in a stainless-steel pan and sealed with a lid. It was heated at a heating rate of 10 ^{o}C/min. DSC results showed no apparent thermal event between 20 and ~180 ^{o}C (Figure 1). The flat line indicates no degradation of the product. The temperature upper limit is the limit of DSC instrument capabilities in our laboratory.

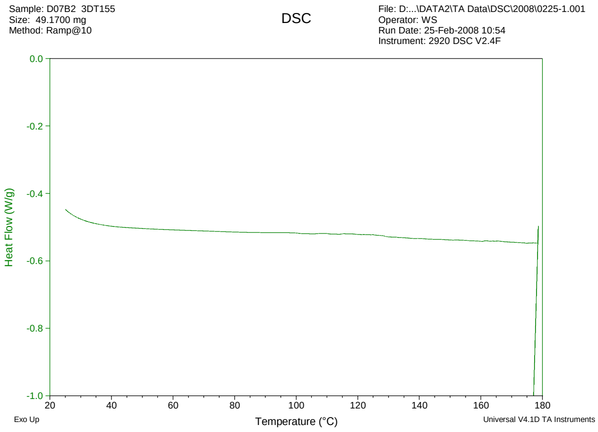

Figure 1. Thermal stability (DSC) plot of silica Inhibitor.

Another way of establishing the hydrothermal stability of the inhibitors was done by heating up 1% solution of the inhibitor in the autoclaveat various temperatures (Figure2)up to 350 ^{o}C. The solution was held at the temperature for two hours. These thermally treated inhibitor solutions were used to inhibit calcium carbonate and silica scale.

3.2 Scale Inhibition

An attempt was also made to simulate surface equipment and injection well conditions. The synthetic geothermal brine (Table 1) was heated in an autoclave and the heated brine was passed through a pre-weighed stainless steel capillary (Figure 3). The experiment was carried out with and without the presence of silica inhibitor.

Figure 2. Autoclave to study hydrothermal stability and scale inhibition

Figure 3. The close up of the capillary

3.2.1 Calcium carbonate scale

To study calcium carbonate inhibition the autoclave was fitted with a stainless steel filtering frit inside the autoclave (Gill and Nicolas, 1979). The filtered brine samples were chilled for collection and then analyzed for calcium content. Scale inhibition was calculated using the following equation.

% Inhibition = $(C_E - C_O)/C_T - C_O)X\ 100$

C_O = Ca concentration with no inhibitor present
C_T= Ca concentration when no precipitation occurs (Initial amount of Ca added)
C_E = Ca concentration when inhibitors are present.

The composition of the brine used for the study is given in Table 1.

Table 1. Brine composition for lab study

Ion	Concentration (PPM)
Mg	100
Ca*	50-1000
Fe	10
Si (SiO_2)*	200-600
Na	9200
Cl	6000
SO_4	10,000
HCO3	300

*Calcium and silica concentration was varied to develop a dose response to varying conditions of silica and calcium carbonate inhibition.

3.2.2 Silica Scale

Similar studies were done for developing the silica inhibitor. In this case we used the weight of coiled capillary to determine the amount of silica deposited as a result of cooling the capillary. Additionally we also monitored the total silica and the monomeric silica. GEO980, which is a copolymer of acrylic acid and hydoxypolyethoxy allylether, has the ability to work as inhibiting/ retarding the rate of silica polymerization as well as dispersing the polymerized silica.

4. RESULTS AND DISCUSSION.

Some of the laboratory data for calcium carbonate inhibition using the brine in Table 1 is shown in Table 2. In this study we used 200 PPM of calcium and 200 PPM of silica as SiO2.

Table 2. Calcium carbonate inhibition at 250°C

Inhibitor	Dose (mg/L) needed for 100 % inhibition
GEO 901	3
GEO 903	2
5200M	2

GEO 901 is a phosphate ester, GEO 903 is a high purity acrylic acid polymer which does not contribute any S,P or N to the geothermal system, and *3 is synergistic mixture of phosphonate and acrylic acid based copolymer. During the selection of the scale inhibitor, it is important to understand that if the brine is, simultaneously, supersaturated with respect to any other scales in addition to calcium carbonate. GEO 901 has been very successfully applied in controlling fouling where the brine is simultaneously, supersaturated with respect to calcium carbonate, barium sulfate, and calcium fluoride. Most commercially available polyacrylic acids has S, or P leftover from manufacturing process (initiators or polymer chain transfer agents), which can cause precipitation of sulfite, sulfide or phosphate scales while GEO 903 (Moya, et.al.,2005) is manufactured using a process which leaves no S or P in the product. 5200M has a very high tolerance for calcium and therefore is especially suited when calcium carbonate driving force is very high or calcium is very high in the brine. This product is also highly effective for calcium sulfate, barium sulfate and calcium fluoride.

Using similar experimental set up and by varying the brine chemistry and the operating conditions, such as temperature and pressure, multiple data points for scale inhibitionare generated for various inhibitors to develop dose predictive models. This is very helpful in applying the correct dose under any conditions.

The new calcium carbonate scale inhibition product, 5200M has been commercialized after several field trials under wide range of calcite saturation index. In cooling water application the product has been used for several years up to 300X calcite saturation and calcium sulfate up to 7-8 X (Gill, and Yorke, 1994). Preliminary results has also shown its efficacy against stibnite inhibition under acidic conditions.

Most common solution for preventing fouling due to silica has been either removing silica by precipitation (Sugita, et.al.,2003)with magnesium lime and landfill or acidified (Gallup,D.L.,2006) the brine < pH 5 to prevent precipitation. Under acidic conditions the rate of silica polymerization is significantly reduced since silica polymerization is catalyzed by OH^- ions. However, both these solutions are very costly and compromise safety. Moreover acidified brine is highly corrosive (Gill, et.al., 2010) to the equipment and the injection well casing. Thus there is a major need for silica inhibitor.

Laboratory studies have shown that Geo 980 can prevent silica fouling up to 2-2.2X the equilibrium solubility of silica based on the solubility curve shown in figure 4. This solubility curve is only a guideline since the silica solubility is influence greatly by the presence of other ions, temperature, pressure and total ionic strength.

The dose curve (Figure 5) of GEO 980 was developed for brine in Table 1 and varying silica, temperature, and pressure.

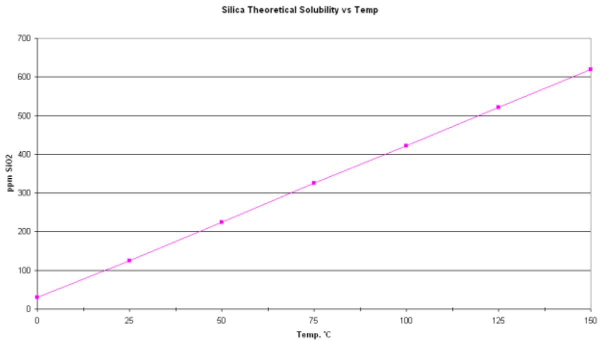

Figure 4. Silica solubility as a function of temperature

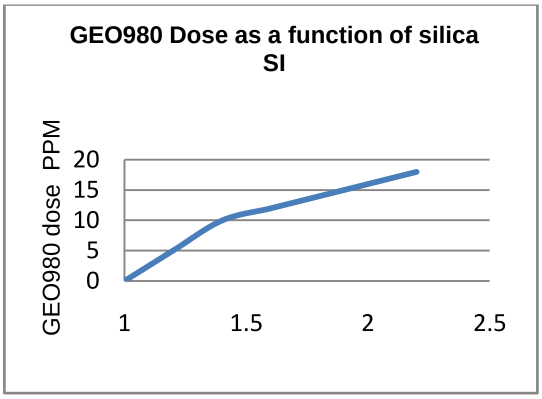

Figure 5. Dose of GEO 980 as a function of silica Saturation Index

This dose is a simplified version of the actual predictive model. The predictive model takes into account the effect of suspended solids and presence of various other species affecting the silica precipitation.

5.FIELD TRIALS

The Heber one facility is a combined flash and binary system. The schematic is given in Figure 6.

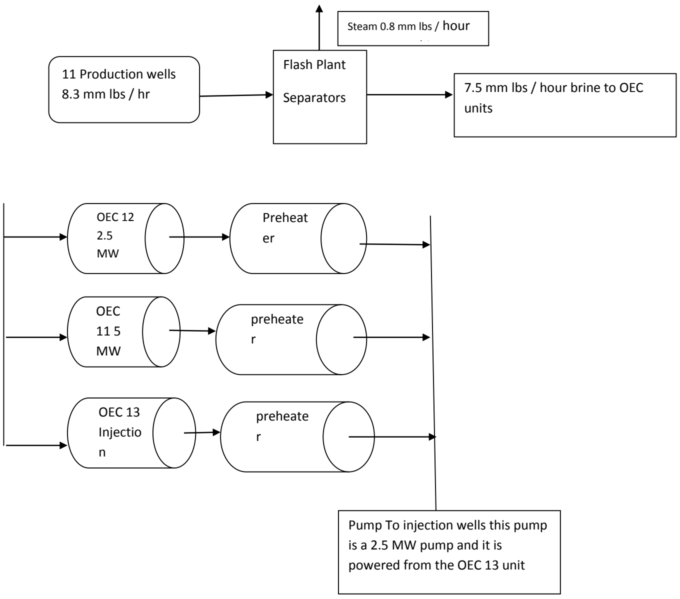

Figure 6. Schematic of the field trial site

The plant has eleven production wells at a total flow of 8.3 million lbs / hour that flow to an HP and LP separator. The separator allows the brine to flash due to a pressure drop and make steam for the flash plant;the steam is sent to a steam turbine and generates approximately 40 MW. The brine continues through the system at a total flow of 7.5 million lbs / hour to three banks of heat exchangers. The heat exchangers are shell and tube heat exchangers with Isopentane on the shell side and brine in the tubes for the vaporizers;water in the tubes and Isopentane on the shell side for the condensers. After the brine goes through the vaporizers it gives up more heat through the preheaters which are shell and tube heat exchangers with Isopentane on the shell side and brine in the tubes, once the brine leaves the preheaters it is sent to the injection wells. These heat exchangers comprise a close loop system for the Isopentane in which the Isopentane is heated up by the brine and sent to a turbine to generate power. The Isopentane is then sent to a heat exchanger to be cooled off before going back to the first heat exchanger to repeat the cycle. This system is known as the Ormat Energy Converter (OEC) system.

The brine enters the flash plant at 270-300 ^{o}F and then enters the OEC units at 220-240 ^{o}F. When the brine leaves the OEC units the temperature is 130-160 F. The brine has about 2400 ppm as CaCO3 and about 250 ppm Si as SiO2. The wells are artesian wells and flashing occurs as the brine flows up through the wells. The brine is treated with GEO904 downhole below the flash zone in each well to prevent calcium carbonate scaling.

As the brine flows through the OEC units and the temperature drops silica begins to drop out and cause scaling. Historically the plant has had scale problems in the OEC units and has lost MW production. Recently the problem has increased due to lower reservoir temperatures. The purpose of the GEO980 is to prevent the silica scaling through the OEC units and the injection wells. The GEO980 has been operating on the system since November 2010. From November through March the GEO980 appears to be working, but since there were not appropriate sample ports and the units had not been cleaned it was hard to evaluate. The OEC units were cleaned in April, 2011 and sample ports were added in effort to get the data required to further evaluate and optimize the treatment. Currently the Real Time Scale Monitoring (RTM) unit has been installed and data is being collected. RTM unit is based on quartz crystal microbalance technology (Figure 7).

Figure 7. RTM an online scale rate monitoring device

Figure 8. Front side of the scale coupon

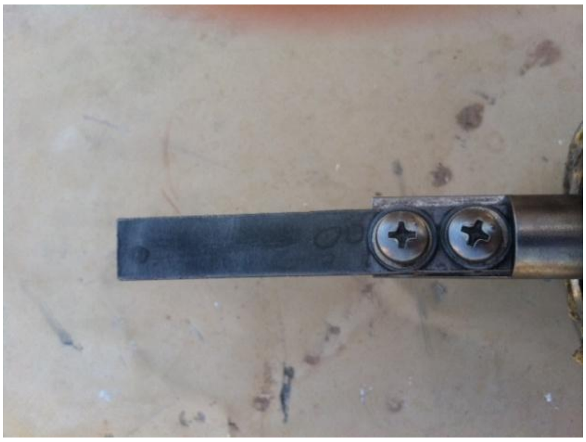

Figure 9. Back side of the scale coupon

Another silica trial using GEO980 was conducted at CFE owned and operated Geothermal Power Plant called Cerro Prieto, a 720 MW installed capacity. The plant is located in Mexico. In the recent years, Cerro Prieto has declined steam production capacity due to fouling of the wells caused by high silica concentration in the brineresulting in low Brine reinjection rates.The objective of this trial was to evaluate Binary Cycle Project viability using GEO980 to prevent fouling caused by silica.

Field Trail Evaluation criteria is based on

1. Scale coupons: Clean and free of deposit.
2. Total Silica Analytical Procedure. Before and after heat exchanger.
3. Field data, Brine Temperature and Pressure: Steady

In the early stages of the evaluation, application of GEO980 shows excellent results with following the measurements

SiO_2 = 550 ppm, $\Delta T = 130 - 100 = 30°C$, and $P = 30 - 25$ psi

GEO980 starting dose was 44 ppm and it was slowly reduced to the target dose of 20 ppm.

The test heat exchanger is shown in Figure 10 and the scale coupon from the exit (the coldest temperature of the test loop is shown in Figure 11, which appears to be completely free of any scale.

All the goals of the trial have been met, however the longer time data is still being collected.

Figure 10. The Test Heat Exchanger

Figure11. The scale coupon from the exit of the heat exchanger

6 CONCLUSION.

The data presented in this paper has identified two new scale inhibitors that can prevent fouling of silica, calcium carbonate, calcium sulfate and other scales in geothermal brines and cooling towers. Silica inhibitor, GEO 980, results are of paramount importance in harvesting energy even from low enthalpy brines that contain high silica level. The current practice of pH modification or silica removal by precipitation is very expensive, unsafe, and environmentally unsustainable. Better heat recovery is possible using GEO980 without fouling heat exchangers (binary systems) or plugging up re-injection wells.

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