

Scale Control in Geothermal Brines – New Inhibitors for Calcium Carbonate and Silica Control

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ABSTRACT

Fouling mitigation and corrosion control are big challenges in harvesting geothermal energy. In the production well, during or after flashing brine, the resulting high Ph water, in combination with high temperatures, can cause calcium carbonate precipitation. Silica/Silicate precipitation becomes a problem when the brine gets cold in the surface equipment and the rejection well. This paper discusses new inhibitors for both calcium carbonate and silica/silicate control.

INTRODUCTION

The appetite for oil and other energy sources is growing rapidly worldwide due to population increases and improvements in living standards. Alternate sources of energy must be found, especially those that are more environmentally acceptable. Geothermal energy has a minimal effect on the environment, depending on how the geothermal energy is produced. Direct use and heating applications have almost no negative impact on the environment. Geothermal plants using 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.

SILICA

In many parts of the world, silica is the 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 formed as a result of its polymerization, coprecipitation with other minerals, precipitation with other multivalent ions, and biological activity in the water. 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. The terms silica and silicates

are often used interchangeably. In fact, silica and silicate represent two distinct families of compounds. The terms should not be used interchangeably. Silica 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_2SiO_3 . 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, as determined by X-ray diffraction. The compound cannot be identified by its characteristic crystallinity since the particle size is so minute.

Silicate refers to compounds that 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 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 that could be present. Results of both water and deposit (elemental only) analyses are reported as SiO_2 regardless of whether the compound present is 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 for 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 that result in deposition.

CALCIUM CARBONATE

Calcium carbonate is another mineral that limits the use of geothermal brines. Precipitation of calcium carbonate is caused by the increase of brine pH during flashing of the brine, resulting in the escape of carbon dioxide. High temperature, in combination with high pH in the production well, represents an ideal atmosphere for calcium carbonate precipitation. Fouling occurs in the production well or in the surface equipment. Even a small (< 5 PPM) amount of calcium in brine is responsible for precipitating enough calcium carbonate to scale-up geothermal production wells.

It is well known that pH modification is one of the most promising methods for preventing scale deposition, but this method has not been commercially applied universally due to its primary shortcoming. The acidic conditions to prevent deposits due to silica¹, where the pH of the re-injection brine is modified to 5.5, results in severe corrosive conditions. Lowering pH, even to the range of 6-7, can also control calcium carbonate; but this can again lead to corrosive conditions. Development of corrosion inhibitors to control corrosion under acidic conditions could be of great value. This paper presents the application of two different chemical molecules to inhibit both calcium carbonate and silica/silicate deposit without the need for acid feed to lower the pH.

EXPERIMENTAL

Calcium carbonate inhibition studies were done using a stagnant flask at 55°C and an autoclave heated to 250°C with a synthetic brine (Table 1) to mimic typical geothermal conditions. The results are compared for various inhibitors and are presented in Tables 3 and 4.

Initially, silica beaker studies were done (similar to calcium carbonate) under stagnant conditions to determine the efficacy of the new molecule (TX13813) and, subsequently, most of the studies were done in a pilot cooling tower (PCT), at much lower temperatures than those encountered in the geothermal brines. However, it was postulated that since silica is much more soluble at higher temperatures than at colder temperatures, and if the molecule was hydrothermally stable at higher temperatures, these results could be applied to geothermal brines. Silica is seldom a problem in the production wells; it causes fouling in the surface equipment and the brine rejection wells. Hydrothermal stability of the inhibitor was evaluated using a 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°C/min. DSC results showed no apparent thermal event between 20 and ~180°C (Figure 2). A sample was heated at 95°C in a heating block for one hour. Molecular weight of the polymer was determined by Size Exclusion Chromatography (SEC). An attempt was also made to create surface equipment and injection well conditions. The synthetic geothermal brine was heated in an autoclave and the heated brine was passed through a pre-weighed stainless steel capillary. The experiment was carried out with and without the presence of silica inhibitor.

RESULTS AND DISCUSSION

The two essential properties of a scale inhibitor, namely surface adsorption and chemical binding with a scale-forming ion in the solution or at the nucleus surface, are not very well defined. It is the lack of this information that is responsible for any definite resolution on mechanism. Molecular modeling techniques, in which one can calculate the various interactive energies between the mineral and the inhibitor molecule, are also hampered by this unresolved mechanism. What is an ideal range of these interactive energies? There is no clear-cut answer that can provide some numerical value; the same is true for adsorption and inhibitor binding. All these measurements, such as binding constants, adsorption/desorption constants, affinity constants, and various other interactive energies, calculated using molecular modeling, must demonstrate a relationship with the inhibition data before these parameters can be used for predicting new inhibitor molecules¹⁰. However, as discussed above, the inhibitor molecule's ability to tolerate high calcium in hot brine remains one of the most desired properties of the molecule.

The water employed in these systems ordinarily will contain a number of dissolved salts, and the alkaline earth metal cation calcium is usually prevalent, as is the anion carbonate. The combination product of calcium cation and carbonate anion will precipitate from the water in which they are carried to form scale deposits when the concentration of the anion and cation comprising the reaction product (e.g., calcium carbonate) exceeds the solubility of the reaction product itself. Thus, when the concentrations of calcium ion and carbonate ion exceed the solubility of the calcium carbonate reaction product, a solid phase of calcium carbonate will form as a precipitate. Precipitation of the reaction product will continue until the solubility product concentrations of the constituent ions are no longer exceeded.

Table 1 – Composition of the Synthetic Base Water Brine*

Ion	Concentration (PPM)
Mg	10
Fe	10
Si (SiO ₂)	200
Na	9200
Cl	6000
SO ₄	10,000
Ca*	50-1000

*Calcium was varied as shown in Table 4.

The new calcium carbonate inhibitor is PolyAmino PolyEther Methylene Phosphonate² (PAPEMP). One of the particular advantages of the PAPEMP molecule is its exceptional calcium tolerance (Table 2). Calcium tolerance is a measure of a chemical compound's ability to remain soluble in the presence of calcium ions (Ca²⁺) under both high pH and high temperature, such as in geothermal brines. As pH and temperature increases, calcium tolerance decreases rapidly for traditional CaCO₃ threshold inhibitors (as shown in Figure 1), e.g., 1-hydroxy ethylidene 1,1-diphosphonic acid (HEDP), amino tri (methylene phosphonic acid) (AMP), and polyacrylic acid. The X-axis in this figure is the amount of HEDP as PPM needed to form precipitation in a water containing 10,000 PPM of Calcium ions. The data for temperature curve was collected at pH 9, while the pH curve represents data at 250°F. At higher temperature and/or higher pH, it requires <10 PPM of HEDP to cause precipitation; as the temperature or pH is reduced, higher amounts of HEDP are needed to cause precipitation of Ca-HEDP. These inhibitors precipitate with calcium at alkaline pH's and high temperature, rendering them useless as threshold scale inhibitors.

While it is a common practice to use an acid feed on the brine to lower pH and thus avoid the calcium tolerance problem and calcium carbonate precipitation for conventional inhibitors, the danger to handlers that such acid feeding poses makes it all the more important to find scale inhibitors that do not require pH adjustment. In geothermal brine, high temperatures make high calcium tolerance even more attractive.

The inhibition data reported in Tables 3 and 4 shows excellent performance for calcium carbonate inhibition with PAPEMP. In Table 3, the data was generated using synthetic calcium carbonate supersaturated water and incubating the flasks for 24 hours at 55°C. At the end of the incubation time the soluble calcium was determined in each flask to calculate % inhibition.

$$\% \text{ Inhibition} = (C_E - C_O) / (C_T - C_O) \times 100$$

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.

Another set of experiments was carried out using Par Tube Autoclaves in which the test solution also contained sulfate ions, in addition to calcium, carbonate/bicarbonate, sodium, and chloride ions. The test solutions were incubated for 24 hours, and at the end of the incubation time the soluble calcium was determined in the filtrate to calculate % inhibition. As shown in Table 4, PAPEMP in combination with AA/AMPS copolymer out performed both PAA and PMA. It must also be noted that this combination inhibited both calcium carbonate and calcium sulfate.

Table 2 – Typical Inhibitor Tolerance

Inhibitor	PPM inhibitor for ppt./1000 Ca ²⁺
PPM	Ca ²⁺
PAA	115
PMA	35
AA/AMPS	>1200
AA/SPME/MA	268
HEDP	17
AMP	44
PAPEMP	>40,000

Separately, the hydrothermal stability of the PAPEMP and AA/AMPS copolymer were evaluated by heating up the molecule in synthetic brine at 250°C. No molecular structural or performance degradation was observed for either polymer.

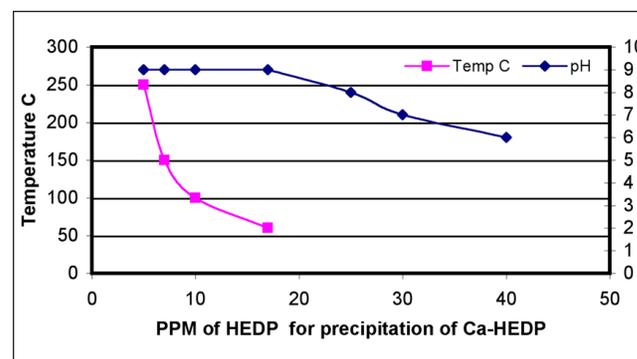


Figure 1 – Calcium Tolerance of HEDP

Table 3 – Comparison of Inhibition at 300X Calcite Supersaturation, pH 9.0, Temperature 55°C

Inhibitor	Active Dose PPM	% Inhibition
AMP	25	41
HMDTMP	25	55
PBTCA	25	57
HEDP-AMP-AA/AMPS Copolymer	23.4	60
PAPEMP	25	100
PMA	25	56
A EC	25	62

HEDP: 1-Hydroxyethylidene 1-1 diphosphonic acid
 AMP: Amino tri (methylene phosphonic acid)
 HMDTMP: Hexamethylene diamine tetra (MPA)
 PBTCA: 2 phosphonobutane-1,2,4 tricarboxylic acid
 AA/AMPS: Copolymer of acrylic acid and 2-acrylamido-2-methylpropylsulfonic acid
 PAPEMP: Polyamino polyether methylenephosphonic acid
 PMA: Polymaleic acid
 AEC: Allyl Epoxy carboxylic acid

Table 4 – Mixed calcium carbonate and calcium sulfate inhibition with PAPEMP, pH 7.5 250°C; SO₄ 1500 PPM

Inhibitor	Dose PPM	% Inhibition at various Calcium PPM			
		50	100	500	1000
PAA	5	100	100	60	
	10	100	100	60	0
PMA	5	100	80	70	0
	10	100	80	60	0
PAPEMP-AA/AMPS	5	100	100	100	72
	10	100	100	100	89

The silica inhibitor is a copolymer of acrylic acid and PEG methacrylate³. The major active component of the co-polymer has a structure where the repeating unit in PEG varies between 5-10.

The DSC curve (Figure 2) remained flat during the entire scan (the instrument had a temperature limitation) indicating no thermal degradation of the molecule. The SEC data also showed that there was no significant change in polymer MW distribution (see the overlay of SEC traces in Figure 3)

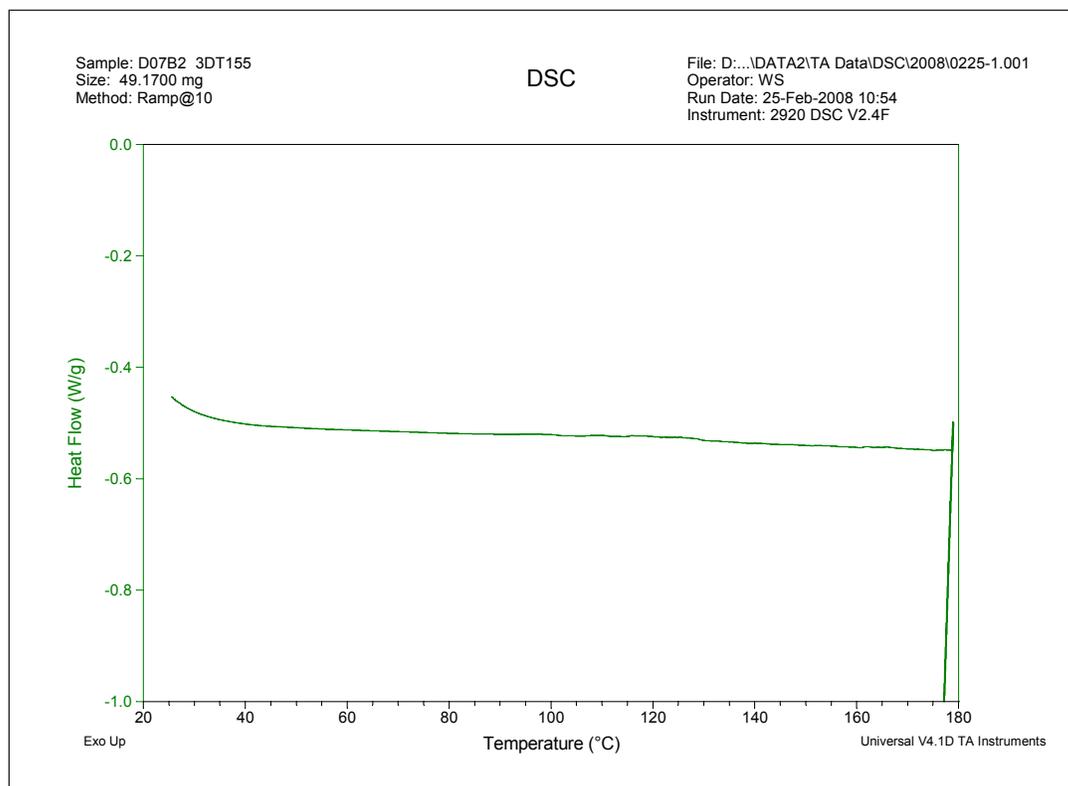


Figure 2 – Thermal stability (DSC) plot of silica Inhibitor

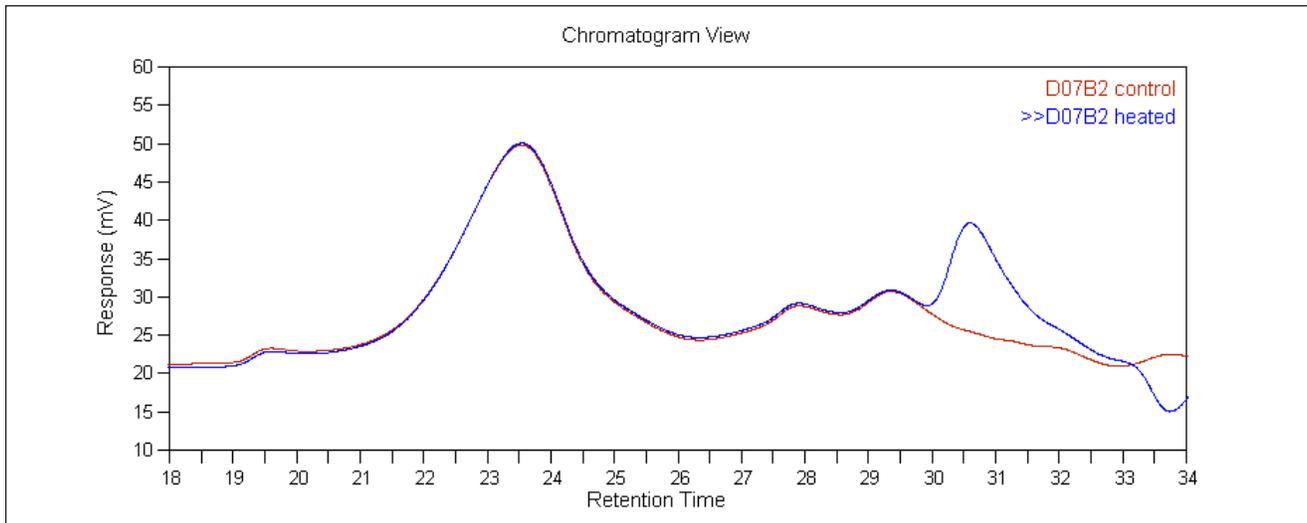


Figure 3 – Molecular Weight Spectra Comparison (Heated vs. Non-Heated)

The preliminary evaluation of this molecule was centered towards inhibition of amorphous silica. Experimental conditions were based on the Figure 4, speciation to avoid the formation of silicates, although other ions such as calcium and magnesium were added to the test solution.

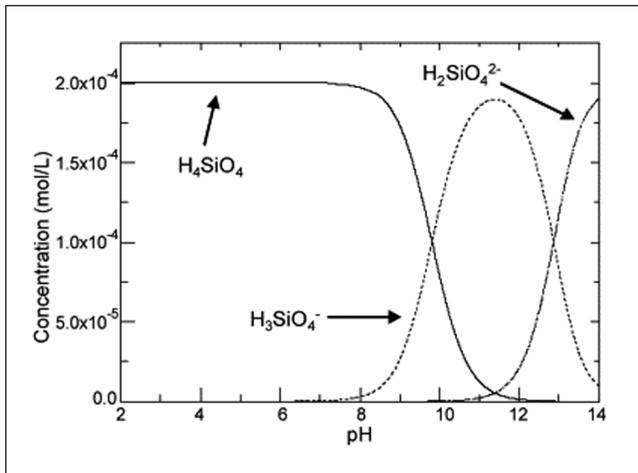


Figure 4 – Speciation curve of silicates calculated with PHREEQC for an initial concentration of $2.0 \times 10^{-4} \text{ mol/L}$ of H_4SiO_4 .

PERFORMANCE TESTING RESULTS

Data from the Pilot Cooling Tower (PCT) testing suggests we could push total silica levels up to 2X the equilibrium solubility of amorphous silica. The pilot cooling study was done with the exit temperature of 95-105°F. At these temperatures, general recommendation is to keep the total silica level between 200-230 ppm total. A number of tests were run under varying conditions.

PCT Testing under conditions similar to our field trial (South-Western Power Plant) were run to evaluate dosages. Examples of the performance testing results are given below.

In a set of beaker studies, calcium chloride (500 ppm as CaCO_3) and magnesium sulfate (250 ppm as CaCO_3) are added, in addition to sodium meta silicate. The starting concentration of silica is 250 ppm as CaCO_3 . The pH of each beaker is adjusted to 7.4. The results are shown in Table 5.

Table 5 – Silica as SiO_2 PPM

Time (minutes)	No Inhibitor	10 PPM Inhibitor	20 PPM Inhibitor
0	250	250	250
50	160	225	240
100	150	225	240
150	140	220	220
200	140	190	220

The data indicate the silica inhibition dependency on both time and product dose. These results do show the importance of kinetics and residence time in determining the optimum dose to inhibit silica deposition. It must be kept in mind that the silica numbers shown in Table 4 are based on a temperature of 25°C.

Pilot Cooling Tower Study

A simulated cooling tower study was used to evaluate the efficiency of the silica inhibitor.

The make up water chemistry of the tower was as follows:

- 84.9 g/250 gal. make up water of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$;
- 147.3 g/250 gal. make up water of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$;
- 233.8 g/250 gal. make up water of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$; and
- 56 ml conc. H_2SO_4 /100 gal. make up water.

The water was cycled until silica precipitation became apparent. The pH of the recycled up water was controlled at 7.8 and calcium carbonate precipitation was controlled using phosphonate scale inhibitor. The silica inhibitor product dose was maintained at 30 PPM.

A typical result from PCT study is shown in the following Figure 5.

Several runs were done to determine the product dose under various conditions and also to determine maximum silica that can be inhibited with a given dose.

FIELD TRIAL RESULTS

Results of two field trial applications are shown below.

The first test site was at a South-Western Power Plant, with a goal of replacing the existing silica treatment on an equal active feed basis, but preventing scaling. This site had a history of silica scaling under the old treatment. The new polymeric molecule based product was initially fed at 20 ppm active, which was subsequently reduced to 15 ppm actives, and was gradually being reduced to a minimum value that precludes scale formation, as identified on the Real Time Monitoring (RTM). RTM is a quartz crystal based scale monitoring device commercialized by Nalco Company.

The product was fed under TRASAR 1 control with data logged using 3D TRASAR® technology with web access via a wireless connection. Dosage was stepped down from 20 to 15 ppm as actives; 15 ppm actives corresponds to an equal or slightly better than equal

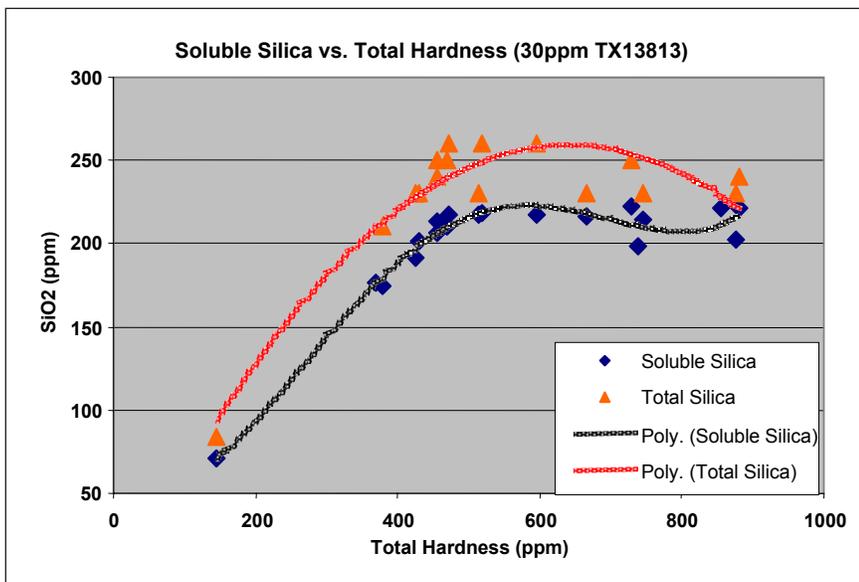


Figure 5 – A typical PCT run

PCT Tower	Program varied Dosage	Limiting Soluble SiO_2 PPM	Limiting Total SiO_2 PPM	Max Total SiO_2 PPM	Notes
D	60 PPM SiO_2 inhibitor + 100 PPM Scale/corrosion	190-200	200-220	240-260	Excellent MS and ADM corrosion
C	30 PPM SiO_2 inhibitor + 100 PPM Scale/corrosion	180-190	190-205	220-240	Very good MS and ADM corrosion
C	10 PPM SiO_2 inhibitor + 100 PPM Scale/corrosion	170-185	180-200	210-240	Excellent corrosion results
D	20 PPM SiO_2 inhibitor + 5 PPM PEG + 100 PPM Scale/corrosion	180-190	190-210	230-260	Excellent corrosion results

cost feed basis compared to the existing treatment cost. The new product feed was suspended for a short while and returned to the old product following this initial test, due to a regulatory approval review at the facility. Drop off in feed during this suspension is indicated by the reduction in the TRASAR 1 signal. The feeding of old product, a terpolymer of acrylic acid/ 2-acrylamido 2-methylpropyl sulfonic acid/ t-butyl acryl amide, resulted in scaling rate increase, which was identified in the RTM signal.

The site contains about 30 ppm of SiO_2 (as SiO_2) in the makeup water, 84 ppm CaCO_3 , and 16 ppm Mg (both as CaCO_3). Tower pH is maintained at 8.0 - 8.2. Some variability in makeup water chemistry may occur as makeup water sources change. The tower operates near 7 cycles. During the test, total and soluble silica were monitored. Higher total and soluble silica levels were maintained with improved scaling protection as verified by RTM data. Total silica levels run during the trial ran between 220 and 240 ppm. Soluble levels were typically 190-195 ppm.

RTM data from the site was collected and the mass uptake slopes are shown before and after the test phase. Mass uptake on the crystal was found to be higher during periods of old treatment. Downward spikes in the data (Figure 6) correspond to regular crystal cleanings to remove deposited scale. During the period of the trial, the slope of the mass uptake on the crystal was found to be lower than during periods of time when the old treatment was in use.

The second test site was another Power Generation Station in Nevada. The site had previously fed a polymeric silica inhibitor. The new silica inhibitor has been fed at this site as a replacement product on two towers (Unit 3 and Unit 4) and is being expanded to others. The product is being fed at this site currently at 10-11 ppm active with no scaling observed via real time monitoring. Total silica levels in the towers vary up to about 250 ppm total silica. Unit 4 operational water information is shown below:

An example of the recirculating water chemistry from Unit 4 at this power plant generating station is shown in Figure 7.

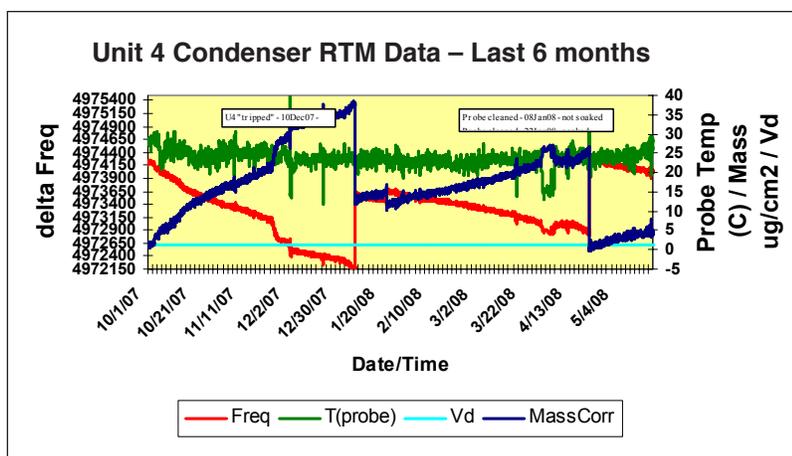


Figure 6 – Real Time Monitor data

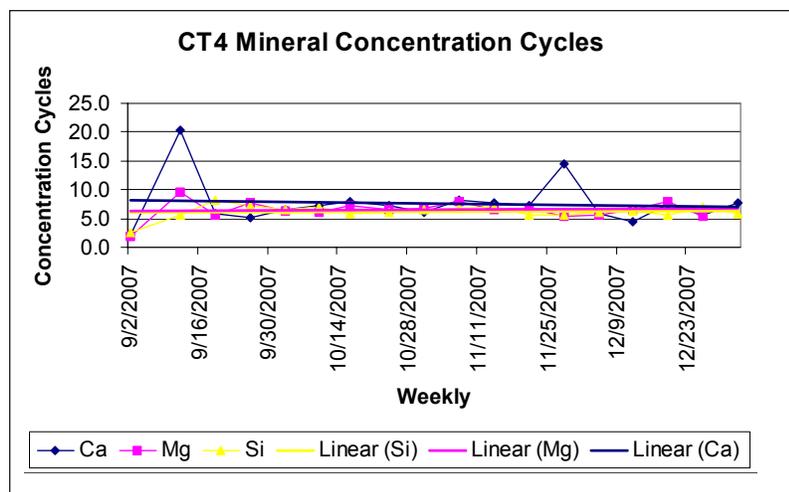


Figure 7 – Water chemistry plot during the field trial of new Silica Inhibitor

A real time monitor to determine if scaling is occurring has monitored Unit 4. No evidence of scale build-up has been identified from the RTM tracking occurring during the 3DT255 application.

Both power plants are continuing with the program and are working to optimize the dosage while keeping silica scaling to a minimum.

In 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 cooling tower and, additionally, geothermal brines.

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