

Minimising Calcium Carbonate and Silica Precipitation in High Efficiency Geothermal Power Plants Through the Use of a Thermally Stable Blend of Polycarboxylate Polymer Additives

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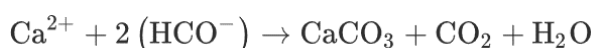
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ABSTRACT

The brine fluids in geothermal power plants usually have high levels of scale forming minerals within them. Typically, calcium carbonate has been the key issue in the past as it is prone to precipitate out in the production well where the high temperatures cause precipitation, usually in the zone below the wellhead according to the reaction:



Ca = Calcium ion, (HCO⁻) Bicarbonate ion, CaCO₃= Calcium Carbonate, CO₂ = Carbon Dioxide, H₂O = Water

Calcium bicarbonate breaks down in the presence of heat to form calcium carbonate, plus carbon dioxide gas. The calcium carbonate so formed is highly insoluble and will readily precipitate.

Control of calcium carbonate is relatively straightforward, and a number of established chemical control methods are available based on either phosphonate or polymer technologies. The key to successful control is having a product with suitable thermal stability to withstand the conditions within the production well and inhibit calcium carbonate deposition. ¹

More recently, with the drive to extract ever more useful heat energy from the brine, silica deposition is also becoming more of an issue. The reason for this is that as the brine temperature is lowered because of additional heat extraction prior to reinjection, there comes a point where silica levels exceed their solubility, and precipitation of silica will result. ²

Silica precipitation can be exceedingly damaging. The deposits can highly impair heat transfer, reducing plant efficiency. Removal of such deposits can be very complicated and often the only solution is to clean with hydrofluoric acid which is not an easy task.

This paper considers the practical use of a thermally stable blend of polycarboxylic acid (PCA) polymers, to not only control calcium carbonate based deposits in the wellhead, but also prevent the precipitation of silica or metal silicates within the heat exchangers as the brine is progressively cooled.

The use of these materials offers an enhanced level of plant protection, improving power output and preventing plant downtime. In addition, PCA based polymers contain extremely low levels of phosphorus. Minimizing use of phosphorus is important as the brine is reinjected, it helps prevent a build up of this material over time as wells age.

1. INTRODUCTION

The development and use of geothermal heat in the production of power is becoming of increasing significance as the world turns to means of carbon neutral energy generation. ³ Geothermal energy has a minimal effect on the environment ⁴. Geothermal power generation plants release a tiny (<5%) proportion of the CO₂ in comparison to plants burning carbon-based fuels to generate steam. Any gases that are contained within the geothermal fluid can usually be managed and / or reinjected into the reinjection well. ⁵

The minerals that are contained within the geothermal brine however can be more of a challenge. Calcium Carbonate (CaCO₃) in the production fluid and silica (SiO₂) deposition in the above ground heat exchanger equipment can both cause issues if not properly addressed.

Cleaning of Calcium Carbonate in comparison to the removal of silica is a relatively straightforward task, however removal of either material can cause significant loss in plant efficiency and expense in terms of the cost of cleaning, plus the monetary loss from lost power generation.

In order to control deposition, there are of course several options. These will vary from plant to plant depending on circumstances, in broad terms however the main choices are:

1) Control of pH to keep Saturation index less than 1.0⁶ (Scaling tendency is usually measured by calculation of the Saturation Index for the species of interest, the higher the value, the more likely is scaling and deposition) with addition of acid.

2) This is possible for control of both Calcite and Silicate, however the addition of acid brings other issues, in particular the control of corrosion which is made much more likely once pH levels become acidic, and to a lesser extent the handling and logistics issues.

3) Dilution with water with a low mineral content: Condensate from the power plant or fresh water source can be used, not an option for calcite scaling but possible in order to prevent silica precipitation. ⁷

4) Use of scale control additive, materials typically used would be either polymer or Phosphonate based, or combinations of the two. This approach can be effective either as a standalone measure or in combination with the other remedial actions listed above. The usual constraint on the use of a polymer can be the dosing rate needed, bearing in mind the high flow rates of brine in a typical geothermal facility.

This paper will now go on to evaluate a PCA blend in two field-based studies.

2. RESULTS AND DISCUSSION

2.1 Geothermal Plant Turkey

A geothermal production facility located in Turkey. The plant characteristics are summarised as below:

	Value
Power Production	16MWe per hour
Brine Flow	2171 Tonnes per hour
Brine Temperature	140 °C
Steam Production	20 Tonnes per hour
Reinjection Temperature	60 to 74 °C

Figure 1. Plant Characteristics

The plant was experiencing both calcite and silicate precipitation issues. Calcite deposition was occurring in the production wells at depths of between 700 and 1200 metres corresponding to the flash point of the brine. The reason for calcium carbonate issues is that as the steam flashes from the brine, it then becomes more concentrated until the solubility point for Calcite is exceeded and precipitation follows. A typical brine analysis of key components is shown below in Figure 2.

ICP OES ANALYSIS RESULTS					
	WELL1	WELL 2	WELL 3	WELL 4	
PARAMETERS					UNIT
[Aluminum (Al)]	0.377	0.488	0.374	0.527	ppm
[Barium (Ba)]	0.716	0.551	0.669	0.512	ppm
[Calcium Hardness (CaH)]	36.55	14.8	35.18	13.52	ppm
[Magnesium Hardness (MgH)]	7.2	17.76	9.24	3.66	ppm
[Total Hardness (TH)]	43.75	32.56	44.42	17.18	ppm
[Crom (Cr)]	0.108	0.078	0.078	0.079	ppm
[Copper (Cu)]	0.062	0.060	0.060	0.060	ppm
[Iron (Fe)]	0.066	0.85	0.116	0.082	ppm
[Potassium (K)]	138.13	136.72	123.18	127.72	ppm
[Mangan (Mn)]	0.143	0.138	0.136	0.134	ppm
[Sodium (Na)]	1324.64	1346.04	1209.53	1230.12	ppm
[Nickel (Ni)]	0.033	0.511	0.033	0.033	ppm
[Phosphate (PO4)]	0.78	3.46	0.83	0.67	ppm
[Sulfate (SO ₄)]	7.03	7	9.2	9.87	ppm
[Antimony (Sb)]	0.518	1.568	2.101	0.675	ppm
[Silicon Oxide (SiO ₂)]	183.63	145.54	176.75	180.65	ppm
[Strontium (Sr)]	1.216	2.011	1.431	0.962	ppm
[Zinc (Zn)]	0.101	0.338	0.044	0.013	ppm
[Molibden (MO)]	0	0	0	0	ppm

Figure 2. ICP Analysis of Brine

Carbon Dioxide and Hydrogen Sulphide also leave the brine with the steam component, further exacerbating this situation. The pH can move from values of 1-3 to between 6-8 in few metres, further driving the production of calcium carbonate.

As calcium carbonate forms and is then precipitated, it will progressively build up on the well surfaces until ultimately brine flow will be reduced.

Silica deposition on the other hand only becomes an issue on the surface of the plant as heat is removed from the brine. Silica unlike Calcium Carbonate is more soluble the higher the water temperature. There will come a point where the Saturation Index will exceed 1.0 however, and it is at this point that any equipment will be vulnerable to precipitation and scale build up.

Prior to the application of the PCA Polymer blend, the plant, on a previous treatment regime had been experiencing both calcite deposition down the well, and silica deposition on vulnerable surface equipment, including vital preheaters as explained previously. Figure 3 shows evidence of silica deposition on one of the coupon test pieces.



Figure 3. Coupon Test Piece Pre PCA-Treatment Showing Silica Deposition

A twice-yearly cleaning regime was accordingly in place to remove deposition by manual and chemical means. As a direct result of this downtime, the value of lost power generation was \$115,000 per annum.

The PCA Polymer blend was introduced immediately following a scheduled plant clean. It was decided to apply the blend down the production well, to a point prior to the steam flash in order to control calcite precipitation. The fact that the additive was being dosed into the high temperatures of the production well also explains the need for high thermal stability. The PCA will then carry through the surface systems and should then prevent the deposition of silica on vulnerable equipment, prior to reinjection.

Following over a year of operation on this treatment regime, the plant has remained scale free. No evidence has been reported of deposition build up in either the production well from calcite, or from silica precipitation on surface equipment. The need for plant shutdown has been reduced by 50% and the only shutdown now is for annual inspection and mechanical maintenance. Figure 4 shows a test piece clean with no further evidence of silica present.



Figure 4. 12 Months Post PCA Treatment implementation coupon clear of Silica deposition

2.2 Geothermal Facility Asia

A geothermal facility in Asia was experiencing silica deposition issues in the cooler sections of the plant where typically the brine temperature had fallen below 90°C. The buildup of material was causing flow issues and plant downtime.

Removal of the deposits which were found to be amorphous silica was time consuming and resulted in plant downtime. The material either had to be physically removed, or cleaned chemically with hydrofluoric acid, both very demanding processes. In extreme cases where pipelines had become blocked, replacement of the entire pipeline was the only solution.

Evaluation of the PCA blend on the plant was therefore agreed. A brine line was divided into two parallel lines. The brine in one line remained untreated and would serve as the blank during the duration of the trial. The other line was fitted with a dosing quill and would be the additive test line. Both lines were fitted with removable test sections. These could be taken out and inspected as necessary to evaluate the effectiveness of the test. Brine conditions are highlighted in figure 4.

Total Silica	800 – 870ppm as SiO ₂
Silica Saturation Index	2.0 – 2.2
Calcium Concentration	190ppm as CaCO ₃
Chloride	5500 as Cl ⁻
pH	7.4
Temperature	95°C
Pressure	0.6 bar
Flow Rate	2.2Kg per minute

Figure 5. Composition of the brine

On the side of the circuit to be treated, two consecutive tests were carried out with the addition of 5ppm and 10ppm of PCA additive.



Figure 6. Untreated Line



Figure 7. Treated Line 10ppm additive

After four weeks operation the test sections were removed. The thickness of the scale deposited on the inner surfaces of the test sections was measured (red arrows on diagrams in figures 5 and 6).

The scale was analyzed by X Ray fluorescence (XRF) and X Ray diffraction techniques and found to consist of over 80% amorphous Silica as referred to previously.

The results of the trial are shown in figure 8 (5ppm dose level) and figure 9 (10ppm dose level).

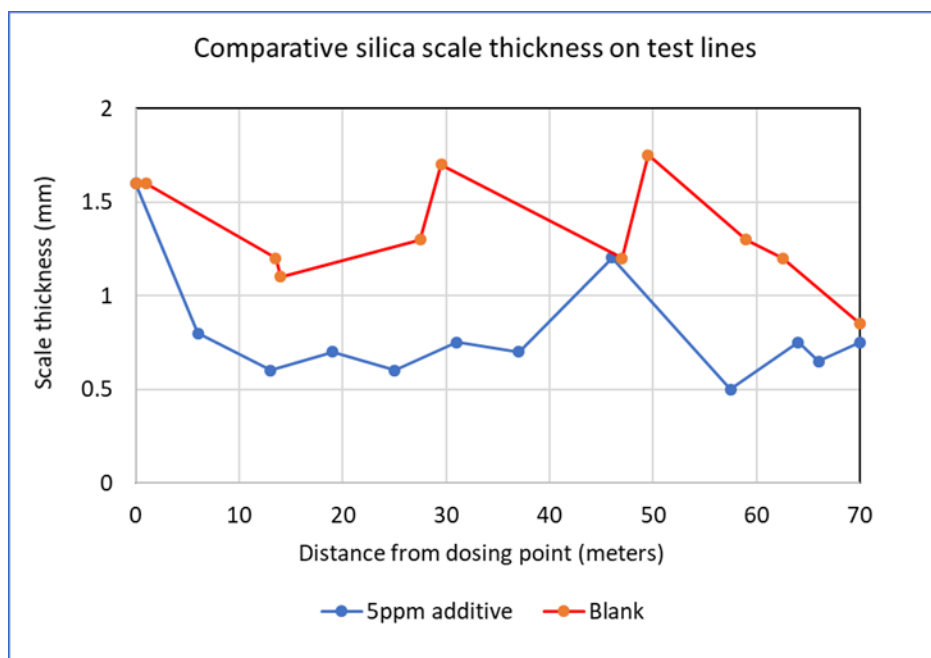


Figure 8. Silica Scale Thickness on Test Lines 5ppm PCA

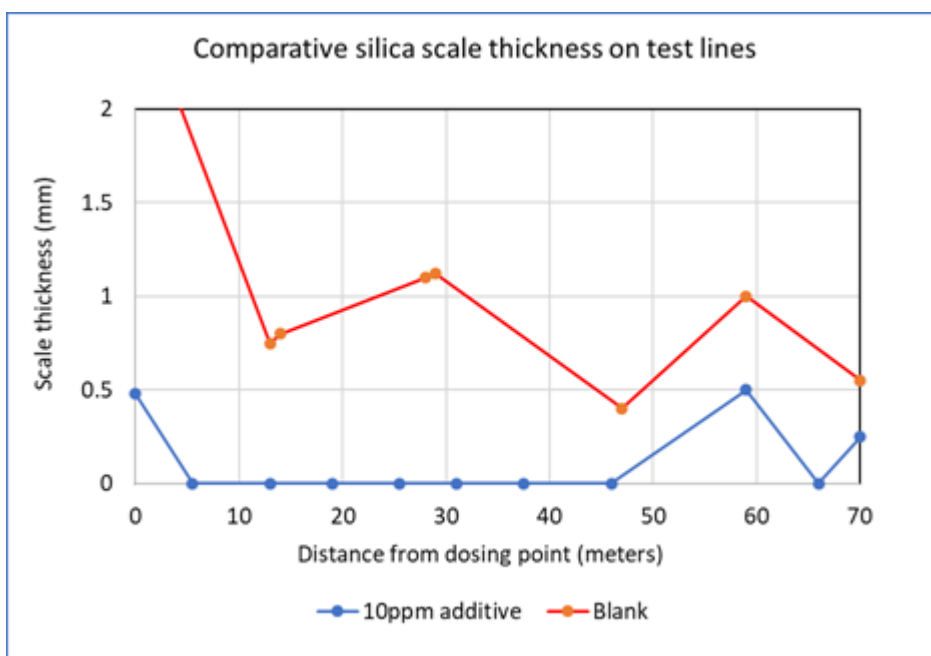


Figure 9. Silica Scale Thickness on Test Lines 10ppm PCA

These results demonstrate clearly that the use of the PCA additive blend reduced the thickness of the scale deposit over the entire length of the line by approximately 35% at a 5ppm dose level and approximately 90% at a 10ppm dosage rate. The effect was more noticeable closer to the point of dosing than at the furthest measured point in this example. More work will need to be undertaken to determine the reasoning behind this.

Some additional work on optimization of the addition rate showed that 8ppm could achieve exactly the same level of inhibition as a 10ppm rate.

A further piece of testing was then undertaken using pre weighed stainless steel coupons so as to determine precisely the scaling rates which were occurring. The 8ppm optimized addition rate of PCA blend was applied to the brine upstream of the metal test pieces, and the system was run for a 14-day evaluation period.

The results are presented in figure 10 as scaling rate vs deposition test coupon number. These results demonstrated clearly that with the presence of 8ppm PCA additive the scaling rate is reduced by a factor of 14 in comparison with the scaling rate of the blank line.

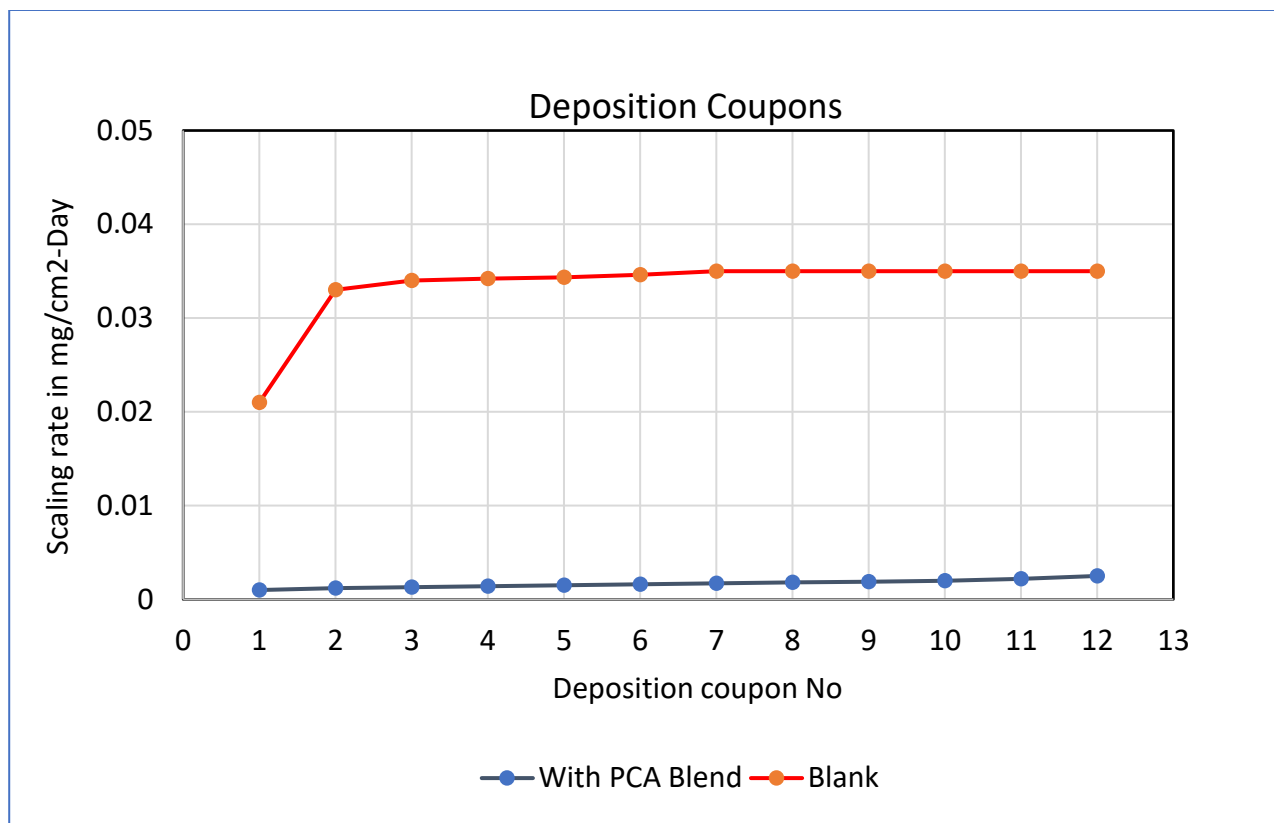


Figure 10. Deposition Rates on Coupons With 8ppm PCA Blend

3. CONCLUSIONS

The two case studies reviewed here both demonstrate clearly the value of the PCA inhibitor blend in preventing both Calcium Carbonate and Silica precipitation in Geothermal brine systems facing both Calcium Carbonate and Silica saturation values in excess of 1.0.

Scale deposition both in the production well and on surface equipment has been controlled and minimized with the simple application of one product, rather than multiple applications or a mixture of solutions.

A blended PCA is capable of both preventing deposition of mainly calcium containing salts in the production well, in addition to helping control silica deposition in the cooler parts of the plant, prior to brine reinjection.

Power output has been maintained and loss of generation through downtime kept to an absolute minimum on both locations.

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