ONLINE CALCITE REMOVAL, SILICA PREVENTION AND REMOVAL, NACE TEST AND CALCIUM ACRYLATE PREVENTION: AN UPDATE ON R&D PROGRESS

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ABSTRACT

At the 2013 NZGW there were discussions about the need for more R&D and how the chemical industry could contribute to moving the Geothermal industry forward by looking into solutions to chemistry problems some plants are facing. In particular silica and antimony was highlighted. This paper is an update on advances made into a series of issues that are, have been or could be faced by the Geothermal power producers. Some solutions have been found, others are work in progress. The topics covered are: online calcite removal, silica inhibition and removal, NACE testing and calcium acrylate deposition.

It was suggested that it is time to work more collaboratively to move our industry forward and be part of the promulgation of clean energy in the face of doubling world energy demand over the next 3 decades.

Initial on site online calcite removal trials show that a combination of PMA and copolymers combinations including carboxylates alkyl ethers and sulphonates, have increased soluble calcium levels in treated brines. This indicates online calcite removal whilst the geothermal well remains in production.

Silica inhibition has been successfully achieved by similar copolymers in an ORMAT run plant and work is now underway to search for methods of dissolving silica which does not involve strong acid. Initial results are presented.

Investigation into the NACE test procedure showed that significant differences in results to screen calcite inhibitors is due to the method used to test the thermal stability of the compounds. As these are used by the industry to make decisions that impact selection of calcite inhibitors and could contribute to calcium acrylate deposition it was thought worthy to uncover the reason for the variances. It was found that the procedure used to test thermal stability is where the inconsistency originates. An oxygenated procedure impacted results from 86% to 540% and varied for each of the 11 inhibitors treated.

The advent of calcium acrylate in boiler and binary plants has been solved by initially adding sulphonate side chains onto acrylate polymers. This has been a significant factor in the development of the copolymer technologies which avoid calcium acrylate deposition completely and are showing improved results for the treatment of silica, calcite and metal sulphides. It is concluded that using unmodified polyacrylates increases the risk of calcium acrylate deposition in binary plants.

1. INTRODUCTION.

With world energy demand set to double in the next 35 years we as a race face unprecedented challenges in energy supply. Our bigger challenge is how we do that and minimise the impact that supply has on the planet's ability to support life.

Geothermal Energy is one of the cleanest power sources in the world. The more we collaborate and make this the intermediary step to looking to the sky for our energy, the better the prospects are for the environment our children will inherit from us.

The speed and efficiency at which we do this is only limited by our ability and willingness to collaborate and work collectively toward solutions and clean advancements. When business structures and corporate values get in the way, we as today's professionals must step up and prioritise the challenge before us and be part of the change to correct this.

At the 2013 NZGW there were discussions about how the chemical industry could contribute to moving the Geothermal industry forward by looking into solutions for chemistry problems some plants are facing. In particular silica and antimony was highlighted. This paper is an update on advances made into a series of issues that are, have been or could be faced by the Geothermal power producers. Some solutions have been found, others are work in progress. The topics covered are online calcite removal, silica inhibition and removal, NACE testing and calcium acrylate deposition.

2. SILICA DEPOSITS: PREVENTION AND DISSOLUTION.

As technology advances and we extract more heat from geothermal brines, mineral precipitation of metal sulphides and silica become more of a plant limiting feature. Silica is particularly troublesome in NZ and it is common to dose sulphuric acid into reinjection lines to slow the polymerization of silica until it reaches the hotter aquifer. However the question of the long term sustainability of pumping concentrated acids into our geothermal aquifers has been raised. It is generally agreed that this is not a practice we can sustain indefinitely and it seems some analyses are showing signs of increased sulphate levels in production wells already. The challenge is the cost, effectiveness and availability of alternatives. Furthermore, once deposited, silica is difficult to remove. It is common in NZ that silica deposits as aluminium silicate; a particularly hard and difficult to remove deposit that 15000psi water blasting often fails to shift. Hydroflouric acid is used but this is a costly and dangerous acid raising H&S and transportation issues.

What is clear is that further R&D is required to develop safer, cost effective solutions. Below we discuss some development work in progress and preliminary results of trials.

2.2 Prevention.

Our first approach is to develop an organic inhibitor that will decompose to CO_2 and water in the aquifer to replace the strong acids currently used that are dangerous and toxic. An organic copolymer was found to be effective up to an SSI of 2.3. The toxicity of this is compound is : LC50 Daphnia magna: 7,551 mg/l, which when compared to table salt LC50 3000mg/l is favorable. This polymer was trialed at the Heber Ormat plant where silica scaling in their ORMAT unit was significant, approximately 4-6 mm/yr. This required hydrofluoric acid cleaning and hydroblasting twice per year. The scaling was worse than we see here in NZ.

A dosage of 2 ppm of the copolymer has meant they ran for 12 months without the need for hydrofluoric acid cleaning. At the annual shuts the units are opened and water blasted to remove any soft build up. This was sustained for three years.

The following two pictures depict the scale coupons used to determine dose rates and clearly show the impact of the polymer dosing.

Figure 1: 8 Days treatment with < 1 ppm Co polymer

Figure 2: 7 Days treatment with 1.75 ppm Co polymer

Based on these results a field trial is now underway in NZ. As each brine is chemically different and plant designs vary significantly, the applicability of the polymer application needs to be modelled for each system, paying particular attention to the cost effectiveness. The results of this trial should be known by the beginning of 2015.

Additional research is underway using the results obtained at TOP Energy, where crystalline stibnite (antimony sulphide) was converted to its colloidal form when dosed at given conditions. This has begun the investigation into the possibility of achieving the same with silica. There are parallels in the mechanisms by which these group 4 and 5 elements form crystal lattices, colloids and compounds with other anions. The use of carboxylate side chains to raise zeta potentials of copolymers has proven to be successful with antimony and it is now a project to explore the applicability to silica. This is work in progress.

2.3 Dissolution

Chemical dissolution of silica is preferential to cutting out pipes and using pigs or hydroblasting IF it is cost effective. As discussed earlier, HF is used but comes with significant drawbacks, despite being effective at removing deposits. Caustic and EDTA have some impact on silica scales but less so on silicate compounds such as aluminium silicate. The challenge therefore, is to find an effective solute for silica deposits that is cost effective and easy to handle. New compounds have been formulated and tested against some known solutions that remove silica, these being EDTA and high levels of the co polymer mentioned above. Initial results are encouraging and are shown below for a 1% solution of the three tested solutions on an aluminium silicate sample taken from a NZ reinjection line.

Dissolution Study				
1% solution of	**Initial weight (g)**	**Final weight (g)**	**Silica loss (g)**	**% loss**
GEO 9XX	1.998	1.627	.371	18.6
Tetra sodium EDTA	1.995	1.899	0.096	4.8
GEO 907	2	1.915	0.085	4.25

Figure 3. Results from comparative silica dissolution test.

Encouraging results, however more work is needed to further enhance performance. The second stage is examining the cost effectiveness of the new silica dissolving compound.

3. ONLINE CALCITE REMOVAL.

When a production well scales it causes two issues for the producer, one is the loss of production from the asset, the other is the cost of cleaning. Traditionally wells have been worked over by drilling out the calcite deposits; recently two new lower cost solutions, broaching and/or Coil Tubing Units have been used. A less intrusive solution would allow for prevention of the calcite from forming and where existing deposits occur, slow, online, removal of the scale deposits to return wells to their full output. This could be used in wells that are not significantly scaled and also would offer a way to overcome deposits caused by plant upsets, equipment failure etc.

Results from six NZ wells indicate that using a blend of traditional scale inhibitors and copolymer technology similar to that used in the boiler industry for the last two decades to transport cations have shown the ability to remove existing calcite deposits. Live trials have been initiated to determine the relationship between dose rate and calcite removal. Results to date indicate that doubling the dose rate that is required for scale prevention seems to be the most cost effective when we use soluble calcium levels as our metric. Whilst the soluble calcium results are encouraging, the primary aim of the trial is to slowly open up calcite affected wells, so gauge rings are being used to measure actual aperture sizes at three month intervals. It will be another six months before we expect any conclusive results. This trial therefore is in progress.

The graphs below (fig. 4, 5, and 6) show the increase in soluble calcium in three wells with different histories.

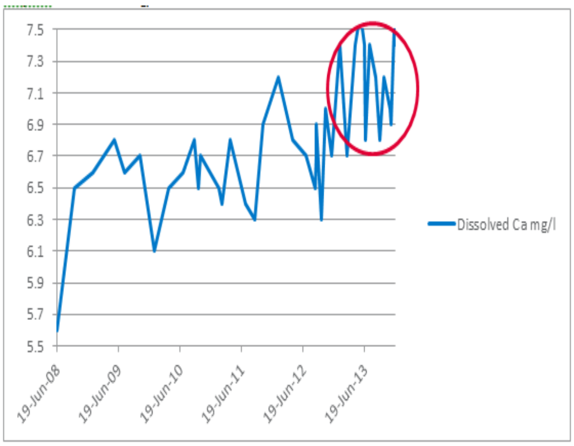


Figure 4: A well historically dosed with PAA then changed to the PMA copolymer blend

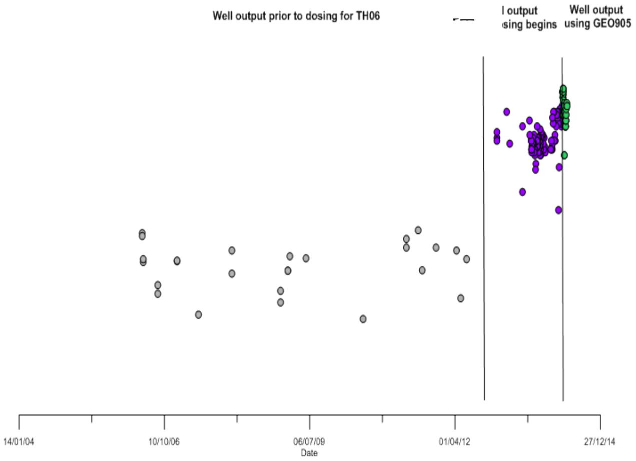
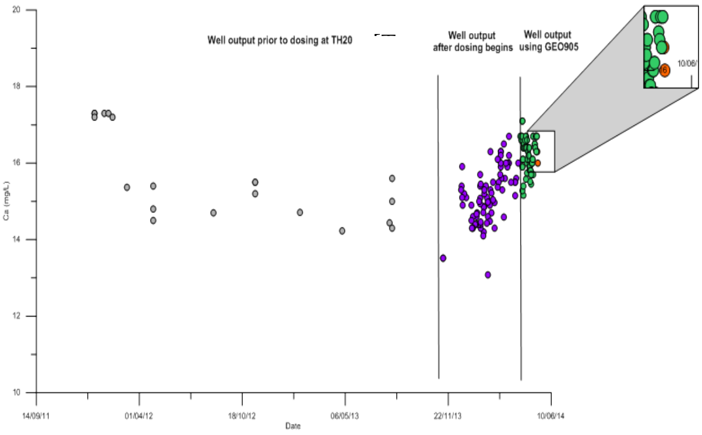


Figure 5: A well worked over, then acidized. Dosed with copolymer (purple) then the PMA copolymer blend (green).



Figigure 6: A scaled well dosed with copolymer (purple) then the PMA copolymer blend (green).

In all three cases, being different wells, in different locations we have observed a jump in soluble calcium levels when shifting to the PMA copolymer blend. This is encouraging news indicating that the potential exists to keep a well in production and slowly remove existing downhole calcite scale.

4. INTERPRETATION OF NACE TEST RESULTS ON INHIBITORS.

Recent test work has highlighted significant differences in NACE test results. The variances are a result in the way the inhibitors are prepared. In geothermal applications people place different weighting on NACE test results in determining inhibitor effectiveness in preventing calcite. The purpose of this investigation was to discover the impacts of sample preparation on results. This is important in determining how much weight gets placed on the results, and what sample preparation method is chosen.

In NZ what is referred to as the “NACE test” is a two part process. First a 10% sample of the inhibitor is filled to 50% level in a 316 ½ inch stainless tube capped by Swagelok fittings and then heated to about 300C for anywhere from 1 to 4 hours. The fluid is then used to conduct the NACE test, which determines the samples’ ability to inhibit calcium carbonate formation after being heated.

In a blind screening it was noted that a high purity polyacrylate performed worse than a low purity polyacrylate of the same molecular weight, concentration and manufacturer. This initiated the question and investigation as to why this would occur. The work and results are described below.

The first part of the inhibitor testing procedure is to test the thermal stability of the compounds. There are two ways this is performed, which significantly affected the results of all inhibitors.

1- A stainless column is filled 50% with 10% solution of the inhibitor. The remaining 50% space in the test column is air.

2- As above but the 50% airspace is blanketed with Nitrogen or other inert gas to displace the oxygen.

So a side by side NACE test was done on a range of different calcite inhibitors to see if they performed differently in the oxygenated vs the non-oxygenated pretest environment. The results are represented below.

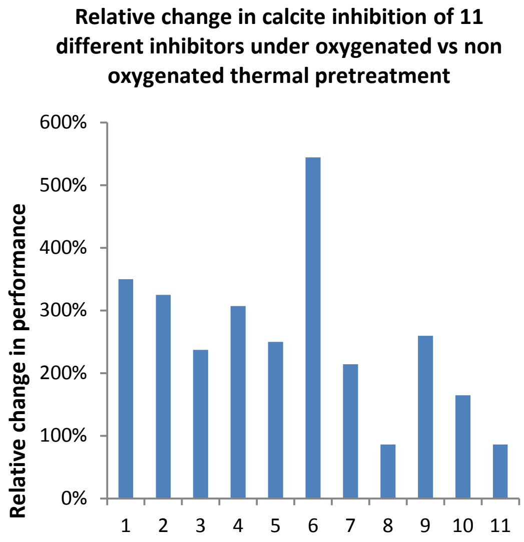


Figure 7. The relative impact on scale inhibition performance of various inhibitors by heating the samples in the presence or absence of oxygen.

What this shows us is that the performance of each individual inhibitor is significantly affected by the method used to test its thermal stability; the results vary considerably. It is suggested that in the oxygenated tube we are not only testing thermal stability, but resistance to oxidation. 10,000 ppm oxygen at 320 degrees is a highly aggressive environment and it is thought that this causes degradation of some of the inhibitors and, therefore, loss of performance.

Such lab tests should simulate the real conditions as closely as possible, as is good analytical practice. The question to ask is “does geothermal brine contain 10,000ppm oxygen whilst in the production well?” Clearly it doesn’t, so by introducing another significant variable in this test method we must challenge how meaningful are the results to the industry. Are we better to stipulate that a deoxygenated environment be used when testing inhibitors?

In practice the only oxygen present in the well environment is that which enters with the product or dilution water down the dosing tube. Practice varies, but in most plants the calcite inhibitor is mixed with cooled condensed condensate which in comparison to the oxygenated test method is low in oxygen, even after sitting in the dosing tank for several days.

Whilst a recommended procedure is not being made here, the results are significant enough to warrant further consideration as to how inhibitor stability tests are performed and interpreted. Decisions based on this test may negatively influence treatment costs, performance and issues as calcium acrylate deposition outlined below.

5. CALCIUM ACRYLATE

During the 1980’s Polyacrylates (PAA) began to replace precipitating phosphate treatments for the control of calcium carbonate deposition in boilers. One of the advantages was a reduction in suspended solids in the boilers, a cause of scale and deposition in boilers and often of foaming and steam purity issues. About the same time polyacrylates were used in geothermal applications, again for the control of calcite formation.

However there became reported cases of a new deposit forming in boilers, a hard tenacious and extremely difficult deposit to remove: Calcium Acrylate. Whilst this was not a universal problem, it was sufficient to have to chemically re-engineer the PAA as the difficulties and costs associated with calcium acrylate deposition were significant. The characteristics of the calcium acrylate polymerization process is that the temperature at which it forms is far lower than the melting point of the product and far less soluble (Costashuk, 1970).The deposit was insulative and extremely difficult to remove requiring > 28000psi water blasting or hydrofluoric acid cleaning in cases.

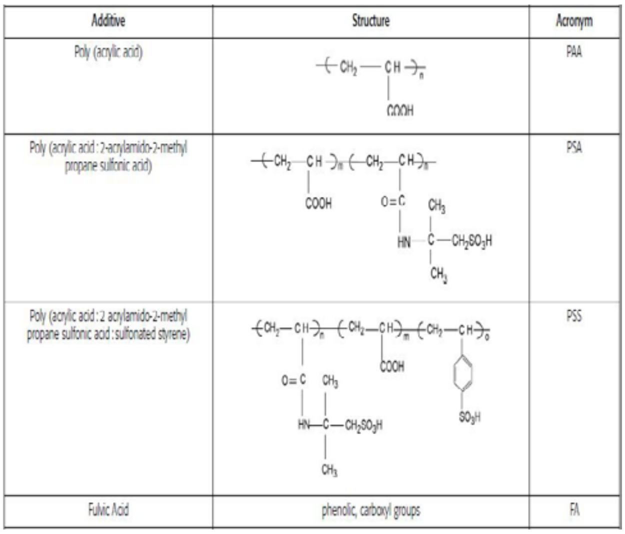
The causes of the calcium acrylate deposition appeared to be many, or a combination of causes. Over-dosing the acrylate seemed to favour the formation of the calcium salt rather than the highly hydrophilic sodium salt which plays it role in the dispersion characteristics preventing calcite formation. Additionally very high or very low pH seemed to impact the calcium acrylate deposition. Chemically the acidic pH’s interfere with the PAA’s ability to act as a highly charged dispersant and in the presence of calcium tend to deposit as the calcium salt. Acid conditions in boilers are not often encountered but it does occur as a result of poor pH control and overdosing sulphite based oxygen scavengers and/or condensate contamination returning to the boiler. Conversely at very high pHs, whilst the dispersion characteristics of the PAA are better, the solubility of the calcium salt reduces.

In Geothermal applications the problem of calcium acrylate deposition was not encountered until the use of binary plants. In a geothermal well with a pH above 5, conditions remain relatively stable and in general, dosing is consistent. It is well recognized that over dosing PAA is not recommended so apart from instances where dosing is left on whilst a well is out of production, or a mistake in dilution, ongoing overdosing is unlikely. However with the advent of binary plants we have another set of chemistries that increase the risks of calcium acrylate deposition, being a sudden and often quite acid change in the brine pH. The injection of condensed steam can cause a significant drop in pH. It is not uncommon to have condensate returning to a binary system at pH 4; a pH that we know PAA does not perform well at all and is one of the postulated reasons for calcium acrylate deposition in boilers in the 80’s and 90’s.

5.1 The solution

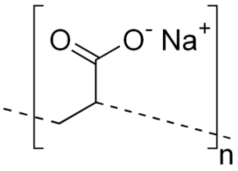
This problem in boilers was a significant stroke of luck for the geothermal industry. Solving this issue of calcium acrylate deposits when using PAA as a calcite inhibitor was one of the initiating factors in the development of co-polymers which play a significant role today in the inhibition of silica, arsenic, antimony and calcium compounds in geothermal applications. The addition of sulphonate groups to the carbon chain (Amjad, 2004) increases steric hindrance and once deprotonated the salt increases the charge density on the carbon chain improving dispersion and zeta potential. This was the first change to the PAA that has prevented calcium acrylate. Further to this the addition of other active groups like PMA and maleic acid side chains has led to the development of co-polymers which have shown to be effective against silica and metal sulphide deposition and have replaced the PAA use in boilers and in may Geothermal applications (Muller, 2013) (Gill and Jacobs, 2011).

Removing the risk of Calcium Acrylate deposits is achieved simply by the elimination of one of the two reactants. As calcium is inherent in the brine, the only other option is to remove the acrylate source. By using a non PAA based calcite inhibitor the risk is avoided.

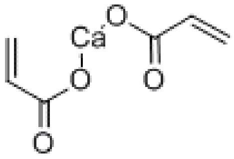


Additive	Structure	Acronym
Poly (acrylic acid)		PAA
Poly (acrylic acid : 2-acrylamido-2-methyl propane sulfonic acid)		PSA
Poly (acrylic acid : 2 acrylamido-2-methyl propane sulfonic acid : sulfonated styrene)		PSS
Fulvic Acid	phenolic, carboxyl groups	FA

Source Amjad, 2004 Table 1 pg 215



Sodium poly acrylate



Calcium acrylate

6. CONCLUSION

All of the work mentioned above has involved the collaboration of industry and suppliers and often independent experts. The significant discovery in the sections above is the speed of what can be achieved when the industry works together.

The challenge of clean energy supply is one of humanity’s greatest challenges and one which we, as industry professionals, must rise to tackle.

ACKNOWLEDGEMENTS

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