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Development of a 'Green' Hydrothermally Stable Scale Inhibitor for Geothermal Wells and Pipelines.

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ABSTRACT

The need for low toxicity, biodegradable and hydrothermally stable scale inhibitors is increasing, and greener chemistries are being sought to meet these challenges.

This paper describes an environmentally friendly inhibitor and uses simple jar and dynamic scale loop tests to evaluate the inhibitor compared to a commercial ‘green’ inhibitor for carbonate scales. Hydrothermal studies performed under differing pH regimens demonstrate stability to 200°C (392°F) thereby showing good potential for Geothermal wells and pipelines.

1. INTRODUCTION

Recent events in the Gulf of Mexico have heightened concerns on environmental pollution. While the Deepwater Horizon oil spill has had significant impact on the local ecosystem there have been far reaching consequences regarding the use of chemicals in hydraulic fracturing (http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/index.cfm) and the fate of chemicals used in performing these operations. The major concern is the migration of chemically contaminated waters into subterranean or surface water sources.

The chemistries used in these operations are varied to achieve the required opening of the formation. A major component is water but this also includes sand, biocides and scale inhibitors.

Geothermal hydraulic fracturing is thought to have less impact on the environment. However public concern and perception needs to be taken into account.

Regulations in the oilfield, industrial cooling water and other industries are in place in some countries. Self regulation, by deployment of chemistries that meet the most stringent regulations that have been introduced in other parts of the world should be adhered to. The selection of chemistries should be based on the most efficient inhibitors to ensure flow, whilst being benign to the environment and still give efficient and cost effective means of keeping wells and pipelines free from scale.

Media attention to ‘green’ issues has also heightened public awareness with cooling towers becoming an easy target for exemplifying global warming with their water vapour plumes being mistaken as carbon dioxide emissions. This global awareness of the impact of chemicals on the environment has been growing over a number of years. (Brown, J.M. et al 1993) (Darlind, D., Rakshpal, R. 1998) (Hater, W. 1998)

The challenge now is to develop either low or non-phosphorus containing inhibitors that work. Another increasingly asked for feature is that of biodegradability. No longer is it acceptable to discharge persistent chemistries into the environment. Achievement of these requests while still meeting hydrolytic and calcium stability is no easy feat, which is why there is no plethora of such products in the marketplace. Some of the biodegradable polymers in existence claim to be scale inhibitors but do not perform well over the wide ranging conditions where the existing non-biodegradable alternatives work.

The definition of ‘green’ chemistry has a different meaning depending on global location. The ‘Twelve Principles of Green Chemistry’ (Anastas, P., and Warner, J 1998) are listed on the US Environmental Protection Agency (EPA) web site as:

- Prevent waste.
- Design safer chemicals and products.
- Design less hazardous chemical synthesis.
- Use renewable feedstocks.
- Use catalysts, not stoichiometric reagents.
- Avoid chemical derivatives.
- Maximise atom economy.
- Use safer solvents and reaction conditions.
- Increase energy efficiency.
- Design chemicals and products to degrade after use.
- Analyse in real time to prevent pollution.
- Minimise the potential for accidents.

There is agreement that ‘green’ chemistry has low toxicity, is biodegradable and has minimum impact on the environment.

One way of improving impact of chemistries on the environment is to introduce less persistent chemicals. One way of approaching this is to design chemistries that are more biodegradable than existing chemistries that are deployed.

There appears to be a fundamental mismatch in requiring efficient biodegradation and an ability to withstand the higher temperatures being encountered in geothermal wells. Existing green inhibitors have not found wide acceptance for deployment due to inherent hydrolytic and thermal stability issues as well as poor performance against calcium carbonate scaling.

The non phosphorus, non nitrogen containing polycarboxylic acid (PCA) inhibitor presented here has performed well in the OECD 306 (OECD 1992a) and OECD 302B (OECD 1992b) test. It has also shown a resistance to hydrothermal degradation over a range of pH and temperature up to 200°C.

It remains to be seen if further development of inhibitors can reach harsher environments in the field and still meet the toxicity constraints and biodegradation hurdle, although the findings presented here gives hope for the future.

2. EXPERIMENTAL

2.1 Environmental Tests

Environmental testing was performed under GLP conditions at third party laboratories using OECD guidelines.

2.2 Calcium Tolerance Test

Various concentrations up to 100 mg/L inhibitor as solids is added to a 1000 mg/L calcium solution. The solution is adjusted to pH 9.0 with sodium hydroxide and stored for 30 minutes at 60°C (140°F). The resultant turbidity of the solution caused by the formation of an insoluble calcium additive complex is measured on a turbidity meter. Increase in turbidity with increasing dose level indicates an increase in the formation of insoluble calcium additive complex.

2.3 Calcium Carbonate Threshold Test 1

This test is designed to assess the ability of additives to inhibit the precipitation of calcium carbonate. Air bubbling is used to facilitate carbon dioxide loss, which moves the equilibrium towards carbonate formation, thereby increasing the test severity.

A solution containing calcium chloride and magnesium chloride is mixed with an equal volume of a solution containing sodium carbonate and sodium bicarbonate which already contains the additive under test. The air bubbled solution is heated at 70°C (158°F) for 30 minutes, after which time the solution is filtered and the calcium remaining in solution determined by EDTA titration. The higher the amount of calcium retained in solution the greater the scale inhibition ability of the product.

2.4 Calcium Carbonate Threshold Test 2

This test is designed to assess the performance of potential inhibitors under simulated high total dissolved solids water conditions to inhibit calcium carbonate precipitation. Two synthetic solutions are prepared, one containing the scaling cations and the other containing the anions. The two waters are mixed in a 50:50 ratio. The anion solution is added to the bottle after the inhibitor solution and then mixed. The cation solution is added with mixing and the bottles shaken in a water bath at 90°C (194°F) for 4 hours. The solution is filtered and the calcium remaining in solution is analysed by titration with EDTA solution.

2.4 Calcium Carbonate Dynamic Scale Loop Test

The same water from the calcium carbonate threshold test 2 is utilised in this test. The two waters are pumped through preheat coils at 90°C (194°F) and mixed in a T-piece prior to the 0.1mm ID 1metre long 316 stainless steel test coil. Calcium carbonate deposition reduces the bore of the test coil causing an increase in pumping pressure. The rate of change in pressure across the coil is monitored with a pressure transducer and data captured for graphical representation later. The test is considered successful if the change in pressure remains below 1psi (6.895kPa) over a two hour period. A schematic diagram of the equipment is shown in Figure 1.

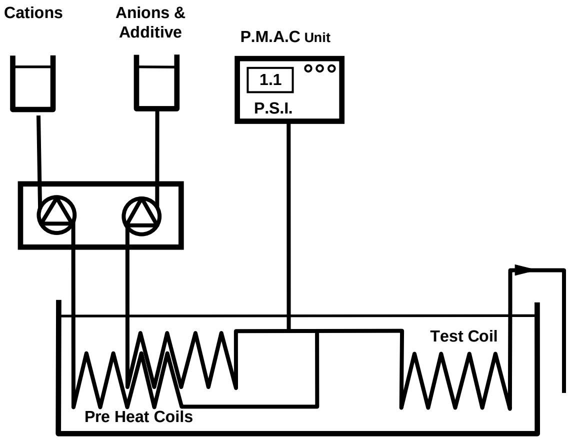


Figure 1: Schematic diagram of the Dynamic scale loop test equipment.

2.5 Hydrothermal Stability Test

A 10% additive solution in synthetic seawater is nitrogen sparged for 2 hours and placed in a Teflon lined autoclave. It is then sparged with nitrogen to minimise head space oxygen before heating at 120°C (248°F), 140°C (284°F), 160°C (302°F), 180°C (356°F), or 200°C (392°F) for three days. The resultant solution is then checked for efficacy in the calcium carbonate dynamic scale loop test.

3. RESULTS

3.1 Environmental Tests

Extensive environmental testing has been performed on PCA under GLP conditions at third party laboratories. The results from these tests performed are listed in Table 1. The results obtained for toxicity testing vs rat and fish at >1000 mg/L and >1000 mg/L respectively, means that

PCA is classified as essentially non-toxic. A significant amount of polymer is required to inhibit algae growth as demonstrated by the >150 mg/L result. This is more than an order of magnitude of in use concentration to control calcium carbonate scaling. It is classified as a non irritant to both eyes and skin. It is not mutagenic and is not a teratogen.

Table 1: Environmental Test Data for PCA.

STUDY	PCA
Toxicity Testing	
Algal growth inhibition Skeletonema costatum EC_{50} 72h (mg/L)	> 1000
Freshwater algal inhibition EC_{50} 72h (mg/L)	>150
Toxicity to rat LD_{50} (mg/kg)	> 1000
Toxicity to fish Scophthalmus maximus juvenile LC_{50} 96h (mg/L)	> 1000
Zebra Fish LC_{50} 96h (mg/L)	> 1000
Bioaccumulation Log P_{ow} (OECD 117)	< 1
Biodegradation % in 28 days (OECD 306)	>60
Biodegradation % in 35 days (OECD 302B)	43.7

The octanol / water partition coefficient (Log P_{ow}) for PCA is <1 and as such it is considered not to bioaccumulate in the environment.

Inherent biodegradability of PCA has been evaluated using the OECD 302B Guideline. The PCA was exposed to activated sludge for a 35 day period. The dissolved organic carbon (DOC) was monitored over the period of the test. The percentage of the total DOC removed from solution is equal to the degree of biodegradation. The degree of DOC removal after 35 days was 43.7%.

These data demonstrate improvements over that obtained for phosphonates and comparable polymers in the OECD 302B test, Table 2.

Further biodegradability studies have also been performed in seawater using the OECD 306 test. Over a 28 day period the PCA biodegraded to greater than 60% again demonstrating its superior potential to biodegrade.

Table 2: Comparative OECD 302B test data.

Chemical	OECD 302B Test Result
Hydroxyethane Diphosphonic acid (HEDP)	33% in 28 days (Steber, J. and Wierich, P 1986)
Aminotris (Methylenephosphonate) (ATMP)	23% in 28 days (Steber, J. and Wierich, P 1987)
Phosphonobutane-1,2,4-tricarboxylic acid (PBTC)	17% in 28 days (OECD SIDS).
Polymaleic acid (PMA)	18% in 35 days
Polyacrylic acid (Mw 2000)	4% in 35 Day

3.2 Calcium Tolerance Test

While calcium intolerance can be improved by the use of other co-additives, it is more prudent to design chemistries that are inherently calcium tolerant. Insoluble calcium salt formation of an additive can contribute to and exacerbate calcium carbonate deposition. To demonstrate the calcium tolerance of PCA a calcium tolerance test was performed. The results for PCA are compared with Polyaspartic acid (PASP) and the calcium intolerant HEDP in Figure 2.

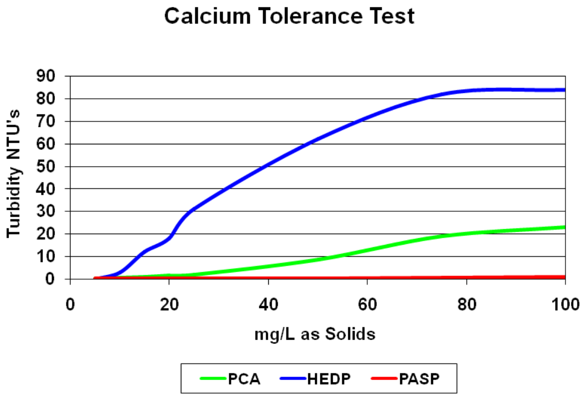


Figure 2: Comparison of PCA, HEDP and PASP in the Calcium Tolerance Test.

The best performer in this test is the PASP which had the highest calcium tolerance. PCA gives close to 20 NTU turbidity units even at the high dose level of 100 mg/L (solids) and compares favourably with the PASP inhibitor.

It also demonstrates that at typical in use concentrations of 5 to 20 mg/L PCA has excellent calcium tolerance.

3.3 Calcium Carbonate Threshold Test 1

This accelerated basic screening test was used to evaluate PCA against Carboxy Methyl Inulin (CMI) and PASP for calcium carbonate scaling efficiency. The water chemistry and test conditions are shown in below.

Table 3: Water Chemistry ‘A’ and conditions for Calcium Carbonate Threshold Test 1.

Calcium as $CaCO_3$	375 mg/L
Magnesium as $CaCO_3$	112 mg/L
Carbonate alkalinity as $CaCO_3$	85 mg/L
Bicarbonate alkalinity as $CaCO_3$	440 mg/L
Aeration	500 ml/minute
Duration	30 minutes
Temperature	70°C

At each of the dose levels PCA is showing improved performance over either PASP or CMI in this severe test. Figure 3 illustrates these points.

A second threshold test with higher total dissolved solids was also used to evaluate the products.

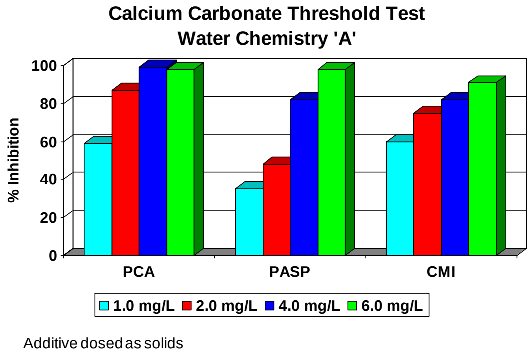


Figure 3: Comparison of PCA, PASP and CMI in Calcium Carbonate Threshold Test 1.

3.4 Calcium Carbonate Threshold Test 2

The water chemistry used in the test is presented in Table 4. Inhibitor levels of 2, 4, 5 and 7.5 mg/L as solids were evaluated in this test and compared with that of PASP. A good result is considered to be greater than 90% inhibition of the calcium carbonate deposition. As can be seen in Figure 4 this is achieved at a 5 mg/L dose level for the PCA. Increasing the dose level to 7.5 mg/L increases the efficiency to 99%. The PASP appears to have reached a plateau in efficiency at 5 mg/L and indeed at the higher dose level of 7.5 mg/L has dropped off in efficacy.

Table 4: Water Chemistry ‘B’ and conditions for Calcium Carbonate Threshold Test 2.

Ion	Concentration mg/L
Calcium	350
Magnesium	56
Sodium	10077
Potassium	283
Bicarbonate	1000
Chloride	16058
TDS	27924
pH	7.8

This is an unusual observation which was reproduced in subsequent testing. Although not investigated, the drop off in efficiency from the 5 mg/L result could be due to a calcium compatibility issue of the PASP giving rise to particulate calcium PASP deposition. This deposition would exacerbate calcium carbonate crystallization by providing growth sites and the subsequent lower dose level after PASP calcium salt formation would be insufficient to control further deposition in this water type.

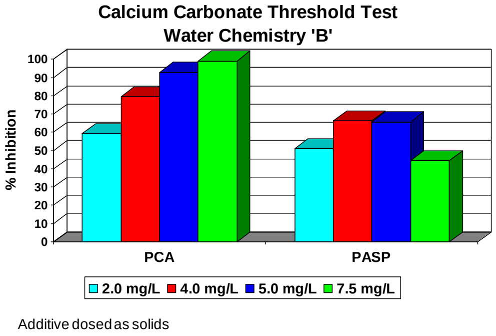
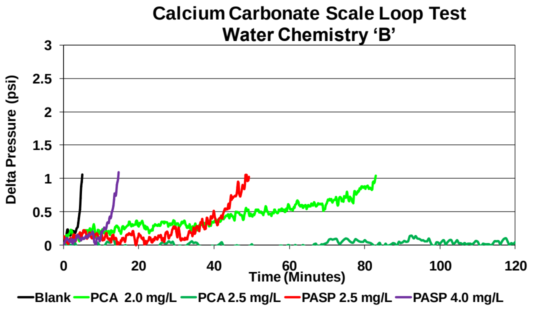


Figure 4: Comparison of PCA and PASP Calcium Carbonate Threshold Test 2.

3.5 Calcium Carbonate Dynamic Scale Loop Test

In some ways dynamic testing is less severe than the threshold static jar test, since replenishment of inhibitor with time favours improved results. In the jar test the inhibitor concentration is decreasing with time once a crystal is formed, but in the dynamic test the constant inhibitor level throughout the test ensures that it is the growth inhibition mechanism that is being studied. The roughness of the metal surface acting as growth sites for initial crystal formation. In this test the water chemistry used is the same as used in the calcium carbonate threshold test 2, i.e. Water Chemistry ‘B’.

Figure 5 illustrates the data for PCA and PASP in the calcium carbonate dynamic scale loop test. Excellent results are obtained for PCA at the 2.5 mg/L solids dose level confirming the findings in the threshold test and demonstrating the additional growth inhibition properties of the inhibitor. At the 2 mg/L dose level the PCA is still giving some inhibition whereas the PASP does not perform to an equivalent level even at a 2.5 mg/L dose level. Increasing the dose level to 4 mg/L for the PASP gives an inferior result to that obtained at 2.5 mg/l mirroring the increased dose level phenomena obtained in the threshold test. Consequently PASP was not able to match the performance of the PCA irrespective of the dosage used.

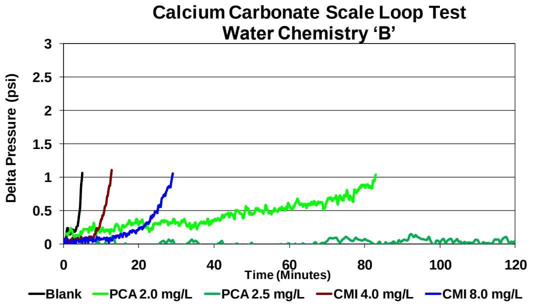


Additive dosed as solids

Figure 5: Comparison of PCA and PASP in the Calcium Carbonate Scale Loop Test.

Figure 6 compares the performance of PCA with CMI. Increasing the dose level of CMI from 4 mg/L to 8 mg/L does not give performance comparable to PCA. These dynamic test results demonstrate clearly the difference in severity between the simple jar test and one performed under flow conditions in the presence of a metal tube.

Inhibitors that perform well in the jar test do not necessarily perform in a dynamic test due to their inability, as in this case, to act as growth inhibitors once deposition of scale has started.



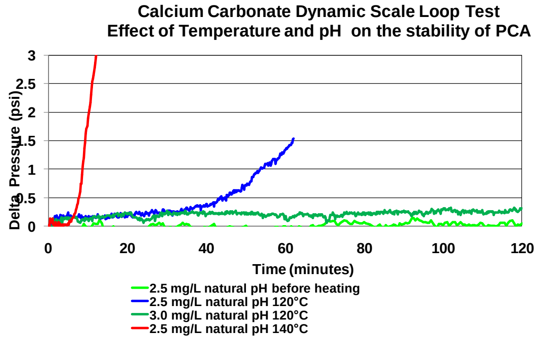
Additive dosed as solids

Figure 6: Comparison of PCA and CMI in the Calcium Carbonate Scale Loop Test.

3.6 Hydrothermal Stability Test

Any chemical being contemplated as a potential inhibitor in geothermal applications must be able to withstand the thermal and aquatic environment encountered in the well and for the duration of the residence time in the equipment. Therefore hydrothermal stability tests were performed on the PCA at pH 1.0, the natural pH of a 10% solution, and 120°C (248°F) for a period of three days.

Performance testing using the calcium carbonate dynamic loop test demonstrated a reduction in activity. Figure 7 shows that a decreased activity was obtained at 2.5 mg/L dose level compared to the original untreated sample. Increasing the dose level to 3.0 mg/L gave similar results to that obtained with 2.5 mg/L of the original untreated solution. This result would indicate either incomplete breakdown or breakdown to species that still inhibit calcium carbonate but with a lower level of activity. At a higher temperature of 140°C (284°F) there was sufficient breakdown to cause more loss in inhibitor efficiency as seen from the 2.5 mg/L result in Figure 7. At this temperature and dose level of 2.5 mg/L the result is identical to a blank condition. No increase of dose levels were performed for this140°C (284°F) hydrolytic stability temperature.



Additive dosed as solids

Figure 7: Effect of temperature and pH on PCA performance in the calcium carbonate dynamic scale loop test.

However the effect of pH has been published elsewhere (Dyer, S.J., et al 1999) and higher pH conditions confer greater hydrolytic stability.

Hydrothermal stability tests were performed on the PCA at a temperature of 180°C (356°F) and 200°C (392°F) at a pH of 7.0 and 8.0.

Subsequent testing of these solutions in the calcium carbonate dynamic scale loop test demonstrates significant improvement regarding hydrothermal stability performed at lower pH.

The results of these studies are shown in Figure 8. After hydrothermal testing at 180°C (356°F) increasing the pH to 7.0 and then to pH 8.0 results in increased hydrolytic stability as demonstrated by the improving results at 2.5 mg/L dose level at these pH’s.

Indeed at pH 8.0 the hydrolytic stability is improved so significantly that no loss in performance is observed even at 200°C for a 2.5 mg/L dose level.

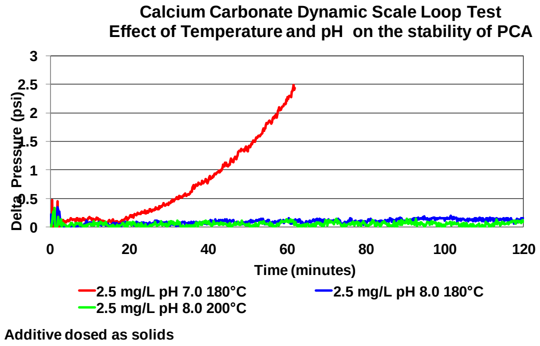


Figure 8: Effect of temperature and pH on PCA performance in the calcium carbonate dynamic scale loop test.

The hydrothermal stability data presented here represent a worst case scenario regarding hydrolytic attack as the residence times in the geothermal systems is significantly less than the three days time that the additive has been subjected to.

Obtaining positive confirmation of efficacy post hydrolytic stability testing using the conventional test method should give confidence for the use of this chemistry in geothermal scale control for calcium carbonate.

4 CONCLUSIONS

1. PCA is a readily biodegradable scale inhibitor, meeting and in some cases exceeding current regulations for 'green' chemistries.

2. PCA an efficient multi-functional scale inhibitor being efficient in the inhibition of calcium carbonate formation.

3. Hydrothermal stability of PCA has been exemplified by no loss in activity after heating at 200°C (392°F) and pH 8.0.

4. PCA is demonstrably a better calcium carbonate inhibitor compared to two other 'green' inhibitors.

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