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# THERMAL STABILITY AND EFFICIENCY OF CALCITE SCALING INHIBITORS

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## ABSTRACT

*A total of eight (8) calcite antiscalant chemicals (Aquaquest 305, Betz Dearbom DG9349, NALCO 9354, NALCO 1340HP, NALCO 1340HP Plus, CHEMCO 6344, Millsperse 815, EC6458A) were tested for thermal stability and % inhibition efficiency. Physical changes like charring and precipitate formation were noted during the thermal stability tests at 250°C and 300°C. Percent calcite inhibition of the chemicais were determined using the NACE test. The abiiity of the heated inhibitor to keep calcium ions in solution provides a simple measurement of its inhibition efficiency. Structural degradation is further confirmed through an FTIR spectmphotometric scan of the inhibitors.*

*After heating at 300°C, all inhibitors except for Aquaquest 305 exhibited frothing. The heated inhibitors eventually formed some precipitates at the bottom of the container which indicate hydrolytic degradation. CHEMCO 6344, Millsperse 815 and EC6458A gave low percent inhibition relative to the other inhibitors. Although precipitation is positive at 300°C in the thermal stability test, some inhibitors still exhibit high percent inhibition. The similar spectra obtained from FTIR scans for one sample treated at two different temperatures suggest that only partial degradation has taken place and most of the functional groups am still intact.*

## 1.0 INTRODUCTION

Formation of calcite scale in geothermal wells can be a serious problem and may occur in all wells during exploitation. In at least one study on geothermal scaling, calcite scale thickness ranged from 0.7 to approximately 3 cm and resulted in costly fluid restrictions of 10 to 45% (Vetter, 1987). Scales can also deposit in fractures and in the formation some distance from the well bore. The usual method of clearing the well is by mechanical reaming (cleaning) a few times a year. This is an expensive exercise that cannot be undertaken during production. Furthermore, traditional mechanical methods of scale removal will have no effect on scale being deposited in the formation area. Scale in the formation is often indicated by a production decline in two-phase or steam-entry wells with pressure drawdown (other potential problems include: inflow of cooler fluids and feed sharing). As the reservoir pressure declines, wells having low permeability will stop producing.

Scaling can be controlled by adjusting the pH (as opposed to cleaning a well with acid) of the geothermal fluid or maintaining excess $CO_2$ pressure through well throttling or downhole injection of $CO_2$. Acidification may not be economic as usually large amounts of acid are required to sufficiently reduce the pH. Well throttling results in decreased output while downhole injection of $CO_2$ has not been tested at pressures greater than about 10 bars. In throttling , the flash point of the well changes with variable operating well head pressures. Throttling helps in that it keeps the flash point within the well-bore longer. Loss of production however, may not make this option worthwhile.

Recently, there has been interest in using antiscalant chemicals to prevent the build-up of calcite in geothermal wells and associated piping. The antiscalants work at threshold concentrations by acting as chelating agents or by inhibiting crystal growth. Corsi et al. (1985) believes that use of these chemicals is the most promising of the scaling control methods, both technically and economically. They identified the major problems to be choosing the most suitable inhibitor and the system for injecting it into the well.

In this work the thermal stability of eight commercially available calcite inhibitors were compared at temperatures of 250°C and 300°C

Table 1. Chemical and physical properties of tested calcite scale inhibitors used. (Candelaria, 2000).

| Product Name | Description | Specific Gravity (kg/ll) | pH | Viscosity (cps) | % Active Component |
|---|---|---|---|---|---|
| **1. Aquaquest 305 Henkel NZ Ltd.** | **aqueous soln. of a Na-polyacrylate** | **1.3** | **7.5-9.0** | | **trade secret** |
| **2. DG9349 Betz Dearborn** | | **1.268** | **7.0** | **3720** | **trade secret** |
| **3. NALCO 9354** | **aq. soln. of an acrylate polymer a $SO_4$ and $HSO_4$** | **1.27-1.32** | **5.4-8.0** | **51** | **trade secret** |
| **4. NALCO 1340HP** | **aq. soln of a polyacrylate** | **1.11** | **4.1** | **15** | **trade secret** |
| **5. NALCO 1340HP PLUS** | | **1.17** | | **no data** | **trade secret** |
| **6. CHEMCO 6344** | | | | | **tradesecret** |
| **7. Millsperse 815** | **polymaleic anhydride (PMA)** | **1.18** | **1** | | **trade secret** |
| **8. EC6458A** | | **1.1 - 1.2** | | **35.6** | |

at a residence time of 30 minutes. The chemical trade names and manufacturers are listed in Table 1 (M.N.R.C, 2000). After testing for physical degradation based on appearance and precipitate formation, the % inhibition efficiencies are tested for the heated inhibitors (250°C and 300°C) as well as the control (unheated ones), and the results are compared with each other.

This project attempts to measure the thermal stability of the calcite inhibitor, the percent inhibition efficiency before and after heating and find clues of structural degradation based on FTIR spectra. These investigations are intended to increase the confidence of the end-user on the inhibitor being purchased for a calcite inhibition system e.g. in Palinpinon.

## *2.0* LABORATORY TESTS

The thermal stability test consists of heating a certain volume of an inhibitor in a sealed vessel at high temperatures (250°C to 300°C) for a period of time (30 minutes or more). After the heating process the volume of the original inhibitor solution is measured to ascertain that no leakage occurred. The appearance of the inhibitor is then recorded and any signs of physical degradation such as precipitate formation or charring are noted. This test simulates the residence time while the inhibitor is being dosed down the well directly into the flash zone. It also takes into account the effect of high temperatures on the antiscalant chemical.

The thermal stability testing was done at GNS, Wairakei laboratory using a salt bath and a stainless steel vessel. Eight commercially available calcite inhibitors (Table 1) were diluted to 10% $({}^{v}/_{v})$ and heated at 250°C and 300°C for 30 minutes in a sealed stainless steel pressure vessel. Three sets of each antiscalant sample were prepared. The' first set comprises the unheated antiscalant, the second set comprises antiscalant heated at 250°C and the third set comprises antiscalant heated at 300°C. The effectiveness of the inhibitors after the heat treatment was evaluated using the National Association of Corrosion Engineers (NACE) standard test method TM-0374-90 (item no. 53023). This test provides a way of quantifying the % inhibition efficiency of a particular inhibitor based on its ability to retain the calcium ions in solution in a supersaturated solution of $CO_2$ and with high levels of calcium ions. The amount of calcium left in solution is the measure of the inhibition efficiency of the inhibitor relative to the other inhibitors. The calcium ions left in solution was measured using a Varian AA1275 atomic absorption spectrophotometer at 422.7 nm wavelength (slit width: 0.20 nm, Integration: 5 seconds, stoichiometric flame). The calibration standards used for the calcium calibration curve consist of 0.2, 1, 5, 10, and 20 ppm calcium as working standards. The flame type used is air-acetylene. The percent inhibition values are calculated based on the formula below:

$$\text{Inhibition(I)} = \frac{Ca - Cb}{Cc - Cb} \times 100 \qquad (1)$$

where: Ca = $Ca^{2-}$ concentration in the treated sample after precipitation
Cb = $Ca^{2+}$ concentration in the blank after precipitation
Cc = $Ca^{2+}$ concentration in the blank before precipitation

Table 2. % Inhibition (equation 1) of antiscalant chemicals.

| Inhibitor | Uncooked | 250°C | 300°C |
|---|---|---|---|
| 1. Aquaquest 305 | 83 - 97% | 74 - 90% | 92-99% |
| 2. DG9349 Betz Dearbom | 83 - 100% | 70-94% | 87-99% |
| 3. NALCO 9354 | 100% | 70-90% | 79-100% |
| 4. NALCO 1340HP | 91-100% | 68-88% | 93-99% |
| 5. NALCO 1340HP Plus | 100% | 66-96% | 99-100% |
| 6. CHEMCO 6344 | <1 - 2% | 0 - 6% | 25-27% |
| 7. MILLSPERSE 815 | 79 - 97% | 7046% | 35-75% |
| 8. EC6548A | 81 -90% | 4-72% | 27-97% |

Another test was done on the 10% samples using a Perkin Elmer PARAGON 1000PC Fourier Transform Infrared (FTIR) spectrophotometer from 4000 to 400 $cm^{-1}$ wave number. This parallel test was done to check for any structural degradation (e.g. disappearance of peaks, decrease in intensity, appearance of small extra peaks). The spectra obtained for the uncooked sample is compared with the heated ones at 250°C and at 300°C. The appearance of small extra peaks show that there is degradation of the inhibitors.

## 3.0 EQUIPMENT AND PRQCEDURES (THERMAL STABILITY TEST, NACE TEST, FTIR SCANS)

The thermal stability test utilizes a pressure vessel made of a stainless steel tube. The inhibitors were diluted to 10% ($^v/_v$). About 50 ml of the 10% ($^v/_v$) solution was transferred to the pressure vessel and sealed. The vessel was then totally immersed in a molten salt bath at 250°C. The molten salt has a high thermal mass (about 90 kg of salt) which gave good temperature control and stability. After 30 minutes in the salt bath the vessel was taken out of the bath and quenched in cold water. The solution inside the vessel could be cooled from 250°C to below 80°C in less than 30 s. The same procedure was repeated for each sample at a temperature of 300°C. The 50 ml volume of 10% antiscalant chemical transferred inside the 90 ml vessel is not an arbitrary volume but is computed based on Standard Temperature and Pressure (STP). Filling the vessel to the brim could cause the vessel to explode under an extremely high pressure. The computation for the safe working volume is:

$$90\,\text{ml} \times \frac{\left(\text{density}_{(\text{water})} @ t^{\circ}\text{C}\right)}{1000} = \text{approx. volume} \qquad (2)$$

In order to know if part of the liquid has boiled inside the tube another equation can be used (Watson, A., pers. comm.):

1. Total mass = $V[(1\text{-}x)\text{density}_{(w)} +$ (3)
$x\ \text{density}_{(s)}]$ @ 20°C
= M is a constant, x = 40190
if V = 50 ml

where:

V = volume of inhibitor used
density(w) = density of water @20°C
density(s) = density of steam @ 20°C

2. At 250°C

M from (1) = $U[(1\text{-}X_{250°C})\text{density}(w)_{250°C} +$
$X.\text{density}(s)]$

3. If $X_{250°C} > 0$ then fluid has boiled.

In this experiment the volume that could be placed at t=300°C inside the vessel is about 64 ml but for safety considerations only 50 ml of the 10% inhibitor was used.

Calcium analysis using atomic absorption was adopted because of its convenience and speed. The % inhibition of the eight calcite inhibitors obtained from the NACE test were in Tabte 2.

The last part of the investigation involves the interpretation of the Fourier transform infrared (FTIR) spectra of cooked and uncooked antiscatants, complementing the results of the NACE test. The thin transparent discs were then scanned using a Perkin Elmer PARAGON 1000PC FTIR spectrometer, in the near infrared region (4000 - 400 $cm^{-1}$). The purpose is to determine any structural degradation that may have occurred during the thermal stability test.

Table 3. Physical appearance of the inhibitors before and after heating.

| **Inhibitor** | **Not Heated** | **250°C, 30 mins.** | **300°C** |
|---|---|---|---|
| 1. Aquaquest 305 | light yellow, fruity odor, sl. pungent when inhaled | dark brown | color |
| 2. DG9349 Betz Dearborn | colorless, fruity odor, yellowish brown, sticky - can't be pipetted. Gel-like consistency | dark brown after cooling | lots of frothing, yellow |
| 3. NALCO 9354 | colorless, pungent odor | light yellow color after cooling | charring, formed ppt. |
| 4. NALCO 1340HP | Colorless | yellow color after cooling. Frothing on surface | yellow turbid solution, frothing on surface after heating |
| 5. NALCO 1340HP PLUS | Colorless | yellow color after heating, frothing on top layer after heating | yellow turbid solution, frothing on surface after heating |
| 6. CHEMCO 6344 | reddish color, strong amine-like odor | dark brown after cooling, no frothing | yellow turbid solution with frothing after heating |
| 7. MILLSPERSE 815 | red-orange color | yellow turbid solution, frothing observed after heating | yellow creamy solution. precipitate observed. |
| 8. EC6548A | Colorless | yellow sl. turbid solution with frothing | yellow creamy solution. |

## 4.0 RESULTS

After the heat treatment at 250°C most of the inhibitors were still able to retain their antiscalant properties. The FTIR spectra support these findings in addition to the NACE test results. At 300°C most of the inhibitors showed to some extent a decrease in their ability to retain calcium ions in solution. Most inhibitors developed some precipitate at 300°C.

The thermal stability experiments at elevated temperatures showed partial degradation of the antiscalant (polymers) in the form of precipitate formation and charting (Table 3) The actual choice can only be made after further field tests involving above ground and long term downhole dosing trials.

Calcite crystals formed as expected in the controls. No crystals were formed in the unheated blanks at room temperature. This means that the heated solutions are supersaturated with $CO_2$ and increase in temperature would decrease the solubility of calcite (retrograde solubility). No crystals were found on the heated samples except for CHEMCO which showed crystal formation at 250°C as well as at 300°C.

The results are listed in Table 4. The blank (before precipitation) and blank (after precipitation) are the maximum and minimum amount respectively of calcium carbonate that could be retained in solution. The total analytical error is estimated at about 0.1 g/l calcium carbonate. Except where indicated each value is an average of two duplicates.

## 5.0 DISCUSSION

The thermal stability test results showed that most of the inhibitors degraded when subjected to temperatures of 300°C for 30 minutes (Table 3). Aquaquest 305 was still thermally stable at 300°C. Duplicate samples confirm the trial results. The solutions showed liffle evidence of decomposition after heating at 250°C. Only a Change in cdor (darkening) and increase in putrid smell was noted. These tests showed that all the inhibitors remained thermally stable after being heated at 250°C for 30 minutes in a salt bath. Under 300°C most of the inhibitors showed signs of degradation either in the form of charring, and formation of a creamy solution and eventually the development of a precipitate. The thermal stability test is the most important factor in determining the antiscalants' effectiveness at elevated temperatures. However actual performance under field

| Inhibitor | Uncooked trial 1 | Uncooked trial 2 | 250°C trial 1 | 250°C trial 2 | 300°C trial 1 | 300°C trial 2 |
|---|---|---|---|---|---|---|
| 1.Aquaquest 305 | 4218 | 4246 | 4333 | 4476 | 4400 | 4320 |
| 2. DG9349 Betz Dearbom | 4134 | 4359 | 4298 | 4512 | 4401 | 4269 |
| 3. NALCO 9354 | 4160 | 4390 | 4300 | 4480 | 4170 | 4420 |
| 4. NALCO 1340HP | 4160 | 4100 | 4280 | 4460 | 4340 | 4400 |
| 5. NALCO 1340HP PLUS | 4290 | 4320 | 4260 | 4530 | 4420 | 4400 |
| 6. CHEMCO 6344 | 3320 | 3365 | 3670 | 3730 | 3550 | 3560 |
| 7. MILLSPERSE 815 | 4000 | 4140 | 4300 | 4440 | 3660 | 4120 |
| 0. EC6548A | 4080 | 4010 | 4320 | 3710 | 4380 | 3600 |
| Blank (before precipitation) | 4275 | 4331 | 4565 | 4637 | 4417 | 4401 |
| Blank (After precipitation) | 3462 | 3433 | 3673 | 3691 | 3247 | 3230 |

conditions cannot be predicted as the inhibiting effect is dependent on a combination of many factors. These laboratory experiments can eliminate unlikely candidates but do not necessarily differentiate between the best performing ones. The choice of the best inhibitor can only be made after field trials.

The solubility of calcite rapidly increases with decreasing temperature. This is the main reason why in the NACE test the samples are heated at 71°C to induce the formation of calcium carbonate crystals. The inhibitor may only have to remain stable until it has had its effect on the calcium ions at the first point of flashing. Thereafter degradation of the inhibitor will not necessarily result in calcite deposition. Calcite saturation at any position in a well can be easily modelled using downhole chemistry computer programs such as WATCH, SOLVEQ, CHILLER and its probable deposition site by WELLSIM (flash point zone determined). The modeling would give some idea at which point the fluid becomes undersaturated with respect to calcite and enable a more realistic estimate of the time required for the inhibitor to be effective. Results of the NACE test showed degradation of some of the inhibitors at 300°C. Correlation of results between 250°C and 300°C however can not be done as the test results were not the same and the tests were done on separate days due to logistics (e.g. glasswares like $CO_2$ bottles, volumetric flasks etc.) and time constraints. The higher percent inhibition efficiency obtained for 300°C may be attributed to the loss of $CO_2$ during the 24 hours heating time at 71°C in the force draft oven. The effect of $CO_2$ loss is a decrease in calcium carbonate crystal formation or even none at all. Which means that calcium ions remain in solution and are thus detected when analyzed by atomic absorption spectrophotometer. At both temperatures, only inhibitor number six showed a significantiy low result compared to the other inhibitors. Even at room temperature it gave a very low percentage of inhibition. Antiscalant numbers 7 and 8 also showed some decreasing trend in percent inhibition as portrayed by a drop in their inhibition efficiencies at 300°C. The NACE test results for the first five inhibitors showed inhibition efficiencies which are higher relative to the other inhibitors. Since the major source of error in the NACE test is the loss of $CO_2$, then the *lower* values for the percent inhibition are the most likely correct results. Actual field trials of these 5 antiscalant chemicals is the next step to validate their capabilities.

Sample preparation for the FTIR spectrophotometric scans took 24-48 hours and the speed of preparing KBr pellets is very important because the samples are extremely hygroscopic. The dried antiscatant chemicals absorb moisture almost immediately after they are removed from the vacuum oven. The moisture could mask any changes in the group frequency and fingerprint regions of the spectra. Consequently, the result would appear as if no degradation occurred even at higher temperatures, e.g. 250°C and 300°C (e.g. NALCO 9354). The amount of mixed sample (1:20 with KBr) placed on the discs is not exactly constant, therefore the intensity shown in the spectra is not always the same. Degradation can only be based on the appearance or disappearance of peaks.

## *6.0* CONCLUSIONS

The thermal stability test showed the effect of elevated temperature and time on the organic antiscalant polymers. This test simulates the harsh condition that the inhibitor solution undergoes during its descent into the stainless steel tube as it is being pumped down into the well to the point where calcite is supposed to form. Physical degradation like charring and precipitate formation is a good indication of partial degradation of these chemicals.

The NACE test is a static test for determining the % inhibition efficiency of the antiscalant chemicals before and after the heat treatment test. The major factor that affects the result is the loss of $CO_2$. All the sample sets must be done at the same day in order to get a coherent result. The number of inhibitor sample tested should only be limited to 3-4 samples or as the logistics will allow. The apparent inconsistency of samples heated at 250°C and 300°C resulted from their analysis on two separate days. Based on the test results it is obvious that even when there are physical signs like charring and precipitate formation the inhibitors could still inhibit calcite crystal formation to some degree. This implies that only partial degradation took place on the inhibitor as it was heated at 250°C and 300°C for 30 minutes. More degradation might occur if contact time were extended.

FTIR spectra of heated and unheated samples showed a very slight difference which makes it a difficult method to use in identifying sample degradation. The difficulty lies in the fact that the inhibitor samples are extremely hygroscopic and have to be dried for 24 -48 hours. They also have to be analyzed quickly as water absorption takes place in a matter of 5-10 minutes. Another reason, is that only partial degradation of the samples took place during the thermal stability test (not all of the sample solution degrade). This was confirmed by the NACE test results.

## 7.0 RECOMMENDATIONS

- Thermal stability tests based on actual residence time of the inhibitor in the injection tubing should be done for a particular well
- It is important to do the NACE test right after the thermal stability test, i.e., when the samples are still fresh.
- The NACE test should be conducted on all sets (uncooked and cooked) of samples at the same time in order to get consistent results. The 10% cooked samples should be shaked/mixed well prior to preparing the 0.1% solution for the NACE test.
- 5 ml aliquot of the 10% antiscalant samples should be vacuum dried for at least 48 hours and mix in KBr quickly to avoid absorbing moisture from the atmosphere. After grinding the sample/KBr mixture it has to be dried in an Oven for 10-20 minutes before pelletizing to get rid of extra moisture. This would result in a clean spectra.
- Aside from FTIR spectra the viscosity of the samples can probably be used to measure antiscalant degradation. A reduction in viscosity might be correlated to polymer degradation.

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