

EFFECT OF FERROUS IONS ON THE PERFORMANCE OF CALCIUM SULFATE INHIBITORS

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ABSTRACT

Inorganic precipitates (scales) are one of the major flow assurance concerns in oil and gas production, and lead to significant reductions in productivity. Scale prevention by use of chemical inhibitors is the most effective solution to the problem.

Calcium sulfate deposition, a common scale problem in oil production, is often controlled by application of commercially available scale inhibitors.

Ferrous ions can be found in many brines accompanying oil and gas production. This study investigates the effect of ferrous ions on two calcium sulfate inhibitors in synthetic brine.

Firstly, some experiments were carried out to study the performance of two scale inhibitors, A and B, in the absence of ferrous ions. The results showed that the inhibitor A is more efficient than inhibitor B.

Also, in this laboratory study, the effect of ferrous ions on the performance of the inhibitors A and B were conducted. The results showed that the inhibitor A was impaired by the presence of ferrous ions. In contrast, the inhibitor B showed an improvement in its performance.

Keywords: Calcium sulfate, ferrous ions, scale, scale inhibitor

INTRODUCTION

Scale is an adherent deposit of inorganic compounds precipitated from water onto surfaces. In oil and gas production systems, the most common scales are $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaSO_4 , CaCO_3 , BaSO_4 , and SrSO_4 . Other scales occasionally encountered are FeCO_3 , Fe_2O_3 , SiO_2 and CaF_2 .

Scale formation frequently restricts flow through injection and flow lines, and tubing strings. It causes pump wear or plugging and creates additional rod loads when it forms on sucker rods. Fire tubes in all types of heaters fail prematurely when scale formation results in overheating. Corrosion is often more severe under a scale deposit. Therefore, effective scale inhibition is of primary importance to the oil producer.

Scale inhibitors can be used in many circumstances to control scale formation, thereby reducing production difficulties. Scale inhibitors are widely used in oil and gas production systems. In the oilfield, the scale inhibitors should be selected on the basis of many factors like cost, effect of pH, thermal stability, compatibility with other chemicals and effect of dissolved iron.

In oilfield-produced waters, the iron ions may be present in reservoir formation water itself or as a result of corrosion of the production tubes, valves and pumps. In an enclosed system, such as that in the oil wells production flow lines and mostly in the surface fluid gathering/ separation systems, the produced waters should remain anaerobic and the iron ions should be in the ferrous state (as Fe^{++}) (Lottes [4]).

Iron in the ferrous state can undergo precipitation as the carbonate in a sweet system and as the sulfide in sour systems. In the presence of oxygen, the ferrous iron may be oxidized to ferric iron (Fe^{+3}) and precipitate as ferric hydroxide or a hydrate form of ferric oxide.

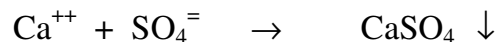
Deposition of such precipitates obviously can cause upsets to oil production and system function.

A few publications generally indicate that both ferrous and ferric ions have a detrimental influence on the performance of some scale inhibitors against common scales, such as calcium carbonate and barium sulfate (Lottes [4]).

In this study, we examined the calcium sulfate inhibition performance of an Alkyl phosphonate (inhibitor A) and an Alkyl Sulphonate (inhibitor B) in the presence and absence of ferrous iron by using NACE standard method TM0374-2001, but modified to simulate the produced brine composition of the desired brines.

CALCIUM SULFATE SCALE

The precipitation of calcium sulfate from water results from the reaction:



Most calcium sulfate deposition found in the oilfield is gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), the predominant form at temperatures below 38°C ; above this temperature anhydrite (CaSO_4) may be found (Nalco Handwork [5]).

Gypsum solubility in pure water increases with temperature up to about 38°C , then decreases with temperature. Above the 38°C , anhydrite becomes less soluble than gypsum, so it could reasonably be expected that anhydrite might be the preferred form of CaSO_4 in deeper, hotter wells. Actually, the temperature at which the scale changes form from gypsum to anhydrite or hemihydrate is a function of many factors, including pressure, dissolved salt content, flow conditions, and the speed at which different forms of CaSO_4 can precipitate from solution.

Pressure drops are one of the primary causes of calcium sulfate deposition in production systems. In addition decreasing the solubility due to thermodynamic considerations, pressure drops across chokes and valves induce turbulence in the water that helps to overcome supersaturation effects and initiate precipitation.

Also, the presence of NaCl or dissolved salts other than calcium or sulfate ions increases the solubility of gypsum or anhydrite up to 150000 mg/l. Further increases in salt content decrease CaSO₄ solubility (Charles [1]).

SCALE INHIBITORS

Scale inhibitors are chemicals that will delay, reduce or prevent scale formation when added in small amounts to normally scaling water.

Most of the scale inhibitors used in the oilfield function by one or both of the following mechanisms:

When scale first begins to form, very tiny crystals precipitate from water. At this point, the scale inhibitor adsorbs onto the surface of the crystals while they are still very tiny and prevents further growth. In some cases scale inhibitors prevent the precipitated scale crystals from adhering to solid surfaces such as piping or vessels.

The most commonly used scale inhibitors function by inhibiting the growth of the scale crystals means that the inhibitor must be present in the water at the point where the crystals begin to form (Charles [1]).

In the oilfield, the scale inhibitors should be selected on a cost /effectiveness basis. Besides cost, inhibitors can be evaluated on the basis of: performance, effect of pH and dissolved iron on inhibition, thermal stability, calcium tolerance (solubility in high-calcium brines), and the availability of a reliable analytical method for determining the concentration of the inhibitors.

The best test is clearly going to be a field test. However, it is useful to first subject the candidate inhibitors to a laboratory test. The goal of all laboratory tests is to reproduce as much field condition as practical.

1. Effect of Dissolved Iron on Calcium Sulfate Inhibition

Most scale inhibitors are less effective in inhibiting calcium sulfate scale formation when dissolved iron is present in the water. The effect is severing in the case of phosphate esters and phosphonates, while most polymers show only slight decreases in performance.

Soluble iron concentrations are typically quite low in sour waters and in waters containing dissolved oxygen, since most of the iron will precipitate as iron sulfide or ferric hydroxide. However, concentrations can be substantial in sweet, air-free systems (Charles [1]).

Since corrosion is the most common source of soluble iron in oilfield waters, an effective corrosion control program is essential for cost-effective scale inhibition. If the source of iron is the producing formation, the use of polymer-type scale inhibitors should be considered.

EXPERIMENTAL PROCEDURES

All the experimental procedures in this study were conducted according to the NACE Standard TM0374-2001, but modified to simulate the produced brine composition of the desired brines.

Two scale inhibitors were used; table 1 shows the chemistry of the two scale inhibitors as received from chemical company.

One percent by weight (1 wt %) dilutions of scale inhibitors A&B were prepared by dissolving the required amount of the scale inhibitors in the de-ionized water.

1. The Effect of Inhibitor A Concentrations on its Performance in the Absence of Fe⁺⁺

Firstly, calcium sulfate precipitation test were conducted to study the performance of the two scale inhibitors A&B in the absence of ferrous ion. The calcium containing brines and sulfate containing brines were prepared as shown in Table2 (brine1) .The salts were weighted out first, and then enough de-ionized water added to bring the solutions volume to 1 liter.

100ppm from the two scale inhibitors A&B were prepared .After that we studied the effect of inhibitor A concentration on its performance by preparing 50,100 and 200 ppm scale inhibitors. Run were duplicated of each scale inhibitors.

2. Test Procedure

Two samples of calcium containing brine (50 ml each) were prepared. The calcium ion concentration of the blanks before precipitation was determines using a standard solution of EDTA according to standard methods (Water standard [6]).

The blanks after precipitation were prepared and handled as described in the next paragraphs, but without scale inhibitors.

The 50 ml of sulfate –containing brine were added to test cell and mixed well. The test cell was capped and the brines and the scale inhibitors were mixed together thoroughly.

All the test cells and blanks were placed in a water bath at 71 °C for 24 hours. After 24-hour the test cells were removed and cooled to 25°C. 1 ml of the test brine was pipette to a 100 ml vessel, and diluted with distilled water. The calcium ion concentration was determined using a standard method⁶ for each of the two scale inhibitors (A&B).

3. The Effect of Fe⁺⁺ on the Performance of Scale Inhibitors A and B

In this experiment, the static test was used to study the effect of ferrous ions on the performance of calcium sulfate inhibitors A& B in three brine systems .The calcium containing brines and sulfate containing brines were prepared as shown in Table2 (25, 50, and 150 ppm Fe⁺⁺).

1 ml from scale inhibitors A were put into the each test cell using the 1 wt % dilutions scale inhibitor A to achieved 100 ppm scale inhibitors. Run were duplicated of each scale inhibitors concentration. The other Procedures were done the same as in section 2.2.

4. The Effect of Inhibitor A Concentrations on its Performance in the Presence of Fe⁺⁺

The calcium containing brines and sulfate containing brines were prepared as shown in Table2 (150 ppm Fe⁺⁺).After that 0.5,1,2 ml from scale inhibitors A were put into the each test cell using the 1 wt % dilutions from each scale inhibitors to achieved 50,100 and 200 ppm scale inhibitor. Run were duplicated of each scale inhibitors. The other Procedures were done the same as in section 2.

5. Percent inhibition calculation

Percent inhibition values has been calculated as

$$\% \text{ Inhibition} = \frac{C_a - C_b}{C_c - C_b} * 100$$

where:

$C_a = Ca^{++}$ concentration in the treated sample after precipitation

$C_b = Ca^{++}$ concentration in the blank after precipitation

$C_c = Ca^{++}$ concentration in the blank before precipitation

RESULTS AND DISCUSSION

1. The Effect of Inhibitors A & B Concentrations on their Performance in the Absence of Fe^{++}

The effectiveness of any inhibitor is measured by its ability to keep calcium in solution. Inhibitor A is an Alkyl Phosphonate type and Inhibitor B is an Alkyl Sulphonate type. Figure 1 shows the efficiency of both scale inhibitors A and B. The efficiency of inhibitor A is 79.00 % and the efficiency of inhibitor B is about 62.53 %. It is clearly shown that inhibitor A is more efficient than inhibitor B in the absence of the ferrous ions.

Figure 2 shows the variation of the inhibitor A efficiency with inhibitor concentration. The inhibitor efficiency increased as the inhibitor concentration increased. The results showed that the inhibitor efficiency was 69.43 % at 50 mg/l of the inhibitor A concentration and 89.24 % at 200 mg/l.

2. The Effect of Fe^{++} on the Performance of Scale Inhibitors A and B

The efficiency of the inhibitors A and B at different ferrous ions concentrations were illustrated in figure 3. From figure 3, it can be seen that the increasing in the ferrous ions concentration increased the calcium sulfate inhibition efficiency for the inhibitor B until a certain ferrous ions concentration. The inhibition efficiency of inhibitor B was 62% in the absence of ferrous ions and improved to 100 at 50 mg/l Fe^{++} , and after that decreased to 94.34 % at 150 mg/l Fe^{++} . In contrast, Figure 4 also indicates that the inhibition efficiency of the inhibitor A decreased from 79 % in the absence of ferrous ions to 45.11 % at 150 ppm Fe^{++} .

Inhibitor A is an Alkyl phosphonate scale inhibitor. This type of inhibitor is affected by the presence of the soluble iron in the system (Kriel [3]). Furthermore, we have done this experiment in an aerobic condition. And in the presence of oxygen, ferrous iron may be oxidized to ferric iron, which also impaired the phosphonate inhibitor (Charles [2]).

3. The Effect of Inhibitor A Concentrations on its Performance in the Presence of Fe^{++}

Figure 4 shows the scale inhibitor efficiency for the different concentration of inhibitor A in 150-ppm Fe^{++} . The results showed an improvement in the inhibitor efficiency when the inhibitor concentration was 200 ppm compared with the same results at 50 and 100 ppm. In general, the inhibitor efficiency increased in the presence of ferrous ions if we increase the inhibitor concentration.

CONCLUSIONS

According to the results obtained from this work, the following can be concluded:

- Static calcium sulfate tests of inhibitors A and B were conducted in the absence of ferrous ions. The results showed that the inhibitor A was more efficient than inhibitor B.
- The calcium sulfate inhibition by inhibitor A increased as the concentration increased.
- The performance of the inhibitor A was reduced by the presence of ferrous ion but its efficiency was improved as we increased the concentration of inhibitor A.
- The results showed an enhancement of the performance of the inhibitor B in the presence of ferrous ion.

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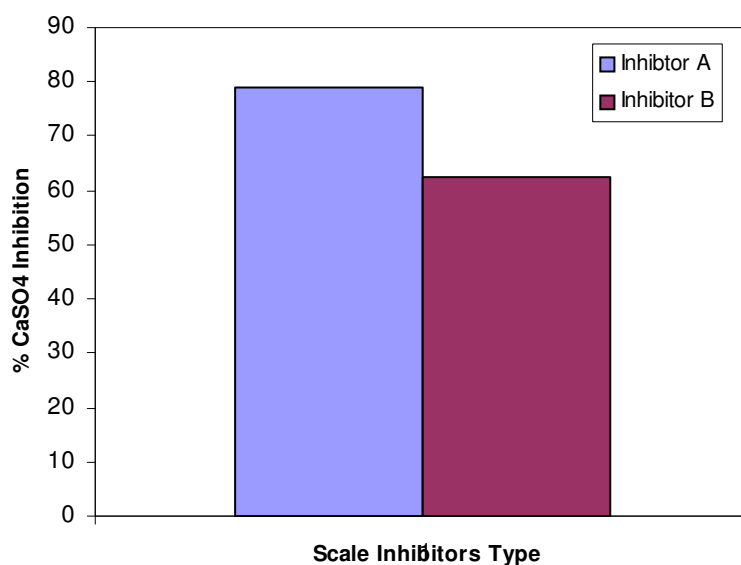
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Table 1 Chemistry of scale inhibitors

Scale Inhibitors	Chemistry
Inhibitor A	Alkyl Phosphonate
Inhibitor B	Alkyl Sulphonate

Table2 Brine Composition

Ion	Brine1 mg/l	Brine2 mg/l	Brine3 mg/l	Brine4 mg/l
Na ⁺	7674	7674	7674	7674
Ca ⁺⁺	3041	3041	3041	3041
Fe ⁺⁺	0	25	50	150
Cl ⁻	15749	15749	15749	15749
SO ⁴ - ₂	7206	7206	7206	7206

**Figure 1 Calcium sulphate efficiency of the Inhibitors A and B**

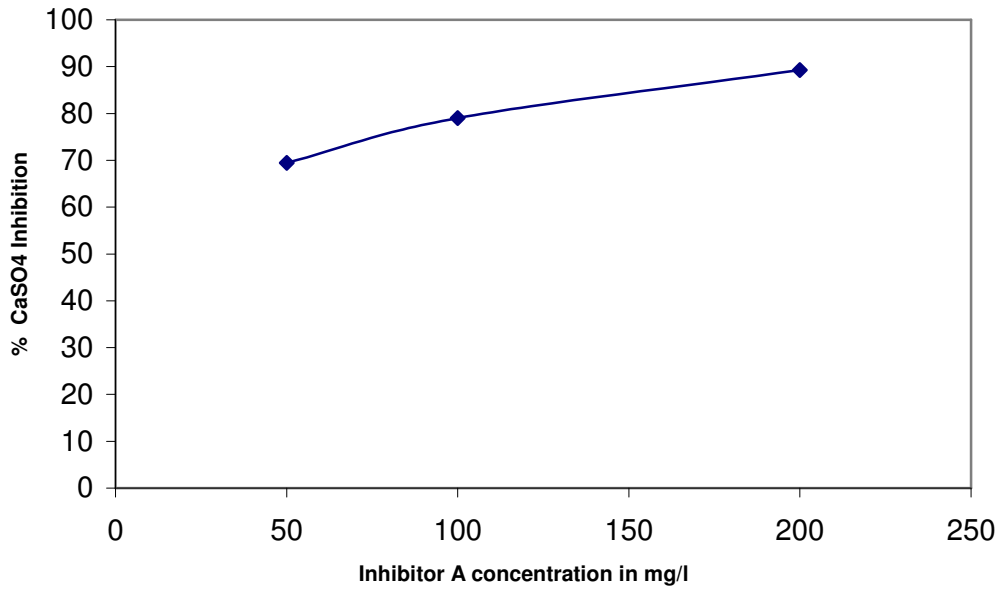


Figure 2 Effect of Inhibitor A concentration on the Inhibitor Efficiency

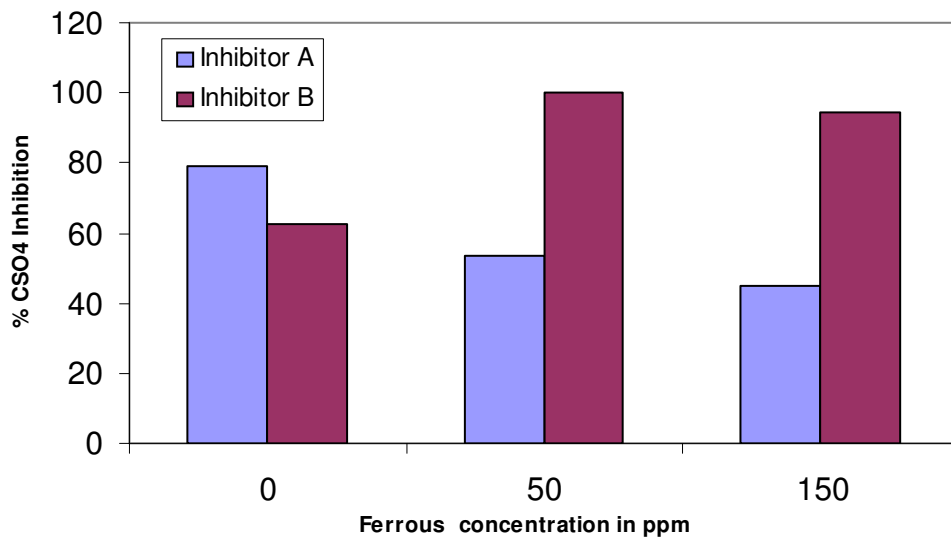


Figure 3 The Effect of Fe⁺⁺ on the performance of scale inhibitors A and B

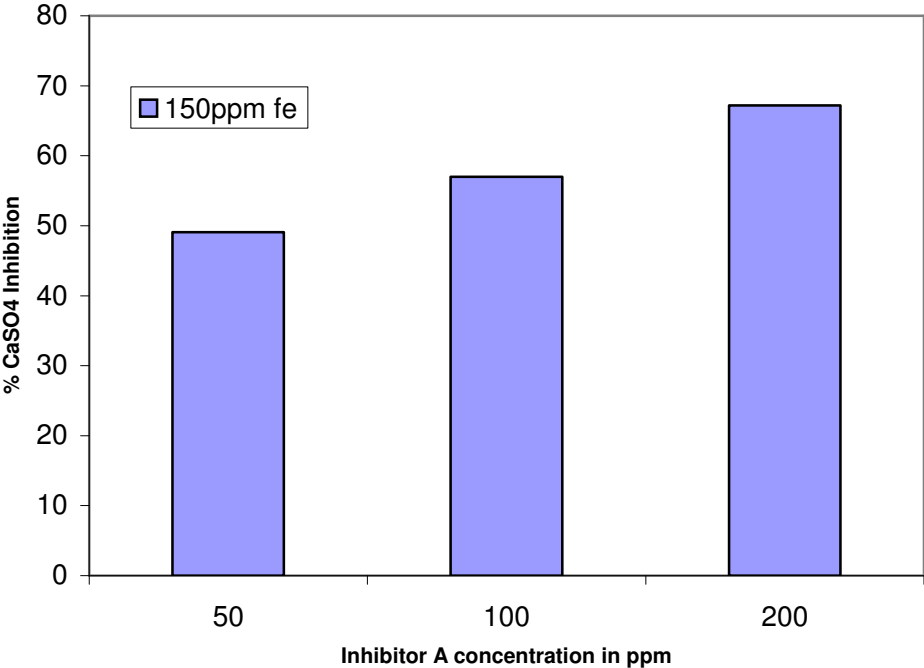


Figure 4 Effect of Inhibitor A concentration on the Inhibitor Efficiency at 150 mg/l Fe⁺⁺