Temperature Effect of Phosphonate-based Scale Inhibitors on Calcium Sulfate Scale in a High Salinity Environment

J Hou¹,*, T Chen², M Han¹,² and M Bataweel³
¹EXPEC Advanced Research Center, Aramco Asia, Beijing 100102, China
²EXPEC Advanced Research Center, Saudi Aramco, Dhahran 31311, Saudi Arabia
*Email: jian.hou@aramcoasia.com

Abstract. Calcium sulfate scale is one of the major scales causing lots of serious operating problems in water injection and oil production. It is necessary to conduct effective treatment when calcium sulfate precipitation occurs. Phosphonate-based scale inhibitors (SIs) are commonly used to control mineral scaling. In this work, the performances for calcium sulfate inhibition by four phosphonate-based SIs were investigated in high salinity and high hardness waters. Experiments at elevated temperatures (65°C, 90°C and 120°C) were conducted to demonstrate the effects of temperature on the scale inhibition efficiency. The results showed that a 100% inhibitive performance could be achieved in the addition of SI-2 at 65°C and 90°C with a dosage of <20 ppm. It was also observed that the inhibition rate on calcium sulfate decreased severely at a temperature up to 120°C.

1. Introduction
Scales caused by the formation of inorganic salts with low solubility, for example calcium carbonate and calcium sulfate, is a significant problem in many water systems, such as reverse osmosis systems, cooling towers and oil field etc. [1,2] In oil production, the inorganic precipitations have led to significant reductions in oil productivity and cost large human resources and time if the scales are allowed to form without any control. [3] Therefore, many methods, including physical and chemical ways are applied to prevent scale formation.

Chemical methods are widely used in oil production as they are low cost and have high efficiency for scale inhibitions. These methods always consist of the addition of scale inhibitors (SIs), such as organic and inorganic acids, to bring down the solution pH or chelating with Ca²⁺ to prevent precipitation of salts. Two applications for scale prevention are regarded as the most effective solutions to the scale problem, applying SIs either by continual injection in the reservoir or by squeeze treatment into the near wellbore formation [4].

Many chemical SIs have been developed and evaluated for field applications [5-7]. Among these SIs, phosphonates, the organophosphorus compounds, are mostly used with high efficacy in industrial water treatment and oilfield scale prevention [8,9]. This is because the inhibitive dosages of these SIs are much lower than stoichiometric quantities. In addition, some of the SIs can work at high saturation indexes for CaCO₃ and CaSO₄.

Calcium sulfate precipitates, usually in three crystal forms: dihydrate (CaSO₄·2H₂O, gypsum), hemihydrate (CaSO₄·1/2H₂O) and anhydrite (CaSO₄), are perceived as a serious scale in water treatment industry because of the low solubility independent of pH. Besides, the insoluble salts cannot be removed by a routine acid cleaning process. Therefore, the formation of calcium sulfate scale
should be inhibited at the very early development stages [10]. There are many factors could have an impact on the nucleation crystal growth and the type of formed calcium sulfate. Some of them must be considered in prevention of the scale, for example, saturation index, temperature and water ionic strength of solutions [11].

In this work, the inhibition performances of four phosphonate-based scale inhibitors on calcium sulfate were investigated at high salinity conditions. The scale inhibition efficiency of the SIs was compared at three temperatures; 65°C, 90°C and 120°C. The optical microscopy images of the precipitations testified the alteration of the morphologies of the calcium sulfate at different temperatures in the presence or absence of the SIs.

2. Experiments

2.1. Chemicals.
NaCl, CaCl$_2$ and Na$_2$SO$_4$ were purchased from Aladdin Chemicals (Shanghai, China). The phosphonate-based SIs (SI-1, SI-2, SI-3, and SI-4) were collected from local market. 4% NaCl with different calcium were prepared in the compatibility tests. The phosphonates were diluted to 1% in ultrapure water as the stock solutions.

2.2. Case$_4$ Inhibition Rate.
8000 ppm Ca$^{2+}$ were prepared in 4% NaCl solution using CaCl$_2$. 8000ppm SO$_4^{2-}$ were prepared in 4% NaCl solution using Na$_2$SO$_4$. 10mL Na$_2$SO$_4$/NaCl solutions were added by 2, 10, 20, 40, 100, 200µL 1% SI solutions respectively before adding 10 mL CaCl$_2$/NaCl solutions. The resulted SI concentration is about 1 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm and 100 ppm. Blank samples were prepared in the same way except being added by 2, 10, 20, 40, 100, 200 µL ultrapure water. The samples were sealed and put in 65°C, 90°C and 120°C in the oven for 24h. After the samples were taken out from the oven and cooled to room temperature in 2 hours, the solutions were filtered through 0.45 µm syringe filters. The collected samples were diluted by appropriate times using ultrapure water for ICP-MS analysis of calcium concentrations. The inhibition rate was calculated as following:

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\text{Inhibition rate (\%) = \left( \frac{C_{\text{after}} - C_{\text{blank}}}{C_{\text{original}/2} - C_{\text{blank}}} \right) \times 100\%}
\]

2.3. ICP-MS Analysis.
The calcium concentrations were measured using Agilent 7900 inductively coupled plasma – mass (ICP-MS) spectrometer. The experiments were performed at no gas mode with $^{43}$Sc as internal standard. $^{43}$Ca and $^{44}$Ca were monitored for concentration determination. The linear calibration range was 1ppm to 50ppm.

2.4. Optical Microscopy
The morphology observation of CaSO$_4$ under different temperatures with and without scale inhibitors were performed on a Zeiss Axio Microscopy. The precipitations after aging 24 hours were washed using ultrapure water for three times and dried at 65°C. The collected samples were directly put on the glass slides and observed using the microscopy.

3. Results and Discussion

3.1. Compatibility at High Salinity Environment
The injected SIs will interact with Ca$^{2+}$ ions affording a calcium-SI complex. This chemical interaction could cause some problems in oil production process. Therefore, the monitoring of calcium compatibility with SIs is important for the SI screening and selection in oilfield applications. The calcium compatibility of four SIs at different concentrations of Ca$^{2+}$ were evaluated. The results when SIs are 100ppm are listed in Table 1. Two concentrations of NaCl (4% NaCl and 20% NaCl) were selected to simulate the injection water and formation water respectively. It showed that SI-3 and SI-4
were the best and the solutions were clear in all tested conditions. SI-1 and SI-2 showed good calcium compatibility in 4% NaCl solutions and low hardness 20% NaCl solutions, but afforded precipitation in 20% NaCl with 10,000 ppm Ca$^{2+}$.

3.2. Effect of Concentration
The performances of the SIs are summarized in Table 2. The experiments were conducted at 65°C for 24 hr in 4% NaCl and the calcium concentration was 4000 ppm. It was observed that the efficacy of SIs increases when the inhibitor dosage increasing, except that SI-4 was not able to prevent calcium sulfate precipitation at present condition. SI-2 showed the highest efficiency and achieved 100% inhibition ratio at 10 ppm concentration. SI-3 showed a relatively lower efficacy and achieved 100% inhibition ratio at 20 ppm. SI-1 achieved 60% inhibition efficiency at most in the tested dosages. The order of the SI performance is SI-2>SI-3>SI-1>SI-4.

Table 2. Inhibition ratio of SIs against CaSO$_4$ at 65°C after 24h.

| SI | Conc. in ppm | 1 | 5 | 10 | 20 | 50 | 100 |
|----|-------------|---|---|----|----|----|-----|
| SI-1 | 0% | 0% | 5.1% | 28.3% | 56.5% | 59.6% |
| SI-2 | 37.4% | 66.1% | 100.0% | 100.0% | 100.0% | 100.0% |
| SI-3 | 1.4% | 0.8% | 49.6% | 100.0% | 100.0% | 99.6% |
| SI-4 | 12.6% | 9.5% | 10% | 17.8% | 2.9% | 10.7% |

3.3. Effect of Temperature
Table 3 presents the inhibition ratio of four SIs against CaSO$_4$ at 90°C over 24h. Compared to the results in Table 2, the inhibition ratios of all SIs were severely decreased at 90°C compared to that at 65°C. When the dosage of SI-2 was higher than 20 ppm, almost 100% calcium sulfate scale was inhibited. In the addition of SI-3, the dosage of 20 ppm achieved 90% inhibition and 100 ppm dosage lead a 100% inhibition. SI-1 inhibited the scale when the concentration was higher than 10 ppm, but the highest ratio was less than 60% even when 100 ppm dose was added. SI-1 and SI-4 can hardly prevent the formation of calcium sulfate scale at this temperature.

Table 3. Inhibition ratio of SIs against CaSO$_4$ at 90°C after 24 hr.

| SI | Conc. in ppm | 1 | 5 | 10 | 20 | 50 | 100 |
|----|-------------|---|---|----|----|----|-----|
| SI-1 | 6.6% | 0.8% | 4.5% | 24.5% | 15.0% | 11.7% |
| SI-2 | 6.7% | 31.1% | 61.8% | 92.0% | 100.0% | 100.0% |
| SI-3 | 1.1% | 4.9% | 11.1% | 89.9% | 91.2% | 100% |
| SI-4 | 9.1% | 12.2% | 4.0% | 1.0% | 3.6% | 5.5% |

When temperature increased to 120°C (as shown in Table 4), the inhibition performance further decreased. The highest inhibition ratio appears at 10~20 ppm dosage of 30% for SI-2 and at 20 ppm of
20% for SI-3. When the dosages were at 50 ppm or 100 ppm, the measured calcium concentration in the resultant solutions were not be able to be detected. The SIs possibly were precipitated with calcium at 120°C when the SI dosages are higher than 50 ppm. It also demonstrates that the temperature has a great impact on the formation of SI-calcium complex which both affect the scale inhibition performance and compatibility of the solutions.

| Table 4. Inhibition ratio of SIs against CaSO₄ at 120°C after 24 hr. |
|-------------------------------------------------------------|
|                | 1 ppm | 5 ppm | 10 ppm | 20 ppm | 50 ppm | 100 ppm |
| SI-2           | 3.8%  | 19.7% | 33.7%  | 32.3%  | 0%     | 0%      |
| SI-3           | 14.1% | 17.2% | 17.0%  | 24.4%  | 0%     | 0%      |

3.4. Morphology of Calcium Sulfate

Optical microscopy observations were conducted for the characterization of the precipitation formed in blank samples and in the addition of the SIs. Figure 1 shows the crystal images of calcium sulfate at different temperatures.

Figure 1. Optical microscopy images of calcium sulfate precipitations at 65°C, 90°C and 120°C with and without scale inhibitors. The scale bar (red) in the images are all 200 µm.
It is observed that at 65°C and 90°C, the blank samples present a needle-like crystals and it resulted to flower-like crystals at 120°C. When the temperature was under 120°C, the precipitations were mainly CaSO₄·2H₂O, while when the temperature is above 120°C, the precipitations were mainly CaSO₄. After addition of scale inhibitors, the crystals are block crystals or layered crystals at 65°C and 90°C. Though it was not effective to prevent precipitation at 120°C, the crystals were still quite different from that in blank samples. The crystalline structures were in a complex morphology.

4. Conclusions
In this study, the performances of four phosphate-based SIs were evaluated. The conclusions can be drawn as following:
1) The phosphonate-based SIs can effectively inhibit the formation of calcium sulfate at high temperature up to 90°C in the high salinity environment. The order of efficiency for the SIs is SI-2>SI-3>SI-1>SI-4.
2) The SIs present good compatibility with calcium (Ca²⁺) in 4% NaCl except SI-1 and SI-2 which precipitate with 10,000 ppm Ca²⁺ in 20% NaCl at 90°C.
3) The performance of SIs against calcium sulfate formation decreases with the increase of temperature, as the temperature can affect the nucleation of calcium sulfate and formation of calcium-SI complex at the same time.
4) The morphology observation on the precipitations at different temperatures with and without SIs using optical microscopy confirming the strong impact of temperature on the formation of calcium sulfate crystals.
5) It is necessary to develop more effective SIs for high temperature (up to 120°C) reservoirs.

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