

Mitigation of Scaling Potential Using Organophosphorus Phosphonates in High-Temperature and High-Hardness Carbonate Formations

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ABSTRACT

Carbonate and sulfate scales are two typical scales formed in oil fields, which can cause tubing blockage, reduce production, and interfere with well intervention. Phosphonate-based scale inhibitors are widely applied to inhibit scale deposition.

In this study, the performance of four different phosphonate-based scale inhibitors (SI-T1, SI-T2, SI-T3, SI-T4) was evaluated at high temperatures like 105~135°C in high total dissolved solids (TDS) brines (>50,000 ppm). A series of tests was applied to evaluate the performance of the scale inhibitors under test conditions, including the brine compatibility test, the inhibition efficiency against three typical scales (CaCO₃, CaSO₄ and SrSO₄), thermal stability, and rock interaction test.

Scale inhibitor SI-T2 demonstrated the highest inhibition efficiency against the three types of scales at 105°C in the high TDS test brines. SI-T2 was thermally stable at a higher temperature of 135°C. It had a strong adsorption capability on the limestone. SI-T3 also presented good inhibition performance, brine compatibility and thermal stability. Interestingly, the thermally aged SI-T2 presented a different inhibition efficiency for CaCO₃ and CaSO₄. The aged SI-T2 kept the same level of inhibition performance for CaCO₃ as the non-aged inhibitor, but lost inhibition performance against CaSO₄ after thermally aged at 135°C. This study provides a systematic evaluation of phosphonate-based scale inhibitors under high temperatures in high TDS scaling brines. It will benefit inhibitor selection for field application in high temperature and high hardness carbonate formations.

Key words: Phosphonate, carbonate scale, sulfate scale, thermal stability, scale imbibition

INTRODUCTION

Scale is an adherent deposit of inorganic compounds precipitated from water onto surfaces. Most oilfield waters contain certain amounts of dissolved calcium, barium or strontium salts. The mineral scale can be formed by chemical reactions in the formation water itself, by mixing of formation water with injected seawater, or by mixing of the well streams of two incompatible oilfield waters. In carbonate reservoirs, when calcium is deposited as calcium sulfate or calcium carbonate scale, a loss of production and increased maintenance expenses can result. Therefore, effective mitigation of scaling potential is of importance to the oil producers.¹

Various techniques have been developed to prevent or minimize the likely scale formation to increase the total revenue from a reservoir.²⁻⁶ To mitigate scale formation in field, it requires the techniques to be able to avoid any damage to the wellbore, tubing, and reservoir. The approach can be mechanical and/or chemical techniques. Mechanical treatment is one the best methods of scale removal in tubulars, either with abrasive jetting or milling.⁷ Chemical treatment is divided into two types, namely, (i) scale dissolution and (ii) scale inhibition. Use of scale dissolver to remove scales, for example use of chelants to remove barite sulfate, can be costly. In general, application of scale inhibitors (SIs) is proven to be an economic and cost-effective approach and have been used in many circumstances to prevent scale formation, thereby facilitating oil and gas production.

The mechanisms of SIs for scale control include sequestration of scaling cations or through intermediate scale formation phases via threshold inhibition, nucleation inhibition, crystal distortion, and/or dispersion mechanisms.⁸ The mechanisms make SIs be often used in very low concentrations in the water phase like 1-50 ppm.

Many SIs have been developed and evaluated in lab research or for field applications, which can be categorized as water soluble polymers and nonpolymeric compounds.⁹⁻¹² Recently, nano-materials are used in squeeze treatment to mitigate scale potential.¹³ Among these SIs, phosphonates, especially the organophosphorus compounds, have been commonly used to prevent the formation of oilfield scales in the forms of calcium carbonate, barium sulfate, and strontium sulfate.^{12,14,15} Some phosphonates adsorb onto specific crystal nuclei surfaces of insoluble salts, poisoning further crystal growth. They are highly effective because the inhibitive dosage is much lower than stoichiometric quantities of scale and can work at high levels of saturation indexes for certain salts, such as CaCO_3 and CaSO_4 .

This work focuses on the investigation of the scale mitigation potential of four phosphonate-based scale inhibitors at a high temperature of 105°C in high total dissolved salinity waters.

EXPERIMENTAL SECTION

Chemicals.

Scale inhibitors

The phosphonates were supplied by THwater (Shandong, China). The scale inhibitors include SI-T1 with three phosphate groups per molecule, SI-T2 and SI-T3 with five phosphate groups per molecule, and SI-T4 with two phosphate groups and a hydroxyl group per molecule. All scale inhibitors contain nitrogen atom.

Salts

NaCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, SrCl_2 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and Na_2SO_4 of chemically pure were purchased from Aladdin Chemicals (Shanghai, China).

The scale inhibitor compatibility tests were carried out in 4% NaCl, synthetic formation water, seawater, and 50/50 seawater/formation water with anions excluded. The compositions of synthetic waters are listed in Table 1. The active component concentration in the product is considered as 100%. The phosphonates were diluted to 2% in ultrapure water as the stock solutions.

Table 1
Compositions of Synthetic Waters.

Ions	Formation Water (mg/L)	Seawater (mg/L)
Na ⁺	64,300	21,800
Mg ²⁺	4,000	2,000
Ca ²⁺	14,000	600
Sr ²⁺	200	10
Cl ⁻	135,000	37,000
SO ₄ ²⁻	1,000	5,300
HCO ₃ ⁻	300	150
Total dissolved solid	218,800	66,860

CaCO₃ inhibition rate.

To do the CaCO₃ inhibition tests, brines were prepared as Solution A of cations without SO₄²⁻ and HCO₃⁻ and Solution B of anions without Mg²⁺, Ca²⁺ and Sr²⁺ based on NACE TM0374 2007 standard.¹ The compositions are as follows: Calcium-containing brine Solution A: 12.15 g/L CaCl₂ 2H₂O, 3.68 g/L MgCl₂ 6H₂O, 4% NaCl (pH=7.39). Bicarbonate-containing brine Solution B: 7.36 g/L NaHCO₃, 4% NaCl (pH=8.27). Saturate both Solution A and Solution B with CO₂ before use to lower the scale formation tendency. For 500mL solutions, half an hour bubbling is conducted. The pH of Solution A and Solution B drops to 3.78 and 6.31, respectively. In the scale inhibition test, 10mL Solution A was put in 50mL penicillin bottle and added by certain SI solutions respectively, and then add 10mL Solution B to the bottles. The penicillin bottles were carefully sealed and put in oven for 24 hours. Blank samples were prepared in the same way without addition of SIs. After the samples were taken out from the oven and cooled to room temperature in two hours, the solutions were filtered through 0.45µm syringe filters. The collected samples were diluted by appropriate times using ultrapure water to make sure the detected calcium concentration by ICP-MS is in the range from 0.1 ppm to 2.5 ppm.

CaSO₄ inhibition rate.

8000 ppm Ca²⁺ were prepared in 4% NaCl solution using CaCl₂. 8000 ppm SO₄²⁻ were prepared in 4% NaCl solution using Na₂SO₄. 10mL Na₂SO₄/NaCl solutions were added by 4, 10, 20, 40, 100, 200µL 1% SI solutions respectively before adding 10mL CaCl₂/NaCl solutions. The resulted SI concentration is about 4ppm, 10ppm, 20ppm, 40ppm, 100ppm and 200ppm. The filtered samples were diluted by 1000~2000 using ultrapure water for ICP-MS analysis of calcium concentrations.

Thermal stability.

SI solutions of 20% in water were bubbled using N₂ gas in glove box to remove oxygen. Then the samples were sealed in penicillin bottles and put in high pressure reactors. The reactors were kept at 135°C for 7 days. The stability was evaluated by high performance liquid chromatography analysis and CaCO₃/CaSO₄ inhibition tests.

ICP-MS analysis.

The calcium concentrations were measured using Agilent 7900 inductively coupled plasma mass spectrometer. The experiments were performed at no gas mode with ⁴⁵Sc as internal standard. ²⁴Mg, ³¹P, ⁴³Ca and ⁴⁴Ca were monitored for concentration determination. The linear calibration range was 5 ppm to 125 ppm. The inhibition rate was calculated as

$$\text{Inhibition rate (\%)} = (C_{\text{after}} - C_{\text{blank}}) / (C_{\text{original}} / 2 - C_{\text{blank}}) * 100\%$$

Adsorption on carbonate.

Limestone crop was crushed and the particles of size between 60 – 80 sieves were selected. 2.5 gram limestone particles were mixed with 25mL (1:10) 250ppm or 2500 ppm SI solutions respectively and kept at 105°C. Time interval is 0 hour, 1 hour, 2 hour, 4 hour, 24 hour. 700μL solution was taken out at 1h, 2h and 4h. 1h, 2h, 4h, and 24h samples were centrifuged at 7000g for 5mins to remove sand. Then the solutions were filtered through 0.45μm membrane to remove the precipitations and diluted by 10, 100, 1000 times for P, Ca, Mg analysis by ICP-MS.

High-Performance Liquid Chromatography (HPLC) analysis.

A Shimadzu LC-20A HPLC system was used to characterize the scale inhibitors before and after thermal treatment. The equipment was gradient programmable and coupled with an Inertsil/WondaSil ODS (C18) column (25 cm × 4.6 mm × 5μm) and evaporative light scattering detector. Mobile phase A is 100% acetonitrile and mobile phase B is 95% ammonium acetate and acetonitrile. The gradient was from 100% B to 0% B in 20mins. The temperature of ELSD was set at 45 degree and amplifier at 6, with N₂ at 350kPa. The sample injection volume is 10μL.

RESULTS

Compatibility with brines

Mixing of scale inhibitors and a brine can cause compatibility issues when they react with each other. Compatibility tests are needed to make sure that the inhibitor dose not precipitate when mixing with formation brines causing formation damage. Too much calcium ions lead to incompatibility with SI, which result in the precipitation calcium-SI complex, instead of common scale formation. Therefore, the scale inhibitors in 100 ppm are first mixed with 0.01%, 0.10% and 1.0% calcium at 4% NaCl or 20% NaCl solutions. The results were shown in Table 2.

Table 2
Compatibility of SIs with Calcium at 90°C for 24h.

SI (100ppm)	4% NaCl 0.01% Ca	4% NaCl 0.1% Ca	4% NaCl 1.0% Ca	20% NaCl 0.01% Ca	20% NaCl 0.1% Ca	20% NaCl 1.0% Ca
SI-T1	clear	clear	clear	clear	clear	clear
SI-T2	clear	clear	clear	clear	clear	Precipitation
SI-T3	clear	clear	clear	clear	clear	clear
SI-T4	clear	clear	clear	clear	clear	clear

Table 3 and Table 4 showed the compatibility of 200ppm and 2000ppm SIs with seawater, formation water and 50/50 mixed water at 105°C for 24h respectively. The synthetic waters are prepared without SO₄²⁻ and HCO₃⁻. All the tested scale inhibitors show excellent compatibility synthetic waters at tested concentrations.

Table 3
The Compatibility of 200 ppm SIs at 105°C for 24h.

SI	seawater	formation water	50/50 seawater/formation water
SI-T1	clear	clear	clear
SI-T2	clear	clear	clear
SI-T3	clear	clear	clear
SI-T4	clear	clear	clear

Table 4
The Compatibility of 2000 ppm SIs with Brines at 105°C for 24h.

SI	seawater	formation water	50/50 seawater/formation water
SI-T1	clear	clear	clear
SI-T2	clear	clear	clear
SI-T3	clear	clear	clear
SI-T4	clear	clear	clear

Scale Inhibition Efficiency

Inhibition against CaCO₃

Table 5 shows the scale inhibition performances of the SIs against CaCO₃ in brines according to NACE-TM0374-2007¹ at 105°C, higher than the 70°C in the standard. The results showed that SI-T2 and SI-T1 could obtain a relatively high inhibitor ratio at low concentration of 10ppm. When the SI concentrations were as high as 200ppm, SI-T4 and SI-T2 have the highest inhibition ratio. It should be mentioned that when the concentrations of SI-T1, SI-T2 and SI-T3 were higher than 40ppm, some white precipitations (possibly SI-Ca complexes) were formed. This work aims to compare the inhibition efficiency of the four phosphonate-based inhibitors. Though the condition is too harsh for the selected scale inhibitors and the scale inhibition efficiency is relatively low, it is found the CaCO₃ inhibition efficiency is SI-T2>SI-T1>SI-T4>SI-T3.

Table 5
CaCO₃ Scale Inhibition of SIs at 105°C for 24h.

SI Conc. (ppm)	4	10	20	40	100	200
SI-T1 Inhibition rate (%)	12.5	47.3	45.4	49.6	44.7	45.0
SI-T2 Inhibition rate (%)	25.4	45.9	43.8	47.5	54.8	61.5
SI-T3 Inhibition rate (%)	17.6	18.2	25.3	40.9	47.2	52.3
SI-T4 Inhibition rate (%)	8.5	7.4	16.0	37.7	49.7	64.6