

Research Article

Inhibition of Barium Sulfate Scale in the Presence of Sodium Tripolyphosphate Inhibitor

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Abstract

The precipitation of barium sulfate from aqueous supersaturated solutions is a well-known problem in the oil industry often referred to as 'scaling'. The formation and growth of barite on surfaces during the oil extraction process can result in malfunctions within the oil facilities and serious damage to the equipment. The effect of STPP which is commercial Tunisian inhibitors for calcium carbonate was examined for barium sulfate. The in situ conductivity and FTIR measurements allowed the identification of barium sulfate precipitation and the deposited barite in the presence of the inhibitor at various temperatures (25, 50°C). So, at 25°C, 50°C, $ph \approx 5$, the 1.5mg STPP inhibits the growth of the dominant barite surfaces by 85%.

Keywords: inhibition; barium sulfate; sodium tripolyphosphate.

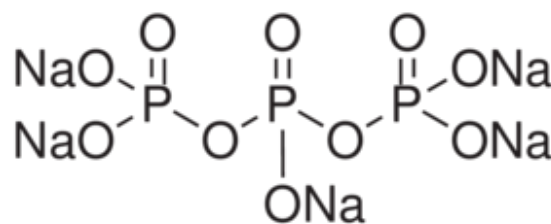
1. Introduction

Inorganic precipitations are one of the major flow assurance concerns in offshore oil and gas production, and lead to significant reductions in productivity and costly work overs if allowed to form uncontrolled. Numerous cases pertaining to oil well scaling by calcium carbonate, calcium sulfate, strontium sulfate, and barium sulfate have been reported (Lindlof and al., July 1983; Mitchell and al., 1980; Shuler and al., 1991; Vetter and al., 1987). Problems in connection to oil well scaling have seriously plugged wells in Russia and similar cases in North Sea fields have been reported (Lindlof and al., July 1983). Some oil fields around the world, such as Saudi, Algeria, South Sumatra in Indonesia, and El-Morgan in Egypt have scale problems because of water flooding where calcium and strontium sulfate scales have been found in surface and subsurface production equipment (El-Hattab and al., July 1982). Scale prevention by the use of chemical inhibitors, applied either by continual injection or by squeeze treatment into the near wellbore formation, has generally been regarded as the most cost effective solution to the problem (Soghomonian and al., 1995). In the post seawater-breakthrough period, however, there is a much more serious problem of precipitation of barium sulfate from an incompatibility between the formation water and seawater. BaSO₄ scale removal is particularly difficult. Thus, BaSO₄ scale treatment must focus mainly on its prevention through the use of scale-control chemicals. Thus, the severity of the scaling problem is determined both by the scaling rate and the efficiency of the chemical

inhibitors (Mavredaki and al., 2011; Jones and al., 2008; Mavredaki and al., 2006; Badr BinMerdhah., 2012).

So, phosphonate molecules are multi protic and their charge depends not only on the pH but also on any interactions with any cation present. Because of chelation with the cation, a number of metal phosphonate compounds have been prepared in the past decades due to their potential important applications in exchange, adsorption, catalyst, and sensor (Cao and al., 1992; Alberti and al., 2001; Clearfield and al., 1998; Clearfield and al., 2001; Lohse and al., 1997; Maillet and al., 2001; Serre and al., 2001; Riou and al 2001; Riou and al., 2000; Soghomonian and al., 1995; Zheng and al., 2000).

In the present study, we investigate to test the efficiency of Tunisian commercial scale inhibitors (sodium tripolyphosphate: STPP: Scheme 1) by conductimetric and FTIR methods both in the absence and in the presence of STPP.



Scheme 1: Sodium Tripolyphosphate

2. Materials and Methods

2.1 Materials

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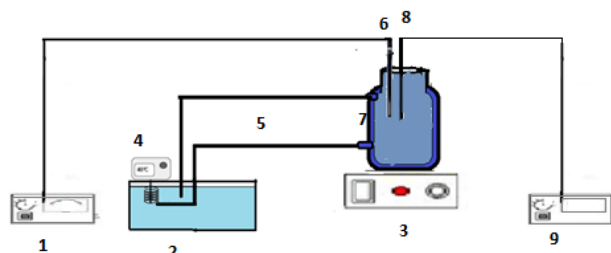


Fig.1

1. Conductivity cell using Proline B 250
2. Thermostatic bath
3. Magnetic stirrer
4. Heating head
5. Pipes
6. Electrode Conductivity
7. Double-wall reactor of 250 ml
8. Electrode pH
9. pH meter Proline B 210

2.2. Types of scale inhibitor

The scale inhibitor who is being tested in this study is the Sodium Tripolyphosphate (STPP) made in the Tunisian **Chemical Society ALKIMIA (the price of 1 kg is close to 1\$)**.

2.3. Chemicals reagents

Solid ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and Na_2SO_4 made to the required concentration using distilled water were of analytical grade from SIGMA-ALORICH and Fluka.

2.4. Experimental procedure

To ensure that the reactions take place under the same conditions, all concentrations were prepared from two stock solutions of BaCl_2 and Na_2SO_4 concentration of 10^{-1}M and 2000 ml volume. To prevent the formation of calcium carbonate CaCO_3 during the precipitation reaction we added a few drops of hydrochloric acid HCl to adjust the pH to 5.

One liter of the solution is prepared with a concentration of $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 5 \cdot 10^{-4}\text{M}$ (68 mg barium) from the mother solutions. Thus, we prepared two flasks of 500 ml containing two solutions of BaCl_2 and Na_2SO_4 with a concentration of 10^{-3}M .

Then the solution of 500 ml of sodium sulfate (Na_2SO_4) concentration of 10^{-3}M is placed in a reactor glass. At time $t = 0$, barium chloride solution (10^{-3}M) is introduced to initiate precipitation reaction. The conductivity of the solution is then measured.

We repeated the same experiments by adding the inhibitor sodium tripolyphosphate (STPP) mass 0.8 mg, 1 mg, 1.7 mg, 2.2 mg, 2.5 mg, to determine its inhibitory effect on the precipitation reaction, at temperatures of 25°C and 50°C .

For all experiments, the stirring speed is set at 300 rev / min and the volume of the test solution was 1000 ml. Precipitation reaction was studied carefully by monitoring three parameters simultaneously measured, that included: pH, conductivity, and temperature.

Solid phase obtained was analyzed by FTIR analyses. Infrared spectra of the samples in KBr pellets were obtained by diffuse reflectance by accumulating 40 scans on an **Affinity-1C Shimadzu** Spectrophotometer, in the range of $4000\text{--}400\text{ cm}^{-1}$ with 4 cm^{-1} of resolution.

3. Results and discussion

3.1. Conductivity study

Scale inhibitor is the main concern of this study. There is one types of scale inhibitors (STPP) that is being tested for its effectiveness in comparison of its ability in preventing scale deposition.

We chose to work at acid pH because phosphonate functional group may be associated with the OH group bonding with the surface as suggested by van der Leeden.

The jar test made at temperatures of 25°C and 50°C without inhibitor has been added in the injection water, shows when the temperature increases, less barium sulfate scales were deposited.

Reproducibility of the experiments was assessed by performing 3 control runs.

At temperatures of 25°C and 50°C , the polyphosphate STPP molecule decreases the rate of precipitation of barium sulfate by decreasing the induction time as the mass of STPP increases. Also, the value of the final conductivity increases, indicating that the mass of the precipitate decreases too. This results may be attributed to the adsorption of the inhibitor will be minimize the number of sites growing crystal clear.

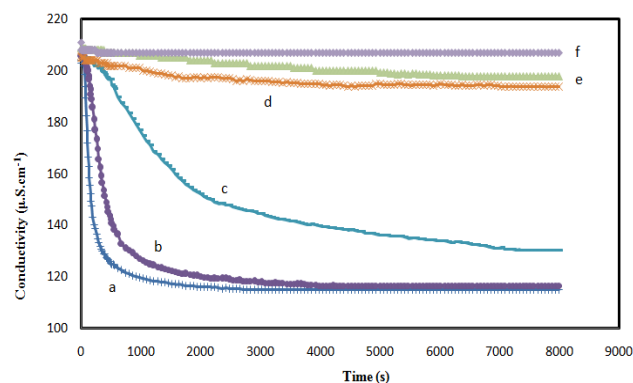


Fig.2. Variation of conductivity as a function of time showing the effect of scale inhibitors at 25°C and under pH 5: a-without STPP, b- $m_{\text{STPP}} = 0.8\text{ mg}$, c- $m_{\text{STPP}} = 1\text{ mg}$, d- $m_{\text{STPP}} = 1.5\text{ mg}$, e- $m_{\text{STPP}} = 2.2\text{ mg}$, f- $m_{\text{STPP}} = 2.5\text{ mg}$.

Fig. 2 shows that in the absence of inhibitor variation of conductivity has two parts. The first part in which the conductivity is a significant drop from $204\text{ }\mu\text{S}\cdot\text{cm}^{-1}$ to $119.4\text{ }\mu\text{S}\cdot\text{cm}^{-1}$ and a second part in which the conductivity is constant (the crystal growth is finish).

The first part in the precipitation reaction of barium sulfate with an induction time $t_{\text{ind}} = 0\text{ s}$ (corresponding to the time of formation of the first stable seeds can grow), and the ending time of barium sulfate precipitation (t_c) equal to 1000 seconds.

The percentage efficiency of the inhibitor can be calculated from equation 1.

$$\text{Percentage efficiency} = \frac{\Delta\mu_0 - \Delta\mu_x}{\Delta\mu_0} * 100 \tag{Eq.1}$$

$$\Delta\mu_0 = \mu_{m6} - \mu_{m0}$$

$$\Delta\mu_x = \mu_{m6} - \mu_{mx}$$

μ_{m6} : the final conductivity value for $m_{STPP} = 2.5$ mg

μ_{m0} : the final conductivity value for $m_{STPP} = 0$ mg

μ_{mx} : the final conductivity value for $0 \leq m_x \leq 2.5$ mg

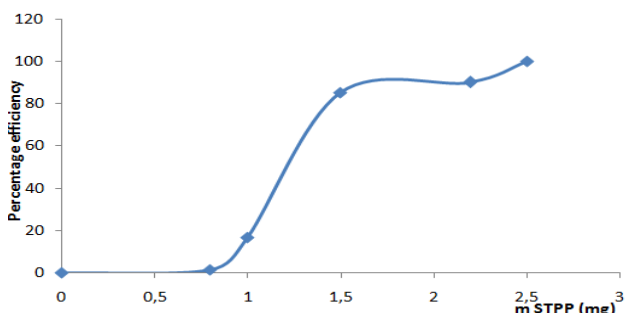


Fig.3 Efficiency Percentage of STPP at 25°C

Values of Percentage efficiency shows that when $m_{STPP} \geq 1.5$ mg, 85% of barium sulfate precipitation was eliminated.

In the presence of 2.5 mg STPP (6.8×10^{-6} M) Barium sulfate (5×10^{-4} M) precipitated STPP was inhibited (Fig.2). This level of STPP is equivalent to 1 phosphonate molecule per 73 barium atoms or 1 phosphonate functional group per 24 barium atoms.

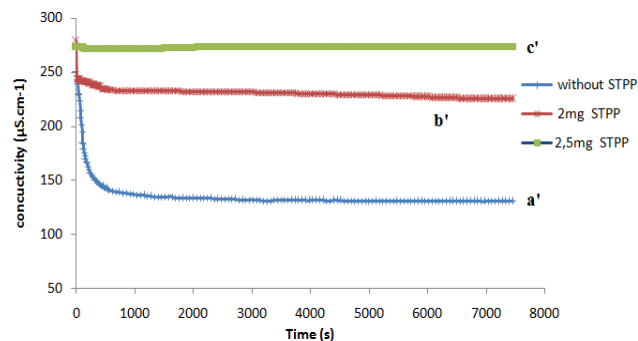


Fig.4. Variation of the conductivity of the solution in the presence of STPP at T = 50 ° C, a'-without STPP, b'- $m_{STPP} = 2$ mg, c'- $m_{STPP} = 2.5$ mg.

3.2. IR Study

To own an idea about the changes in vibration modes of BaSO₄ molecule in the solid state with the addition of STPP we characterized the precipitate obtained by the infrared spectroscopy.

When adding the solution of sodium sulfate, a white precipitate was immediately formed quickly. This part consists of an identification of the nature of the precipitate obtained during the experiments. For this, the final solution was filtered, the precipitate was placed in a drying oven at a temperature T = 105 ° C. A pellet with 90% in KBr is prepared. Lastly the IR spectrum is obtained using a FTIR spectrometer capable Affinity-1CE

Schimadzu. The spectrum obtained is shown in the following figure.

3.2.1. Spectrum of BaSO₄

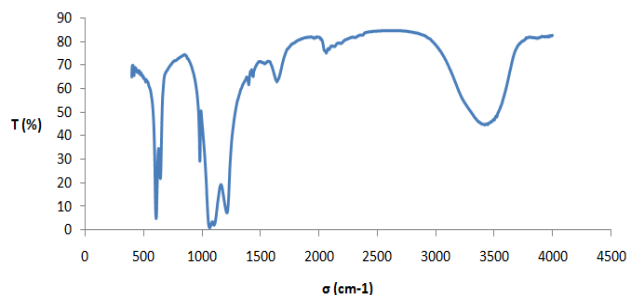


Fig.5. Infrared spectrum of BaSO₄

According to the literature the infrared spectrum obtained for the precipitate formed during the precipitation reaction is that of the compound BaSO₄.

- The bands at 608 cm⁻¹ and 644 cm⁻¹ are the characteristic bands of the vibration of SO₄²⁻ off level.
- The sharp peaks between 1080 and 1130 cm⁻¹ correspond to the vibration of pure BaSO₄.
- The bands centered at 1050-1200 cm⁻¹ and shoulder 981.27 cm⁻¹ correspond to the symmetric vibration of SO₄²⁻.
- The weak bands at 2855 cm⁻¹ and 2925 cm⁻¹ corresponds to the CH₂ and CH groups.
- The bands 1641 cm⁻¹, 3419 cm⁻¹ and 3441 cm⁻¹ correspond to the water molecule absorbed.

3.2.2. Spectrum of Sodium Tripolyphosphate (STPP)

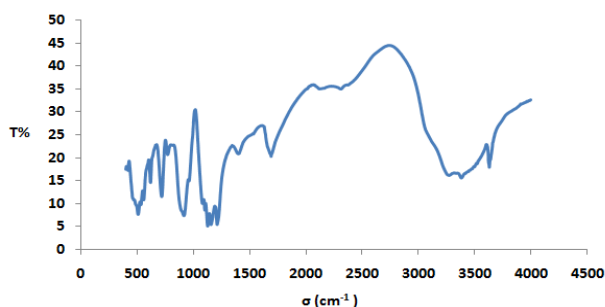


Fig.6. Infrared spectrum of the inhibitor STPP

The infrared spectrum of the sodium tripolyphosphate has several peaks;

- A peak around 916 cm⁻¹ corresponding to the asymmetrical stretching vibration of POP.
- A peak at 1211 cm⁻¹ corresponds to the asymmetric stretching vibration of PO₂.
- A peak at 1126 cm⁻¹ corresponds to the asymmetric stretching vibration of PO₃.
- Two peaks toward 1691cm⁻¹ and the other to 3383 cm⁻¹ is related to absorption bands of water molecules.

3.2.3. Spectrum of BaSO₄ in preens with sodium tripolyphosphate (STPP)

When comparing the IR spectrum obtained in Fig 7 with

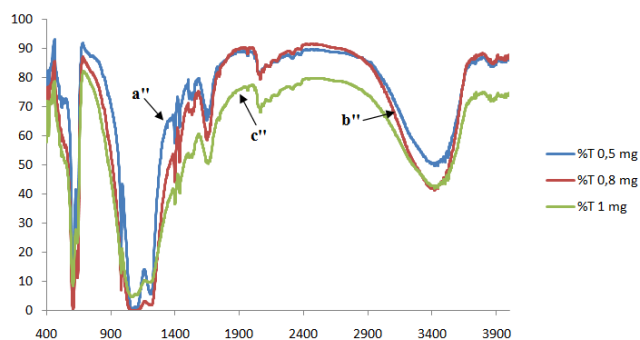


Fig.7. Infrared spectrum of the product obtained by the reaction of barium sulfate precipitation in the presence of STPP at $T = 25^{\circ}\text{C}$, a'' - $m_{\text{STPP}} = 0.5$ mg, b'' - $m_{\text{STPP}} = 0.8$ mg, c'' - $m_{\text{STPP}} = 1$ mg

that of STPP (Fig 6) and BaSO_4 (Fig 5), we can see that if the mass of the STPP increases the intensity of the band of BaSO_4 decreases gradually. This can be attributed to the gradual decrease in the number of free molecules of BaSO_4 without STPP adsorbed. Also, we can say that the adsorption of STPP decreased the vibration mode of the SO_4 group.

Band in 916 cm^{-1} corresponding to the asymmetrical stretching vibration of POP in STPP is missed reason to adsorption of STPP in Barium sulfate molecule.

Conclusions

In The work carried out it was found that sodium tripolyphosphate made in Tunisia with low cost was an effective crystal growth modifier in controlling the crystallization of BaSO_4 . Usually a general indicator into the inhibition strength of additives on the precipitation of barium sulfate is the number of phosphonate groups within the molecule. However, this should be used with care as other factors also determine degree of inhibition as shown by the strong inhibition observed in the presence of STPP. So, at 25°C , 50°C , $\text{ph} \approx 5$, the 1.5mg STPP inhibits the growth of the dominant barite surfaces by 85%.

Conductivity and FTIR studies show that for high barium ions concentration formation water, apparently STPP appeared to be the best BaSO_4 inhibitor compare to the others in literature.

In a solution containing a concentration of 1 mg STPP yielded small traces of precipitated barium sulfate, this is the one that was unable to IR spectroscopic analyses.

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