Journal of Petroleum Science and Engineering ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol

Fast evaluation of inhibitors for calcium carbonate scale based on pH continuous measurements in jar test at high salinity condition

Maria F.B. Sousa*, Filipe Signorelli, Celso A. Bertran

Chemistry Institute, University of Campinas, P.O. Box 6154, Campinas 13083-862, Brazil

ARTICLE INFO

Article history:
Received 21 December 2015
Received in revised form
22 July 2016
Accepted 4 September 2016

Keywords:
Scale
Inhibitor evaluation
Calcium carbonate
High salinity brines

ABSTRACT

Scale formation from calcium carbonate deposition is a major drawback in many industrial facilities, including oil and gas industry, leading to obstruction problems then causing productivity reduction and economic loss. Several anti-scalant formulations, known as inhibitors, are used to control $CaCO_3$ deposition. The evaluation of inhibitors performance is a time-consuming challenge. In the present work a fast approach for evaluation of inhibitor towards calcium carbonate scale controlling is proposed based on continuous pH measurement under jar test condition. Two commercial inhibitors, phosphino polycarboxylic acid (PPCA), usually regarded as a nucleation inhibitor, and diethylenetriamine pentamethylene phosphonic acid (DETPMP), normally considered a growth inhibitor, were evaluated. It was possible to assess their efficiency at same concentration level (5.0 ppm), and DETPMP was the one presenting a better performance at the investigated conditions. The main mechanism of action of each inhibitor was also recognized by this methodology.

1. Introduction

The oil and gas industry uses inhibitors to control the formation of scale onto its facilities, such as pipelines and valves. The performance of the inhibitor depends on the characteristics of the scaling brine to which they are applied, such as ionic concentration, temperature, pH, pressure, etc. Therefore, it is very important to develop rapid methods of assessing the suitability of an inhibitor to a particular fouling environment. Many techniques have been used and several methods have been developed to measure the efficiency of scale inhibitors in different areas such as cooling towers and heat exchanger systems (Marín-Cruz et al., 2007; Touir et al., 2009), water desalination processes (Euvrard et al., 2007; Zhang et al., 2012) oil and gas production (Sousa and Bertran, 2014; Tantayakom et al., 2005a, 2005b), among others (Adel-Aal and Sawada, 2003; Gal et al., 1996; Karoui, et al., 2010).

In oilfield operations, static jar tests and dynamic tube blocking tests are very usual for screening scale inhibitors performance, based on the amount of solid precipitated in bulk and/or scale deposit formed onto surfaces (Wilson and Harris, 2015). However, the jar tests are less time-consuming and demand simpler devices, therefore, in general, they are used as a first selection test at field conditions. For in bulk static experiments, several criteria can be adopted for measuring and monitoring the precipitation process, such as solution turbidity (Demadis and Lykoudis, 2005; Tantayakom et al., 2005a, 2005b) conductivity (Drela et al., 1998), pH of solution (Gal et al., 1996; Kiaei and Haghtalab, 2014; Zhang et al., 2012), induction time (Morizot and Neville, 2001; Xiao et al., 2001) as well as precipitate mass and morphology of the precipitate (Neville and Morizot, 2000; Tantayakom et al., 2005a). Among these properties, turbidity shows sometimes a lack of sensibility to precisely detect the beginning of the precipitation, and conductivity is limited to conditions of low salinity.

For calcium carbonate deposition, whose precipitation is pH driven, measurements of pH variation is a fast, efficient and low-cost methodology to evaluate inhibitors for this type of inorganic deposit. Beyond that, by following pH variation during $CaCO_3$ precipitation more precise information can be obtained in comparison with other methodologies, as those appointed above.

Strategies based on the pH variation have been the object of some studies where two separate solutions, one containing scaling cations and the other containing scaling anions are slowly mixed, producing potentially scaling brines. For example, Gal et al. (2002) conducted kinetic studies of $CaCO_3$ scale formation and inhibition, by measurements of pH as a function of time, during and after the slow addition of NaOH solution to a solution containing $NaHCO_3$, $CaCl_2$ and HCI, in the absence and presence of Amino Trimethylene Phosphonic Acid, (ATMP), a phosphonate-type inhibitor. An evaluation method for selection of $CaCO_3$ inhibitors before reverse osmose dynamic test, based on pH measurements was reported by Zhang et al. (2012). From pH data the authors calculated the supersaturation value at which the precipitation of calcium

---

* Corresponding author.
E-mail address: mfabr@iqm.unicamp.br (M.F.B. Sousa).

http://dx.doi.org/10.1016/j.petrol.2016.09.007
0920-4105/© 2016 Elsevier B.V. All rights reserved.

Please cite this article as: Sousa, M.F.B., et al., Fast evaluation of inhibitors for calcium carbonate scale based on pH continuous measurements in jar test at high salinity condition. J. Petrol. Sci. Eng. (2016), http://dx.doi.org/10.1016/j.petrol.2016.09.007

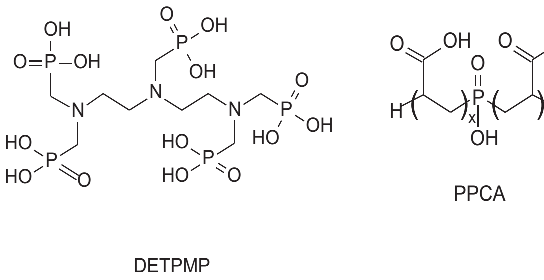

Fig. 1. Structures of commercial scale inhibitors used in this work: DETPMP (diethylenetriamine pentamethylene phosphonic acid) and PPCA (phosphino polycarboxylic acid).

Table 1
Experimental conditions for fast and slow addition of Na_2CO_3 0.020 mol L^{-1} at 30 °C.

Condition	[a]$CaCl_2$ mL	Inhibitor DETPMP ppm	PPCA	[b]Na_2CO_3 mL	[c]Na_2CO_3 mL
UNINHIB	50.00	0.0	0.0	10.0	2.39
W_{DETPMP}	50.00	5.0	0.0	10.0	6.38
W_{PPCA}	50.00	0.0	5.0	10.0	7.65
Mixture	50.00	2.5	2.5	10.0	7.62

[a] 0.45 mol L^{-1} $CaCl_2$ in NaCl 3.42 mol L^{-1}.
[b] Fast addition.
[c] Slow addition.

carbonate started in the presence of each considered inhibitor. Kiaei and Haghtalab (2014) also used the pH variation as function of time to investigate the effect of inhibitors concentration on the precipitation of $CaCO_3$.

In all above cited studies, the measurement of pH variation to evaluate the efficacy of scale inhibitors for calcium carbonate have been applied in experiments at low salinity levels (ionic strength, $I < 1$ mol L^{-1}), in which is performed slow stepwise addition of the anion-containing solution. Those are basic solutions that cause a gradual increase in pH in a medium containing Ca^{2+} ions and some of carbonate species (H_2CO_3, HCO_3^- or CO_3^{2-}),until the pH shows a sharp drop, evidencing the beginning of the $CaCO_3$ precipitation.

The aim of the present work was to investigate the practicability of applying a faster methodology, also based on pH measurements, to evaluate the anti-scaling performance of two commercial scale inhibitors (Fig. 1): diethylenetriamine pentamethylene phosphonic acid (DETPMP) and phosphine polycarboxylic acid (PPCA). PPCA is usually regarded as a nucleation inhibitor and DETPMP is normally considered a growth inhibitor. The pH variation was measured as a function of time, after prompt addition of sodium carbonate solution to a high salinity brine composed by sodium and calcium chlorides, with an ionic strength similar to that salinity found in formation waters of oil wells ($\approx$ 4 mol L^{-1}). Herein, it is important to point out that high salinity can shift to higher values the saturation ratio (SR), a crucial parameter in scale formation.

2. Experimental

2.1. Materials

All solutions were prepared with deionized water (Milli-Q Plus Water System, Millipore) and analytical grade reagents ($CaCl_2$, NaCl, and Na_2CO_3) from Synth.

2.2. Calcium carbonate precipitation applying the prompt addition

As it is usual in jar tests, the precipitating solution (sodium carbonate solution) was quickly added to the brine containing Ca^{2+} ion to precipitate calcium carbonate. A beaker was used to add 10.00 mL of 0.020 mol L^{-1} Na_2CO_3 solution to 50.00 mL of the high salinity brine composed by sodium chloride 3.42 mol L^{-1} and calcium chloride 0.45 mol L^{-1}, both solutions at 30 °C. To keep the temperature at 30 ± 0.1 °C, the experiments were carried out in a water-jacketed glass vessel coupled to a thermostatic bath (ECO RE 415, Lauda).

In inhibited experiments, the inhibitor was previously added to the high salinity brine at the tested concentration (Table 1).

Before the addition of the carbonate solution to the brine, a calibrated combined glass-Ag/AgCl electrode (6.0262.100 - Metrohm), connected to a Titrino Plus 848 unit (Metrohm), was immersed in this medium. In the experiments with inhibitor, the initial pH value of the brine was adjusted with NaOH solution to match the initial pH value of the solution without inhibitor (pH 6.3). The system was magnetically stirred at a constant rate of 625 rpm. The pH values were measured and computer collected every 2 s; starting before the prompt addition of Na_2CO_3 solution, and continuing for 2000 s after.

2.3. Calcium carbonate precipitation applying the stepwise addition

For comparison purpose, a stepwise slow addition was also applied. In these experiments, 50.00 mL of the same high salinity sodium chloride brine containing calcium ions were titrated with Na_2CO_3 0.020 mol L^{-1} solution at 30 °C until the pH started falling. The titration was performed at a rate of 0.1 mL/min, by means of Titrino plus 848 unit (Metrohm). A different final titration volume of the 0.020 mol L^{-1} Na_2CO_3 solution was reached for each experimental condition, with and without inhibitors, as shown in Table 1. For slow addition experiments, in the presence and absence of inhibitor, the pH was measured and recorded, immediately before and during the titration process, every 10 s for approximately 6000 s. All other experimental conditions replicate those used in the prompt addition of sodium carbonate solution.

2.4. SEM and XRD characterization of calcium carbonate particles

At the end of the pH measurements, suspended $CaCO_3$ particles precipitated at prompt addition experiments were quickly separated from the mother solution by filtration under vacuum, using cellulose nitrate filter with pore size of 0.45 μm, washed with deionized water at 30 °C and dried for 2 h at 50 °C.

For SEM imaging, $CaCO_3$ particles were spread out over carbon tape, metallized with Pt and imaged by secondary electrons, applying an accelerating voltage of 3 kV, using a scanning electron microscope (SEM), model Quanta 250 (FEI).

X-ray diffraction analysis was performed by means of a Shimadzu XRD – 7000 diffractometer on $CaCO_3$ particles obtained from inhibited and uninhibited prompt addition experiments. The equipment was operating with Cu-Kα radiation at 30 mA and 40 kV in the 2θ range 5–50° at a scan rate of 2° min^{-1} and 0.02° per step.

3. Results and discussion

3.1. Supersaturation Ratio (SR)

In order to define appropriate evaluation methods for inhibitors performance, it is important to understand the process of calcium carbonate precipitation. As for any sparingly soluble

Please cite this article as: Sousa, M.F.B., et al., Fast evaluation of inhibitors for calcium carbonate scale based on pH continuous measurements in jar test at high salinity condition. J. Petrol. Sci. Eng. (2016), http://dx.doi.org/10.1016/j.petrol.2016.09.007