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Kinetics study of barium sulphate surface scaling and inhibition with a once-through flow system

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Abstract

The deposition and subsequent growth of inorganic scale on completion equipment is a major problem within the oil and gas industry. An in-situ flow cell was designed to investigate barium sulphate surface fouling on stainless steel. The set-up allows real-time analysis of the formation of scale as well as following various scaling parameters such as the surface coverage or number and size of crystals growing on the surface. The experimental results were fitted to a diffusion-controlled crystallisation based model. The effect of PolyPhosphinoCarboxylic Acid (PPCA) scale inhibitor on the growth of crystals was studied and showed that the Minimum Inhibition Concentration (MIC) is different for the surface and bulk solution. The results show that the inhibition mechanism was controlled by the mass transport of scale inhibitor molecules to the active sites of the growing crystals.

Keywords: Scaling; Surface deposition; Inhibition; Barium Sulphate; Crystal growth

1 Introduction

The formation and deposition of mineral scale has long been a major problem within the oil and gas industry. In offshore production, the formation of sulphate scales is usually common during secondary recovery (water flooding). To improve the productivity of oil wells, seawater (containing sulphate ions, SO_4^{2-}) is injected into the reservoir, where it can mix with the cations present in the formation water (Ba^{2+} , Ca^{2+} , Mg^{2+} and Sr^{2+}) and leads to precipitation of mineral scale. Regardless of where scale is being formed, it impedes flow, resulting in a reduction in production and also damage to equipment. Typical sulphate scales encountered by the oil industry are barium sulphate (BaSO_4), strontium sulphate (SrSO_4) and calcium sulphate (CaSO_4). Barium sulphate (BaSO_4) is particularly tenacious due to its high resistance to chemical and mechanical treatments (Graham et al., 2004). It is therefore of paramount importance to understand the mechanism and kinetics of BaSO_4 formation in order to accurately predict its occurrence. In preventing mineral scale fouling, there are various techniques used; surface modification (Cheong et al., 2013; Vazirian et al., 2016), scale inhibitors (Chen et al., 2009; Graham et al., 2001; Hinrichsen, 1998), short pulse plasma discharge (Nam et al., 2016) and magnetic treatment (MacAdam and Parsons, 2004). A recent study by Charpentier et al (Charpentier et al., 2015) shows the

prospect of using novel coatings for the prevention of mineral scale fouling. In this work, infused porous surfaces were used to reduce the deposition of calcium carbonate.

The most popular approach for mitigating barium sulphate is generally through the use of chemical scale inhibitors. These chemicals tend to reduce the driving force for crystallization and successive growth of crystals by disrupting the thermodynamic stability of growing nuclei and/or by blocking the active sites of crystals thus preventing further growth (Graham et al., 2003; Sorbie et al., 1992; Sorbie et al., 1994). In reality, scale inhibitors are known to exhibit both mechanisms; though one of these mechanisms might be predominant for a specific inhibitor. For instance, the study by Laing et al (Laing et al., 2003) showed that PPCA can function both as a nucleation inhibitor and crystal growth blocker, but the predominant mechanism was as a nucleation inhibitor. On the other hand, the inhibition efficiency of phosphonate (DETPMP) was low during the first residence time but constant during a long residence time; thus it implies that it functions mainly as a crystal growth blocker.

The performance of scale inhibitors in oilfield operations is of foremost concern to operators. Information is needed to make efficient decisions to ensure the control and prevention of scale. These decisions are based on evaluating the performance of scale inhibitors under various environmental conditions such as temperature, pH, hydrodynamic conditions and brine composition. Although an extensive body of literature is available for bulk precipitation reactions (Amjad, 1994; Boak et al., 1999; Shaw and Sorbie, 2013; Shaw, 2012; Tomson et al., 2005) only limited numbers focus on the evaluation of surface studies on fouling mechanisms and crystal growth at solid interfaces. Studies have shown that the mechanisms and kinetics controlling bulk and surface deposition are different (Chen et al., 2005; Mavredaki, 2009; Morizot and Neville, 2000; Sanni et al., 2015; Setta and Neville, 2011). Chen et al. (2005) used an electrochemical technique to study the surface deposition of mineral scale on stainless steel. In this research, it was found that bigger crystals were formed on the stainless steel when compared to the size of crystals formed in the bulk solution. Morizot and Neville (Morizot and Neville, 2000) illustrated the difference of inhibition mechanisms of PPCA on barium sulphate scale both in bulk precipitation and surface deposition. The results from this research showed that when 25ppm of PPCA was applied, bulk scaling was greatly reduced; but enhanced surface deposition occurred.

A similar study by Bukuaghangin et al (Bukuaghangin et al., 2015) and Graham et al (Graham et al., 2006) revealed that using an inhibitor concentration below the Minimum Inhibitor Concentration (MIC, from standard bulk jar test determination) reduced bulk precipitation, but enhanced surface scaling. Hence, if common chemical inhibitors such as PPCA are wrongly applied at sub-optimal levels it can reduce bulk precipitation while at the same time enhancing surface deposition. These studies mentioned were carried out in a closed system (e.g. bulk jar test) and, as such, the saturation ratio was decreasing as a function of time. It is therefore not clear if the

same rates and mechanisms would occur in a system more closely replicating the constant supersaturation conditions seen at a particular location in the field.

In the current paper, a flow cell was designed to study barium sulphate surface fouling in an open system. An optical technique was used to follow the nucleation and growth process of barium sulphate on a stainless steel in-situ and in real time. The kinetics of barium sulphate formation were studied under a range of thermodynamic and kinetic conditions; the effect of PPCA on the growth step of barium sulphate crystals was investigated. This research aims to enhance the design of scale inhibition strategies and their implementation.

2 Experimental Details

2.1 Material

2.1.1 Metal Samples

Stainless steel samples (UNS S31603, cylinder, 10mm diameter) were used for the surface deposition tests. Prior to each test, the active surface was ground with silicon carbide paper (1200 grit) and polished with diamond paste (3 μ m). Afterwards, the sample was rinsed with acetone, distilled water and dried with compressed air (see supporting information).

2.1.2 Experimental Set-up

A schematic of the flow cell is shown in **Fig. 1**. The set-up allowed surface fouling and bulk precipitation to be assessed simultaneously. The design is inspired from the cell developed by Euvrard et al (Euvrard et al., 2006), which was used in a closed system where the saturation ratio would decrease with time, therefore restricting kinetic studies to short periods of time. In this work, the set-up was adjusted to include a once-through flow system (Sanni et al., 2015). The flow cell was designed to work under atmospheric pressure and can be adjusted to allow experimental conditions (e.g. saturation ratio, inhibitor concentration) to be kept constant at the point where the imaging is done.

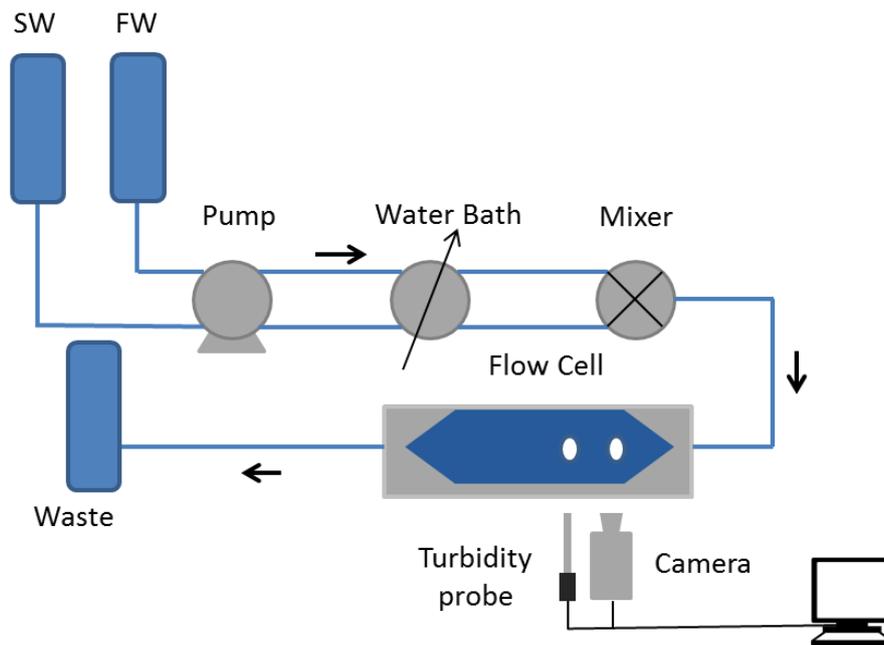


Fig. 1 Schematic of Experimental Set-up

A more detailed geometry of the flow cell (cell volume of 15 ml) where the surface deposition occurs is shown in **Fig. 2**. The flow channel was designed to give a laminar flow regime for the set of flow rates used (see supporting information). The flow is uniform across the cell and no fluid recirculation is occurring within the cell. The surface deposition is analysed using a camera to allow real-time observation of surface fouling. The images were processed to assess the number of particles and their size as well as the barium sulphate surface coverage (Sanni et al., 2015). Similarly, real time measurements of the bulk precipitation were performed using a turbidity probe.

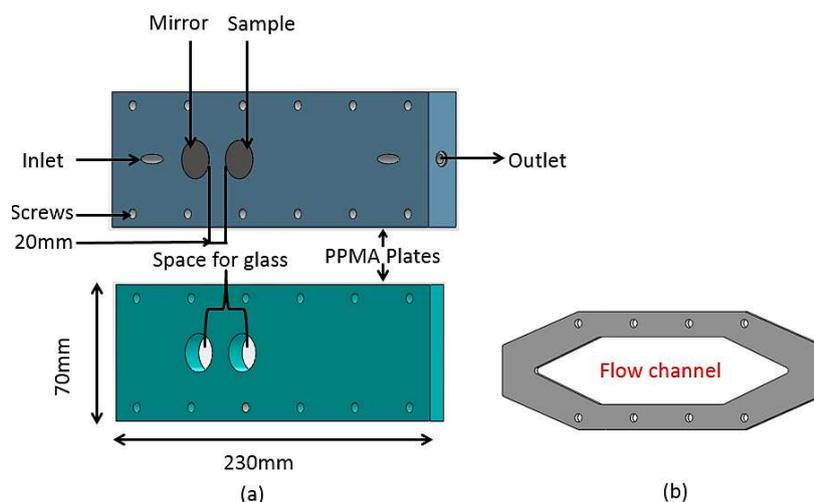


Fig. 2. Flow cell consists of: (a) two PPMA plates and (b) a Teflon gasket with volume of 15 ml

2.2 Chemical

The supersaturation conditions necessary for the formation of barium sulphate scale was achieved by mixing two incompatible brines. Seawater (SW) provided the source of anions (SO_4^{2-}) while Formation Water (FW) the source of cations (Ba^{2+}). The composition of the brines used is presented in **Table 1** and **Table 2**; the brines were mixed 50:50 at a temperature of 50°C. The temperature selected was based on the temperature observed in an oilfield topside operation (Barker, 2012). The saturation ratio used was predicted by using MULTISCALE software (NTNU, 1993). The additive used during the study was PPCA, which is a commercial product commonly used in the oilfield.

Table 1
Composition of Sea Water (SW) and Forties Formation Water (FW)

	SW	FW
Ion	ppm	ppm
Na⁺	10866	31747
Ca²⁺	428	2000
Mg²⁺	1368	739
K⁺	460	654
Ba²⁺	0.00	See Table 2
Sr²⁺	0.00	771
SO₄²⁻	See Table 2	0.00

Table 2
SW and FW SO_4^{2-} and Ba^{2+}

	SO₄²⁻	Ba²⁺
SR	ppm	ppm
15	300	57
20	350	64
30	500	65
80	800	110

2.3 Growth and Nucleation model

The nucleation/growth model used during this study was developed by Beaunier (Beaunier et al., 2001). The model assumes that diffusion controls the crystallization process and that the unit area of a substrate has a finite number of nucleation active sites, N_0 (μm^{-2}); and that all nucleation events are independent of each other. Hence, at time t , the probability of nucleation depends only on the number of nucleation sites available. For 2D growth on a substrate, the actual fractional area of the surface covered by the scale, $S(t)$ is related to the extended area $S_{\text{ext}}(t)$. The area that would be covered by all the nuclei at time t without the overlapping effects is given by:

$$S(t) = 1 - \exp(-S_{\text{ext}}(t)) \quad \text{Equation 1}$$

Beaunier et al (2011) found a relationship between the $S_{\text{ext}}(t)$ for both instantaneous and progressive nucleation. Instantaneous nucleation $S_{\text{ext}}(t)$ is directly proportional to time, whereas progressive nucleation $S_{\text{ext}}(t)$ has a parabolic relationship with time.

3 Results and discussion

3.1.1 Bulk Precipitation

The turbidity of the solutions was measured in the flow cell next to the steel sample and it was found to be 0 FAU which indicates that no bulk precipitation of barium sulphate occurred in the flow cell for the range of thermodynamic conditions considered. BaSO_4 bulk precipitation was observed in the collection vessel but this occurred after the fluid had passed the working section of the flow cell. The scaling brines arrive at the sample in less time than the (bulk) induction time for scale precipitation; as such the growth of mineral scale on the steel surfaces was solely due to a nucleation/crystal growth process taking place at the interface of the steel sample.

3.1.2 Effect of saturation ratio on surface deposition

The effect of saturation ratio on barium sulphate surface fouling is shown in **Fig. 3**, which presents the surface coverage (**Fig. 3a**), the average size of crystals (**Fig. 3b**) and the number of crystals growing on the steel surface (**Fig. 3c**) as a function of time. The results show that despite the absence of bulk precipitation, surface fouling occurs which is also apparent from the optical images shown in **Fig. 4**. This implies that the induction time for surface fouling is shorter than bulk precipitation for the range of saturation ratios considered. These results are in agreement with the classical nucleation theory which predicts a lower energy barrier for heterogeneous nucleation (surface fouling) than homogenous nucleation (bulk precipitation) (Myerson, 2001; Setta and Neville, 2011).

Fig. 4c shows the number of crystals growing on the surface as a function of time and offers valuable insights into the crystallization process. Indeed, at low saturation ratios (SR=15 and SR=20) the number of crystals growing on the surface increases throughout the experiment (Fig. 5b) which is in agreement with a progressive nucleation, where nucleation and crystal growth occurred simultaneously throughout the duration of the scaling tests. At higher saturation ratio (SR 30) the population of crystals reaches a plateau within an hour. At SR 80 the slight reduction in the number of crystals observed was attributed to the agglomeration of crystals. These results are in agreement with an instantaneous nucleation process where surface fouling occurs in two steps: an initial phase where nuclei are formed on the surface and all the nucleation sites are filled; followed by a second phase of crystal grow. Similar findings were reported (Beaunier et al., 2001) during a study on surface deposition of calcium carbonate. Their research was conducted in a closed system and as such the kinetics of crystallization were studied for a short period.

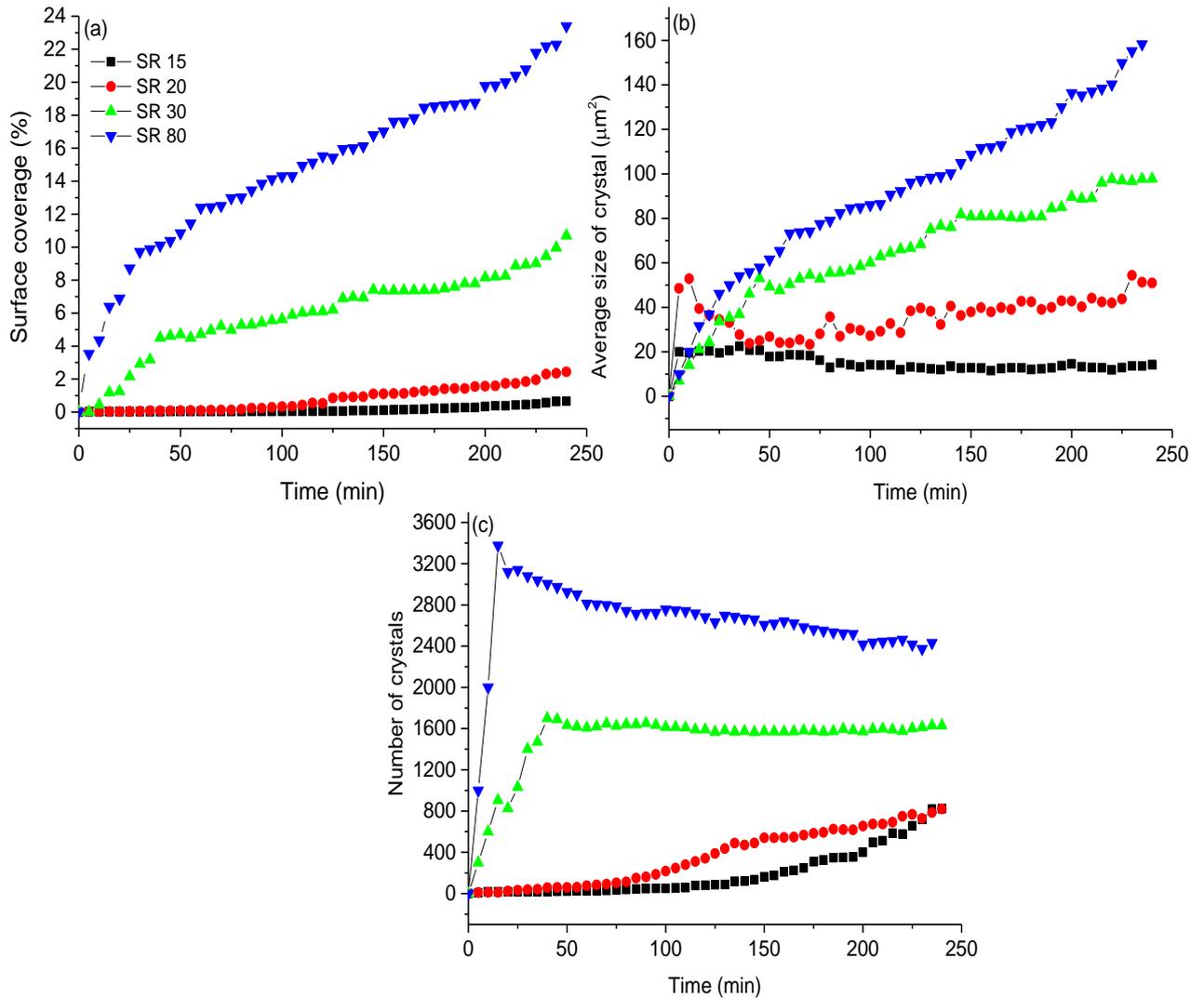


Fig. 3. (a) Surface coverage (b) Average size of crystal and (c) Number of crystals at 50°C for range of SR15, 20, 30 and 80

Fig. 3a presents the effect of saturation ratio on surface coverage. As expected, surface coverage of the crystals increased as the SR was increased. However, the factors controlling fouling change depending on the saturation ratio considered. Surface coverage for SR=30 & SR=80 was controlled by an increase in nucleation and subsequent growth of crystals; whereas in the case of lower saturation ratios (SR=15 and SR=20) the surface growth was driven by the constant formation of new nucleation sites (crystals). **Fig. 5** presents the plots of S_{ext} (%) as a function of time for low (SR=15) and high (SR=80) saturation ratio. The plots show that S_{ext} (%) was linear with time for SR=80, while it follows a quadratic trend at lower saturation ratio. These results are in agreement with the model developed by (Beaunier et al., 2001), where high saturation ratios favour instantaneous nucleation, while lower ones tend to promote progressive nucleation.

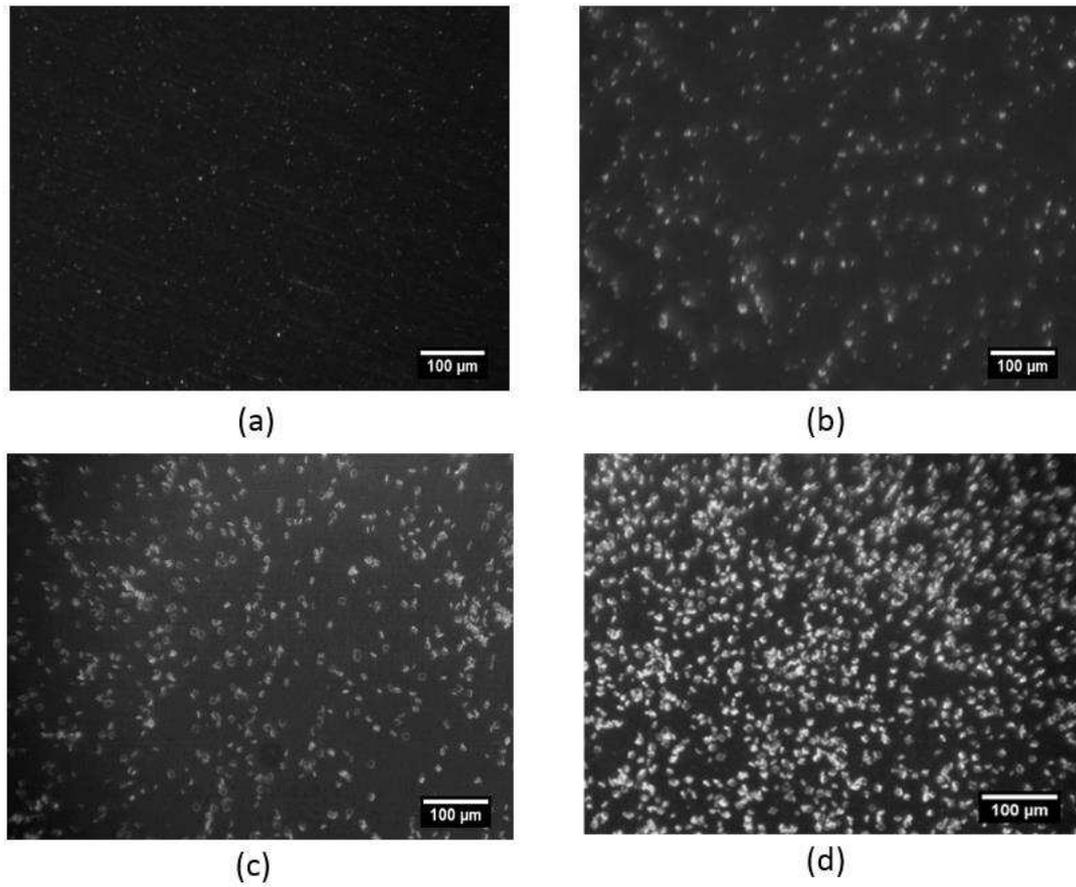
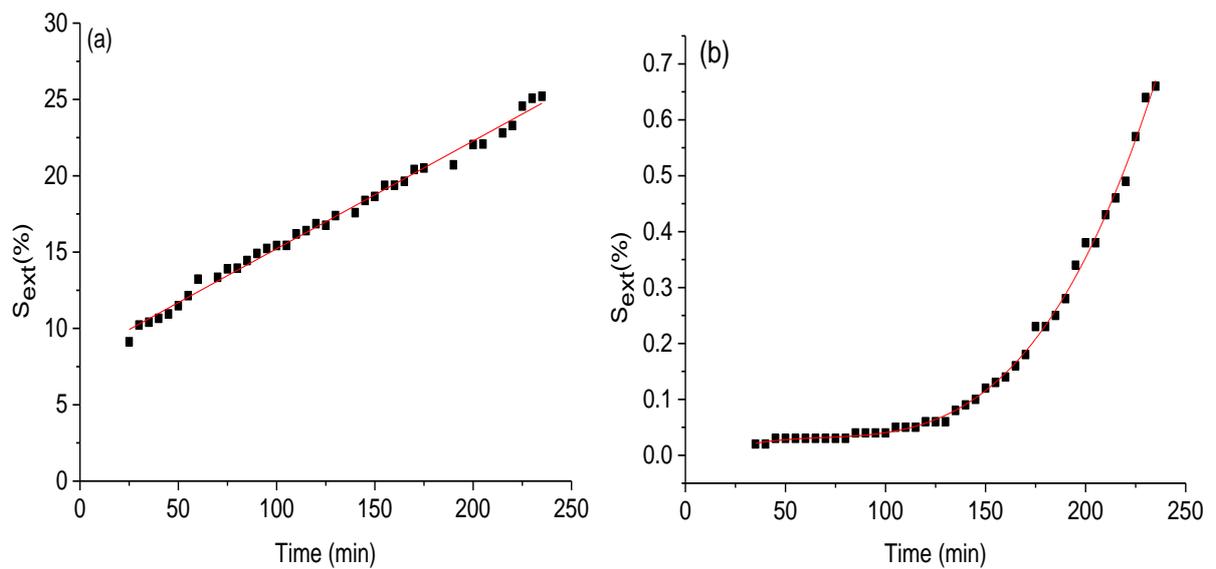


Fig. 4. Image of scale formed on the stainless steel sample (a) SR=10 (b) SR=20 (c) SR=30 and (d) SR=80 at 50°C



3.1.3 Effect of saturation ratio of PPCA

Chemical scale inhibition remains one of the most effective methods to prevent the nucleation and subsequent growth of scale crystals. **Fig. 6** and **Fig. 7** show the effect of continuous injection of 1 ppm PPCA on surface scaling (surface coverage and average crystal size) at low (SR 30) and high (SR 80) saturation ratios respectively. In both cases, the concentration of PPCA is above the minimum inhibitor concentration (MIC) (see supporting information) and was added after a pre-scaling period of 1 hour during which no inhibitors were present.

At low saturation ratios (**Fig. 6**), the surface growth of crystals stopped almost immediately after injecting the inhibitor, with a surface coverage and an average crystal size of 3.44% and 53.35 μm^2 respectively. PPCA is known to have good adsorption properties on minerals (Dupont et al., 1993; Leung and Nancollas, 1978; Liu and Griffiths, 1979) and the instantaneous inhibition of surface scaling observed was attributed to the inhibitor molecules being adsorbed and blocking all the active sites of the crystal lattice (Graham et al., 2003; Graham et al., 1997).

However, when PPCA is injected at higher saturation ratio (SR 80), surface growth continued for 60 minutes before reaching a plateau as shown in **Fig. 7**. The affinity of PPCA molecules for barium sulphate crystals is unlikely to have changed and this suggests that after the scale inhibitor is injected, both processes of adsorption of inhibitor molecules on the active growth sites and diffusion/incorporation of the scaling ions on the crystal lattice occur concurrently. The occurrence of these 2 competitive processes therefore delay the time necessary for the PPCA molecules to be adsorbed and fully block the active growth sites; but ultimately once all the sites have been blocked, growth stops. From these results, it can be observed that the inhibition of surface scaling by PPCA was significantly affected by the saturation ratio. These findings strengthen the need to differentiate the MIC for bulk precipitation and for surface fouling. Also, it encourages the adjustment of current testing procedures to take into consideration surface scaling phenomena. In terms of the effect of scale inhibitors on the morphology of the scale formed, the morphology of crystals formed for SR= 80 were rhombic as in the case of the uninhibited test shown in **Fig. 8**.

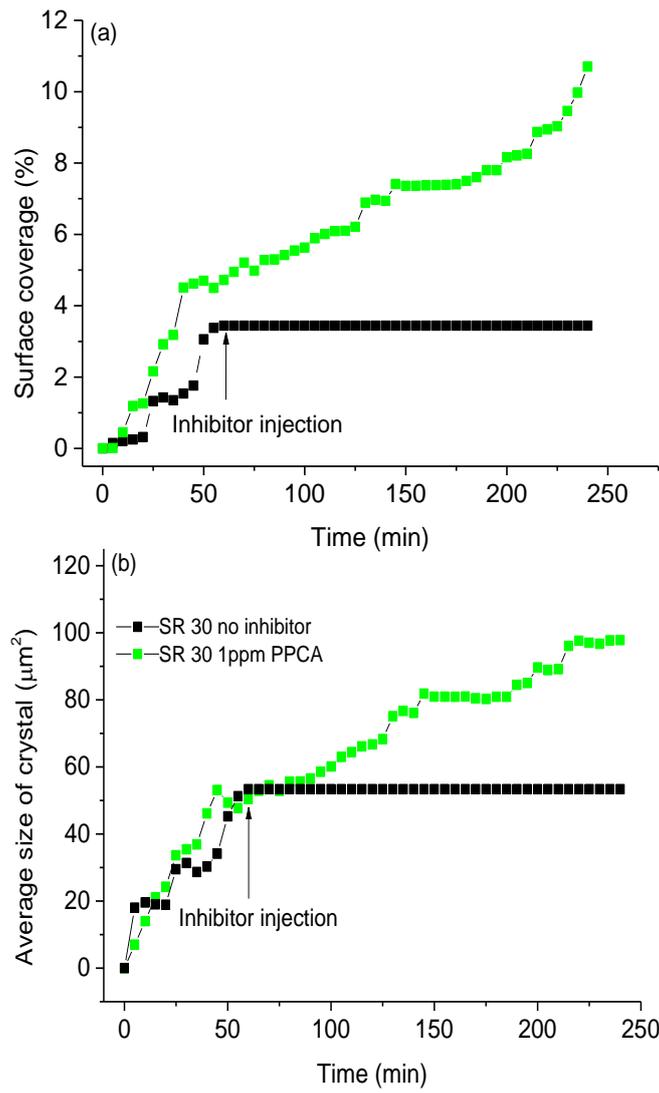


Fig. 6. Effect of 1ppm PPCA on SR=30 at 50°C on (a) Surface coverage and (b) Average size of crystals

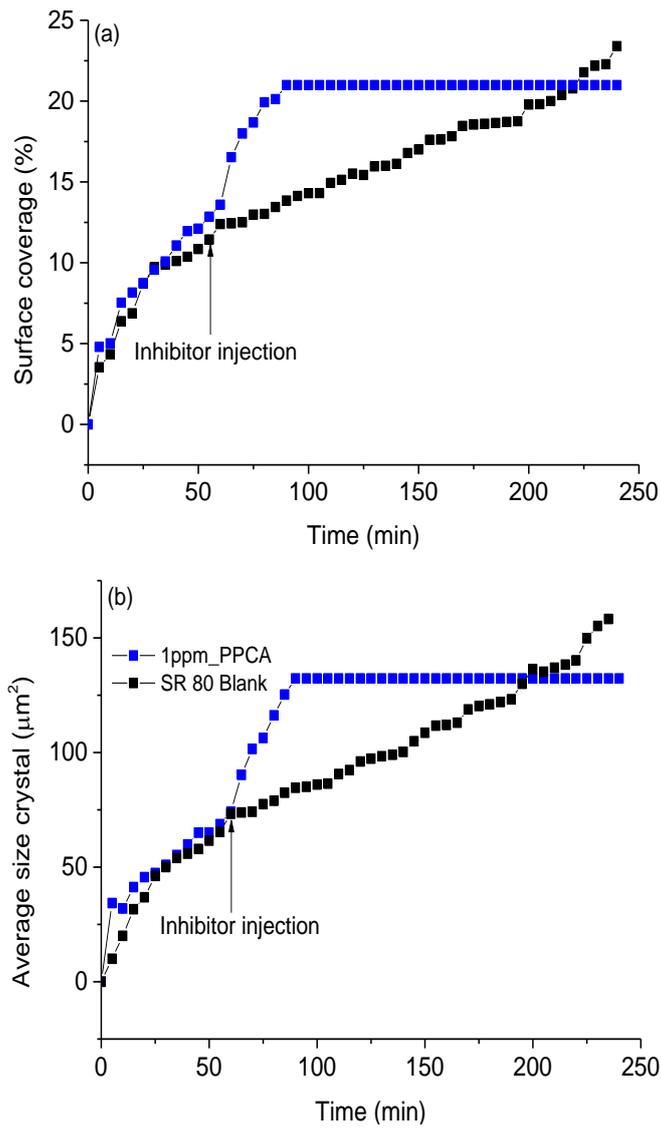


Fig. 7. Effect of 1ppm PPCA on SR=80 at 50°C (a) Surface coverage and (b) Average size of crystals

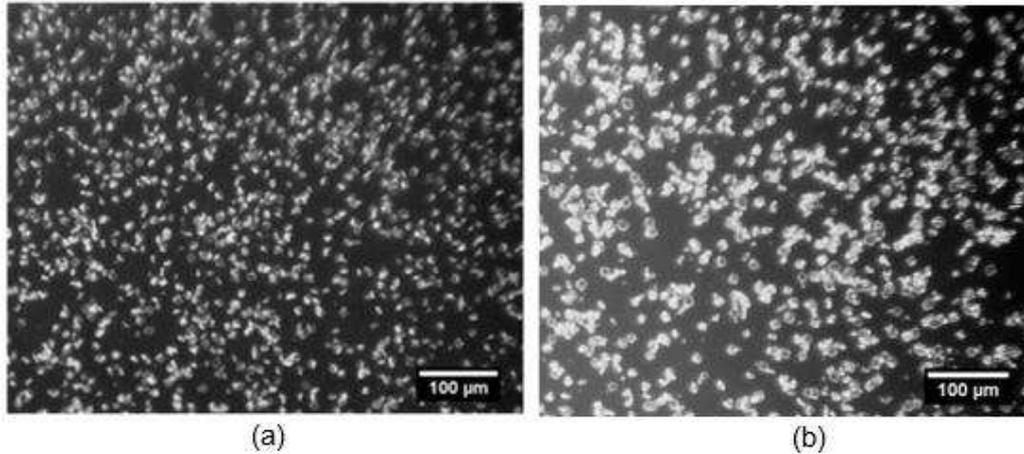


Fig. 8. Image of scale formed on the stainless steel sample for SR 80 (a) Blank and (b) inhibited at 50°C

3.1.4 Effect of inhibitor dosage and kinetic of adsorption

Fig. 9 shows the effect of PPCA concentration on surface coverage and average size of crystals using a scaling brine at SR=80, 50°C; and a constant flow rate of 20 ml min⁻¹. Prior to adding PPCA, all test samples were subjected to a pre-scaling period of 1 hour which gave a barium sulphate surface coverage of 12 ±0.5% and an average crystal size of 95±2 μm². The results show that the inhibitor concentration has a strong effect on the surface scaling. At the highest concentration at 5ppm, barium sulphate growth stopped 4 minutes after injection of PPCA to reach a surface coverage and average crystal size of 12% and 107 μm² respectively. At the lowest inhibitor concentration (1ppm), crystal growth continued for 57±3 min before reaching a plateau where the surface coverage and average crystal size stabilized at 21% and 132 μm² respectively.

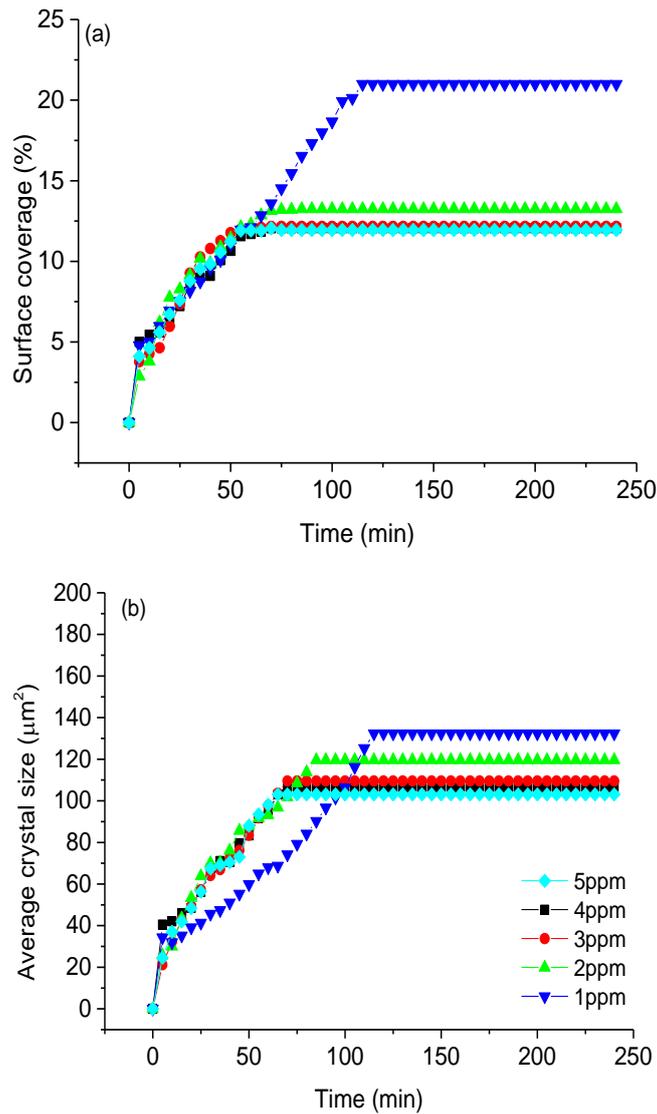


Fig. 9. Effect of inhibitor concentration on (a) Surface coverage and (b) Average size of crystals at SR=80 and 50°C

Barium sulphate crystallization rates at constant saturation ratios and in the presence of PPCA at different concentrations were determined using the slope of the barium sulphate surface coverage versus time graph. **Fig. 10a** shows the crystallization rate as a function of the concentration of scale inhibitor and highlights the relationship between concentration and scale growth rate. At a concentration as low as 1 ppm, the crystallization rate is reduced by 60%, and 80% at 5 ppm when compared to the non-inhibited case. The inhibition mechanism of many polymeric scale inhibitors can be described as an adsorption process at the crystal growth sites of the mineral surface of interest. Many inhibitors have been reported to display an adsorption process that fits to the Langmuir isotherm (Amjad, 1987) shown in equation 2:

$$\frac{R_0}{(R_0 - R)} = 1 + (K \times C)^{-1} \quad \text{Equation 2}$$

Where R and R₀ are the rates of crystal growth in the presence and absence of PPCA respectively, K is the adsorption constant affinity of the inhibitor for the barium sulphate surface and C is the PPCA concentration. According to the equation, a plot of R₀/(R₀ - R) versus 1/[C] should give a straight line that extrapolates to unity at high concentrations (Amjad, 1987). However the plot shown in **Fig. 10b** exhibits the presence of at least two linear segments. This strongly suggests that the inhibitory mechanism of PPCA deviates from the Langmuir adsorption isotherm. This implies that the assumptions of the Langmuir adsorption model are not verified; the adsorption sites at the surface of barium sulphate crystals are not uniform, and intermolecular interactions between PPCA polymer chains are likely to exist. Such findings are in agreement with the study by Mavredaki et al (Mavredaki et al., 2011) that showed that PPCA adsorbed preferentially on certain crystallographic planes of barium sulphate.

While standard bulk jar tests provide useful data regarding the threshold below which scale precipitation is likely to occur; they offer limited information into the kinetics of inhibition. The flow cell used in the current project allows crystallisation rate studies under constant experimental conditions, such as saturation ratios or the concentration of barium sulphate crystals present in the bulk solution. This allows efficient scale inhibition strategies to be developed where the dose rate can be adjusted in time i.e initially a high concentration of inhibitor is used to instantly block the active sites on any pre-scaled surface, and is later reduced to an optimal level that prevents precipitation.

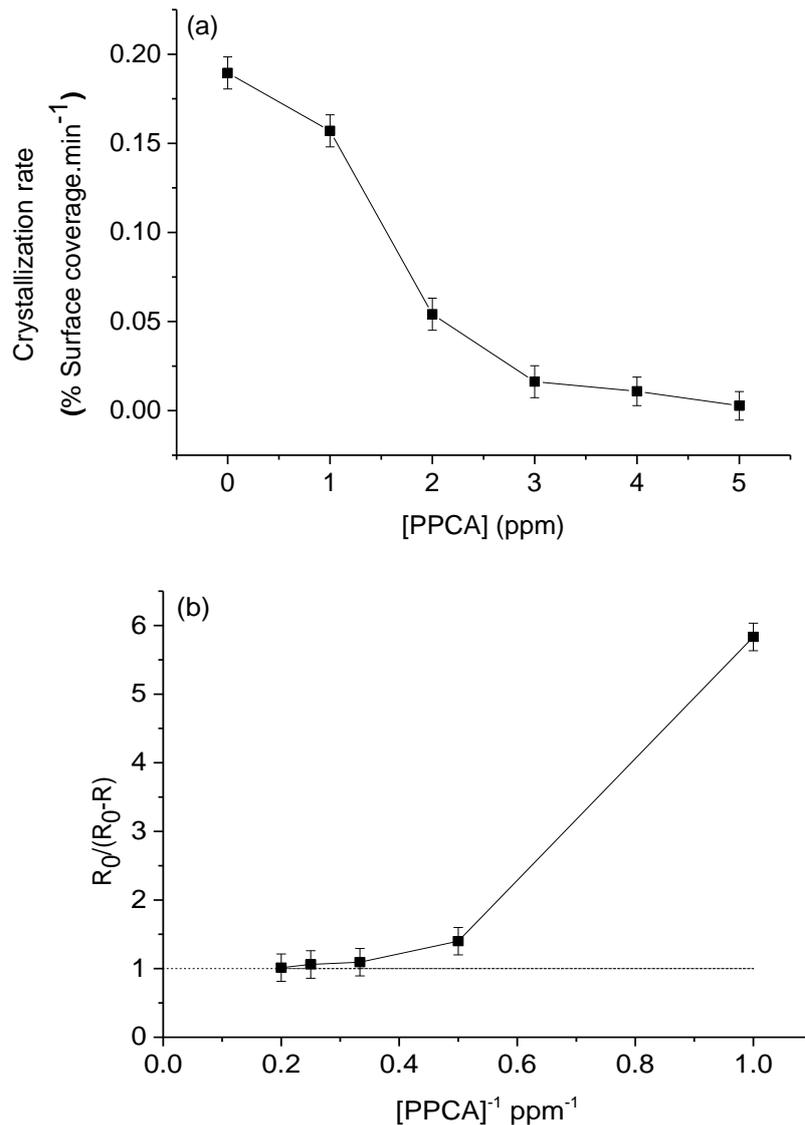


Fig. 10. Effect of PPCA concentration on growth of barium sulphate on surfaces (a) Surface coverage and (b) rate of barium sulphate formation as a function of the reciprocal of the PPCA concentration

4 Conclusions

The current study investigates barium sulphate surface fouling under a range of experimental conditions using optical techniques. The novel flow cell used allows experiments to be carried out under constant thermodynamic conditions which provides a more realistic scaling environment than conventional bulk jar tests. The key findings are:

- The result confirm that the deposition of scale on surfaces can occur solely by heterogeneous nucleation and subsequent growth; rather than the adhesion of scale from the bulk solution. Therefore, it implies that surface fouling as a result

of heterogeneous nucleation and growth on surfaces should be taken into consideration when designing a scale treatment plan.

- The study shows the strong effect of saturation ratio on nucleation and growth mechanisms of barium sulphate on stainless steel surfaces. A distinct two-step mechanism with instantaneous nucleation followed by growth of crystals was observed at high saturation ratios. Whilst at lower saturation ratios, progressive nucleation was observed with the formation of new nuclei and growth of existing crystals occurring simultaneously throughout the experiments.
- This study highlights the link between crystallization rates and inhibitor concentration and also demonstrates the affinity of PPCA to specific barium sulphate bonding sites.
- The results of this work highlight the limitations of current procedures used to evaluate the minimum inhibitor concentration required to stop bulk precipitation but disregard surface fouling aspects.

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