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Evaluation of laboratory techniques for assessing scale inhibition efficiency

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Abstract

Injecting chemical inhibitors is the most common method to mitigate mineral scaling in the oil industry. As such, the effectiveness of the techniques employed to evaluate performance of chemical scale inhibitors and apply the appropriate dosage is a very important aspect to be considered during the design of a scale prevention treatment. In this paper, the kinetics of scale formation and its inhibition are studied using a conventional bottle test, a dynamic tube blocking rig and a recently developed in-situ flow visualization rig. Calcium carbonate scaling brine was prepared at two saturation indices (SI) of 2.1 and 2.8 at 50ºC and run through the rigs at flow rate of 20ml/min. The conventional polphosphinocarboxylic acid (PPCA) inhibitor was used for the inhibition study at concentration ranging between 0.5–10ppm. The MIC_{bulk} determined from bottle test and supported with the in-situ turbidity MIC_{bulk} for SI of 2.1 and 2.8 are 1ppm and 8ppm respectively. For the same SI values, a considerably lower concentration of PPCA, 0.5ppm and 4ppm for the surface inhibition test using the capillary rig were obtained compared to $MIC_{surface}$ of 4ppm and 8ppm from the in-situ visualization technique. The surface visualization technique enables the range of concentration of inhibitors at which both bulk and surface scaling are completely controlled to be determined. The different techniques are shown to give complementary information for different stages of crystallization process and inhibition.

Keywords: Scaling; $CaCO_3$; Techniques; Crystal growth; Inhibition

1 Introduction

The performance and efficiency of chemical scale inhibitors to prevent mineral scaling in bulk solutions and on surfaces of equipment in the oilfield industry cannot be compromised. Great attention has been given to inhibition of bulk precipitation reactions (Amjad, 1994; Boak et al., 1999; Shaw and Sorbie, 2013; Shaw, 2012; Tomson et al., 2005).

The conventional bottle tests used for evaluating the efficiency of scale inhibitor usually focus on the inhibition of bulk scale precipitation processes. Bulk jar test consists of mixing brine in a beaker or a jar and carrying out an assessment of the precipitation process (Graham et al., 2005). At the range of temperature (5^{o}C, 50^{o}C and 95^{o}C) usually encountered in the production system, it was demonstrated that the dosage of inhibitor marginally below the required minimum concentration can actually enhance surface scale growth (Graham et al., 2005; Morizot, 1999a).

Dynamic tube-blocking rigs have been widely used for the study of scaling phenomena and in particular for the ranking of scale inhibitors (Dyer and Graham, 2002; Liu et al., 2012; Liu et al., 2016). A typical tube blocking rig experiment involves measurements of the differential pressure across a small diameter bore tubing of approximately 1-2m length (Bazin et al., 2005; Bazin et al., 2004; Dyer and Graham, 2002). The time for the pressure across the cell to increase and deviate from the baseline value gives a measure of the scaling time. Such technique is often used to assess the efficiency of scale inhibitors before being deployed in the production lines. Tube blocking tests were used by Zhang et al (Zhang et al., 2001) to perform bulk measurements at the outlet of the tube and to develop a kinetic model to predict downhole scaling. Dyer and Graham (Dyer and Graham, 2002) studied the effects of temperature and pressure on barium sulphate and calcium carbonate precipitation. The relative efficiency of two inhibitors combined with temperature and pressure effects on scale formation was also assessed using the dynamic tube blocking rig with good success. Inhibitor efficiency is measured by the ratio of the time needed to block the tube in the presence of inhibitor divided by the time needed to block the tube without inhibitor (Bazin et al., 2004). The drawback of this technique is that the reduction of ionic species as scale is formed in the 1-2m long tubing coil with residence time of above 3s at 20ml/min, will cause a decrease in the saturation ratio and possibly uneven distribution of deposited scale along the tubing. It is therefore difficult to use the methodology to develop a robust kinetic models where the experimental conditions should remain constant across the working section. The possibility of scale gradually building up in the capillary or tube without effectively detecting it could also lead to incorrect assessment of the Minimum Inhibitor Concentration (MIC).

An in-situ flow visualization technique with associated image analysis of scale build-up in real-time was recently developed to study the kinetics and mechanisms of surface scaling under constant condition (Sanni et al., 2015; Sanni et al., 2017). It was used to assess the inhibition of $BaSO_4$ surface and bulk scaling using phosphino-polycarboxilic acid (PPCA) and di-ethylene triamine penta methylene phosphonic acid (DETPMP) (Bukuaghangin et al., 2016). Scale precipitation and surface deposition is followed in-situ and in real-time in a once-through flow rig that allows control and assessment of various parameters such as temperature, flow rate, inhibitor concentration, brine chemistry and scaling indices. Having a constant supersaturation across the working section is important to be able to accurately predict scaling kinetics and effectively evaluate the MIC.

Recent studies are now being focussed on the evaluation and inhibition of surface fouling and crystal growth rates at solid interfaces (Bukuaghangin et al., 2016; Charpentier et al., 2015; Keogh et al., 2017). Chen et al (Chen, 2005) reported that at 4 ppm of PPCA, the inhibition efficiency of surface deposition is greater than the inhibition efficiency of bulk precipitation. It is assumed that the inhibitor film formed on the metal surface at the highest concentration of PPCA (4 ppm) prevent the adsorption of scale crystals on the metal surface. Other studies have shown that the mechanisms and kinetics controlling bulk and surface deposition are different and scale inhibition efficiency varies between surface and bulk processes (Chen et al., 2005; Mavredaki, 2009; Morizot and Neville, 2000; Sanni et al., 2015; Setta and Neville, 2011).

As such, there is need to evaluate existing bulk inhibition methods and establish their suitability to assess surface inhibition by focussing on the distinction between bulk and surface mechanisms and the effects on inhibition strategies. The current paper, therefore assesses and compares the inhibition performance of PPCA using the conventional bottle, dynamic tube blocking rig, a new capillary system as well as the newly developed once-through in-situ flow visualization technique. The new technique has been used at the same condition as the conventional methods in order to simultaneously and distinctively study the inhibition of both homogeneous bulk precipitation and heterogeneous surface deposition in a single system. The results are further analysed to show effects of chemical inhibition on crystallization mechanisms using a model developed by Beaunier et al (Beaunier et al., 2001) and subsequently modified by Euvrard et al (Euvrard et al., 2006). It describes the types of nucleation as either instantaneous or progressive. Instantaneous nucleation describes the situation when, in the initial stages of crystal formation, nuclei are formed and then grow. The nucleation and growth processes are separated, and no further nucleation occurs when the growth is occurring while progressive nucleation describes the process when nucleation occurs and the crystals grow but new nuclei continue to be formed.

For instantaneous nucleation:

$$S_{ext}(t) = -\ln\big(1 - S(t)\big) = \frac{MK_1N_o t}{\rho} \quad (1)$$

For Progressive nucleation:

$$S_{ext}(t) = -\ln\big(1 - S(t)\big) = \frac{MK_1N_o At^2}{\rho} \quad (2)$$

$S_{ext}(t)$ is the extended surface coverage, S(t) is the actual covered surface area, A is the nucleation rate, k_1 is the lateral growth rate (mol/μm/s), M is the molar mass of $CaCO_3$(100g/mol), ρ is the density of the crystals (ρ=2.71 X 10^{-}12g/μm^3 for calcite), N_o is the number of active nucleation sites (equivalent to detected number of crystals).

Instantaneous nucleation occurs when $S_{ext}(t)$ is proportional to time, whereas progressive nucleation takes place when $S_{ext}(t)$ is proportional to time squared (t^2).

2 Experimental Details

2.1 Chemical

2.1.1 Brine Composition

Two brines were mixed at 50:50 at a temperature of 50℃ and at mospheric pressure. The saturation ratio of these brines was calculated using the ScaleSoftPitzer (Version 4.0) (Tomson, 2009). Saturation ratio is calculated generally using equation (3).

$$SR = \frac{[Ca^{2+}][CO_{3^{2-}}]}{K_{sp_{CaCO_3}}} \quad (3)$$

The composition of the brines used is presented in Table 1 and Table 2. The seawater (SW) is the source of carbonate ions (CO_3^{2-}) while the Formation Water (FW) is the source of calcium ions (Ca^{2+}) in the experiment. Each brine shows a simple composition to prevent the influence of impurities on the formation of $CaCO_3$ scale.

The scaling tendency can also be expressed in terms of Saturation Index (SI), which is the logarithm of Saturation Ratio (SR)

$$SI = \log_{10} \mathrm{SR} \quad (4)$$

Table 1: Brine Composition in g/l for SI 2.1

	NaCl	**$NaHCO_3$**	**$CaCl_2.2H_2O$**
Formation water	46.36	0	7.35
Sea water	31.02	5.51	0
Supersaturation index SI (50:50)	2.1 (SR = 126)		

Table 2: Brine Composition in g/l for SI 2.8

	NaCl	**$NaHCO_3$**	**$CaCl_2.2H_2O$**
Formation water	46.36	0	14.70
Sea water	31.02	11.70	0
Supersaturation index SI (50:50)	2.8 (SR = 630)		

The two concentrations were selected to induce both homogeneous bulk and heterogeneous surface precipitation within a reasonable time frame. The temperature

of 50ºC selected was based on temperature observed in an oilfield topside operations(Graham et al., 2005).

2.1.2 Additives

The chemical additive used during the study is PPCA, which is a commercial product commonly used in the oilfield because of its good quality, low cost and environmental acceptability. PPCA is a standard polymeric scale inhibitors widely applied in the field to prevent both carbonate and sulphate scales (Farooqui et al., 2014)

The molecular weight of PPCA IS 3600g/mol and its molecular structure shown in Figure 1.

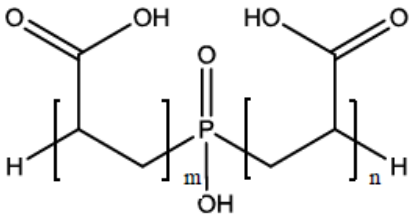


Figure 1: Schematic structures of PPCA (Amjad, 1998)

2.1.3 Cleaning solution

In order to reduce error and increase good reproducibility, the rigs were cleaned up after each experiment with a solution containing 25g of ethylene-diamine-tetra-acetic acid (EDTA) and 25g of potassium hydroxide (KOH) in 500 ml (pH of ~11).

2.2 Experimental Set-up

2.2.1 Bulk Jar/Bottle Test

This is the common test method used to evaluate the efficiency of chemical scale inhibitors in bulk solution. The test procedures for the conventional bottle test performed are as described in the NACE standards (NACE, 2001). The experiment involves the mixing of brine in a beaker/jar the precipitation is then followed by measuring the concentration of free calcium ions in solutions over time (t). The efficiency of the inhibitor is calculated by using the equation:

$$I.E = 100\left[\frac{C(t) - C_b(t)}{C_0 - C_b(t)}\right] \quad (5)$$

Where C (t) = test sample Ca^{2+} concentration at time, t, $C_b(t)$ = Ca^{2+} concentration in the blank solution (no scale inhibitor) and C_O = control sample Ca^{2+} concentration at time, t = 0 (ppm).

$CaCO_3$ brine solutions at SI values of 2.1 and 2.8 are prepared separately and tested. PPCA inhibitors at different concentrations ranging from 1ppm – 10ppm were added to each solution and the solutions were incubated at 50ºC for 2 and 22 hours.

Uninhibited $CaCO_3$ brine serves as baseline conditions. After incubation, 1 ml sample is taken from each bottle for chemical analysis using the Atomic Absorption Spectrometry (AAS) analysis to determine the free calcium ion concentration remaining in solution. 9 ml of a quenching (KCl/polyvinyl sulfonate) solution is added to each sample to prevent further precipitation. The concentration of gas-phase atoms is measured by the AAS using light absorption (Seeger et al., 2019). The analyte atoms or ions is vaporized in a flame or graphite furnace. The light source is a hollow cathode lamp in which the cathode is made from the same metal that is being analysed, in this case calcium. The calcium atoms are excited on heating and their electrons go to higher energy levels. When the electrons fall back to lower levels, visible radiation is given off. The energy of the emitted photons corresponds to the energy difference of the Ca atom electron levels. Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration. Calcium ion standard solution of 1.0 mg ml–1, was prepared by dissolving an appropriate amount of CaO in diluted hydrochloric acid.

2.2.2 Capillary flow rig

The dynamic tube blocking test is a well-known technique used in the oil and gas industry to investigate the effectiveness of scale inhibitor in dynamic conditions (Dyer and Graham, 2002; Frenier, 2008; Graham et al., 2005). The set-up is equipped with a temperature controlled device and a pressure transducer which is used to measure the pressure difference across the tube as illustrated in the schematic diagram shown in Figure 2. The brine solutions (SW and FW) are injected into the coils using a reciprocating pump. The residence time of the fluid to travel from the mixing section to the cells is 0.54s at flow rate of 20ml/min. Supersaturated solutions flow through a thin tube of 1mm in diameter and scale builds up on the surface of the tube results in differential pressure between the inlet and outlet of the tube (Frenier, 2008; Koutsoukos and Kontoyannis, 1984) . In this study, two capillary tubes with lengths of 10mm and 1000mm (both internal diameters of 1mm) were used during the experiment. The short capillary tube is the adapted version of the conventional tube blocking rig where the saturation ratio of the flowing fluid is considered constant within the capillary cell with a very short residence time of 0.03s.

The performance of scale inhibitor is assessed by injecting scale inhibitor solutions upstream of the mixing point of the waters. The inhibitor was injected into the seawater brine solution containing carbonate ions. The scaling time is first evaluated for the baseline conditions for both the long coil and short capillary cell. The effectiveness of the inhibitor concentration is measured by the time period at which the inhibitor prevents or delays the increase in differential pressure. The concentration of PPCA inhibitor used for the different tests and SI values range from 0.5ppm – 10ppm as in the bottle test for bulk precipitation.

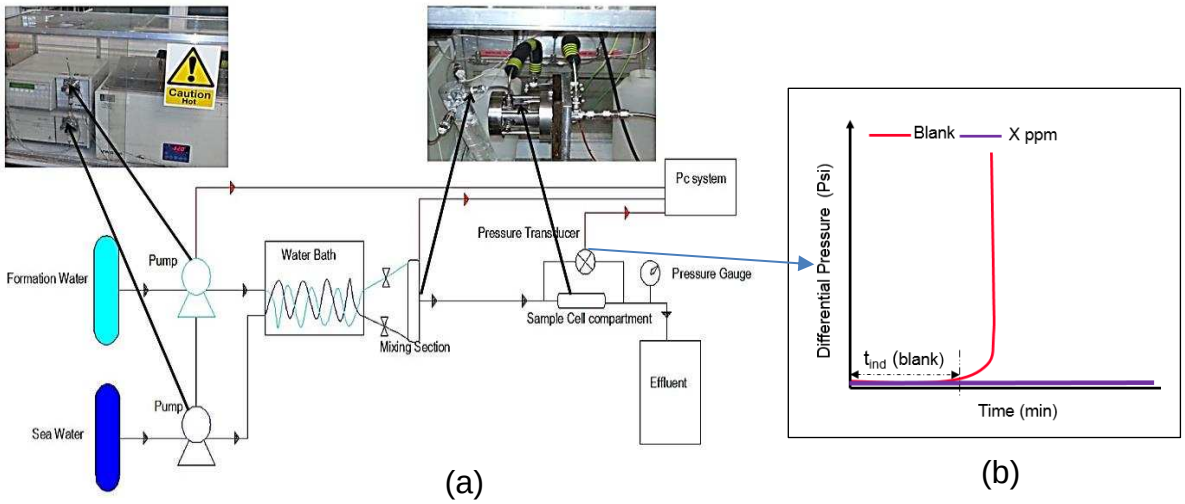
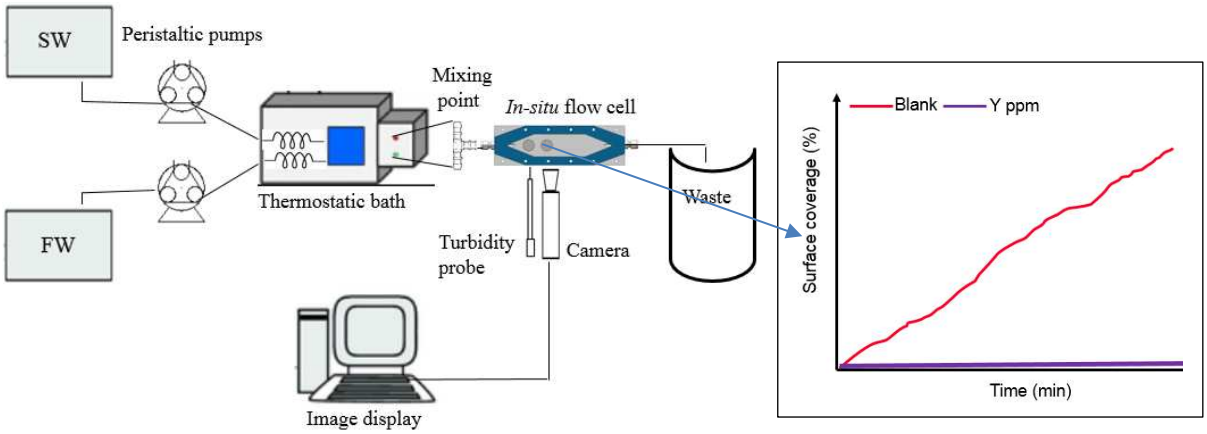


Figure 2: (a) Schematic diagram of the capillary rig (b) typical data (Bello, 2017)

2.2.3 In-situ visualization cell

The in-situ visualization set-up presented in Figure 3, has been described in detail previously (Sanni et al., 2017). The set-up was designed to work under atmospheric pressure and allows experimental conditions to be kept constant at the point where the images are recorded. In addition, the set-up allows surface fouling and bulk precipitation to be assessed simultaneously. The images captured were processed to assess the number of crystals and their sizes as well as the $CaCO_3$ surface coverage. Similarly, real-time measurements of the bulk precipitation were performed using a turbidity probe.

Prior to the start of the experiment, the thermostatic bath is set to the desired operating temperature. The two brine solutions are pumped through the thermostatic bath to be heated up to the desired experimental temperature, they are mixed in a tee chamber close to the flow cell. The residence time of fluids from the mixing point to the cell is 0.03s at 20ml/min. In the flow cell, the camera takes images of the scale formed on the substrate every 5 minutes during the course of the experiment.



(a) (b)

Figure 3: Schematic diagram of the in-situ visualization rig (Sanni et al., 2017)

The inhibition performances and mechanisms at different SR on both turbidity and surface scaling were assessed in-situ and in real time.

$CaCO_3$ scale inhibition tests were carried out in the flow rig with the two SR values of 2.1 and 2.8 at 50ºC using polyphosphinocarboxylic acid (PPCA) at 1, 2, 4, 6 and 8ppm. The inhibitor was prepared and added into the seawater (SW) solution, containing CO_3^{2-}, prior to mixing.

2.3 Test conditions

Tests were carried out to assess the effectiveness of each technique regarding scale inhibition. The test conditions for the static and dynamic flow tests are shown in Table 3. The temperature used is 50ºC to represent a realistic temperature at top side oil production facilities. The flow rate used for the study is 20ml/min and the total time of study is 4hours.

Table 3: Experimental conditions

Parameters	Conditions		
	Bottle	In-situ visualization	Capillary rig
Flow rate (ml/min)	Static	20	
Duration of test (hours)	2 & 22	4	
Mixing Ratio	50:50		
Pressure	Atmospheric		
Temperature (℃)	50		
Inhibitor Concentration (ppm)	1, 2, 4, 6, 8, 10		

2.4 Surface profilometry

The surface contact profilometer was used to determine the scale thickness or growth in direction normal to the surface (refer to z- direction in the remaining of the paper). The contact profilometer measures the vertical characteristics of the surface deviation. The scale deposition was performed in the visualization rig on four samples under the

same condition of saturation index, flow and temperature. The scaling time considered are 60 minutes, 120 minutes, 180 minutes and 240 minutes corresponding to the induction period observed in the short capillary (10mm) cell for brine with SI values of 2.1 and 2.8. The scale was deposited on one half of the sample surface while scale on the other half is prevented with a masking tape. The scale average thickness is measured relative to the unscaled part of the sample with the evaluation length, L, set at 8mm at three different sections (Figure 4).

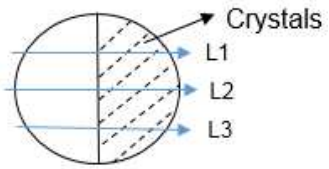


Figure 4: Sample profile for surface roughness

3 Results and discussion

3.1 Bulk Solution Minimum Inhibition Concentration (MIC)

The static bottle test was used to establish the bulk MIC for the $CaCO_3$ brines. The rate of consumption of ionic species (Ca^{2+}, CO_3^{2}) in the bulk solution gives an understanding of the precipitation rate of calcium carbonate scale ($CaCO_3$). The MIC was determined for the brine mixing ratio of NSSW/FW (50:50) at 2 and 22 hours residence times. The inhibition efficiency at different concentrations of PPCA in the bulk solutions of $CaCO_3$ at 50°C are shown in Figure 5. The acceptable industrial standard for bulk MIC (MIC_{bulk}) is the concentration of inhibitor that gives an 80% or more inhibition efficiency at 2 and 22 hours (Graham and Sorbie, 1997; Graham et al., 2001). For this study, the bulk MIC is taken as the concentration level of inhibitor that maintains a 90% inhibition efficiency. For saturation values of 2.1, the MIC_{bulk} is 1ppm as the inhibition efficiency is 90%. At SI of 2.8, the 90% efficiency is attained at higher amount of PPCA concentration of 8 ppm

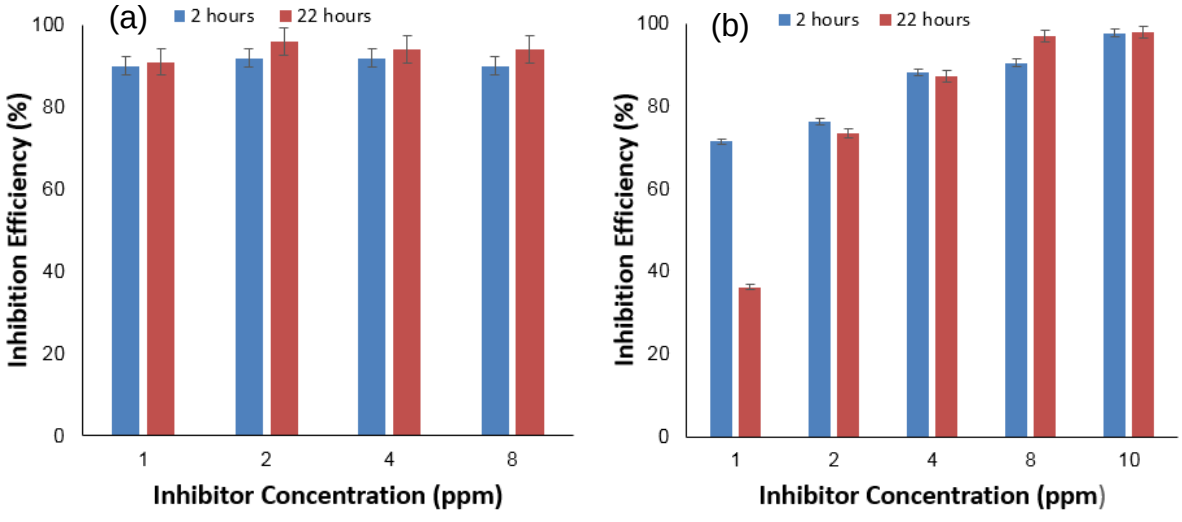


Figure 5: Inhibitor efficiency at different levels of scale inhibitor (a) SI = 2.1 (b) SI = 2.8

Increase in SI and scaling ions requires greater concentration of PPCA to control the formation of calcium carbonate in the bulk solution. This is consistent with previous results by Graham et al.(Graham et al., 2005; Graham et al., 2001) and (Setta and Neville, 2011)

3.2 In-situ turbidity measurement

The turbidity measurement from the in-situ flow rig for the blank tests plotted in Figure 6 are 95 and 166 FTU for SI values of 2.1 and 2.8 respectively with zero induction time. The system is such that the saturation ratio is kept constant throughout the flow cell which consequently maintains constant values of the turbidity measured (Sanni et al., 2017). The inhibition effects and mechanisms for bulk precipitation at different SR were assessed in-situ and in real time. The results presented are in agreement with the MIC_{bulk} obtained from static bottle tests. It can be seen in Figure 6 (a) that for SI value of 2.1, there was no bulk precipitation occurring with the addition of PPCA at 1ppm concentration while for SI of 2.8, the bulk scaling is completely inhibited with the injection of 8ppm of PPCA. At these points, the values of the turbidity measured are zero indicating that there are no crystals precipitating in the solution.

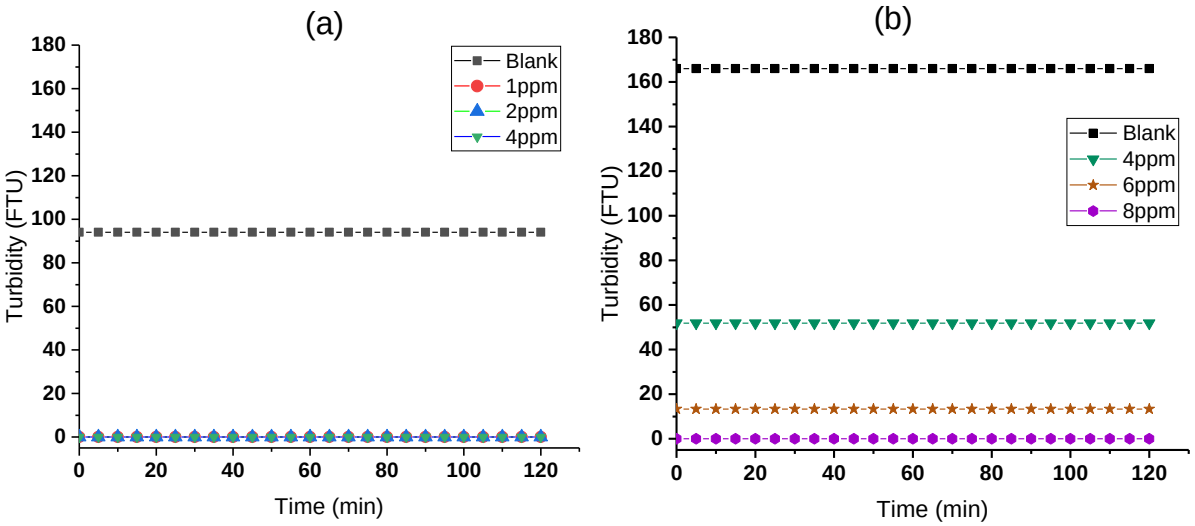


Figure 6: In-situ bulk turbidity for (a) SI = 2.1 (b) SI = 2.8

The real-time in-situ turbidity measurement makes it possible to follow the gradual decrease in turbidity with increasing concentration of PPCA up to the MIC. As shown in Figure 6b, at concentrations below MIC_{bulk} (8ppm), the bulk turbidity values only reduced when compared with the blank turbidity indicating that the precipitation has not been completely controlled.

3.3 Surface scaling in capillary rig versus conventional tube blocking rig

The surface scaling times for the uninhibited tests for both the conventional long coil of 1000mm and the adapted short 10mm capillary are presented here. The residence

time of the fluid in the long coil is about 3.0s at flow rate of 20 ml/min, and for the short capillary cell, the residence time is 0.025s at the same flow rate of 20 ml/min.

For the brine solution with SI value of 2.1 (Figure 7a), the surface scaling induction period is 90 minutes for the conventional tube blocking rig (1000 mm coil length) compared to the induction period of 200 minutes observed for the short capillary rig (10 mm). A similar trend is observed for SI of 2.8, for longer coil length, faster induction time of about 10 minutes and it resulted in faster scale build up as it took shorter time (50 minutes) to reach the threshold differential pressure of 5psi (Figure 7b). However, the induction time for the short capillary for SI 2.8 is observed to be 45 minutes.

Homogeneous precipitation and heterogeneous crystallization processes take place in the two cells with a more constant thermodynamic condition in the short capillary. Primary nucleation is a stochastic process which manifests in crystallization at different scales, as such, detection time of crystals may not be identical in many experiments despite identical experimental conditions (Mazzotti, 2015).

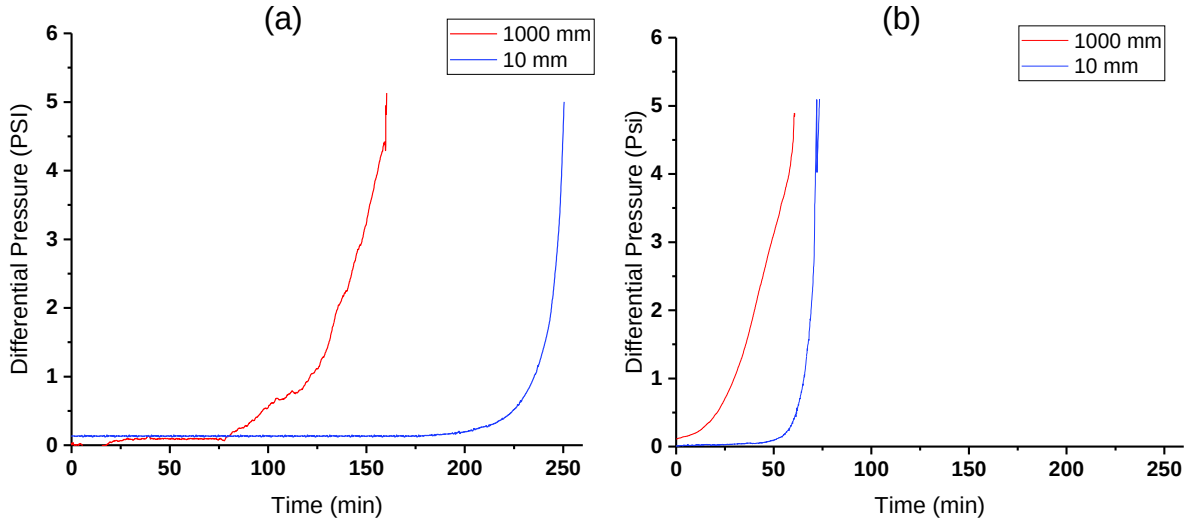


Figure 7: Effects of capillary length on scale deposition (a) SI = 2.1, (b) S.I = 2.8

The difference in the scaling time observed in these two systems could be attributed to the different lengths and configuration of their cells. The long capillary means greater surface area that can facilitate crystallization by heterogeneous nucleation. Heterogeneous nucleation sites include surface defects, joints and seams in tubing. The hot spots created by the coil system of the long capillary can act as high energy region for surface reaction and could facilitate interaction between the adsorbed hydrated calcium ion and the substrate thereby leading to faster crystallization on the scale (Flaten et al., 2010; Nielsen, 1984; Yamanaka et al., 2012).

3.4 Inhibition in capillary rig

The capillary rig test is designed to assess scale inhibition under dynamic flow conditions at constant saturation ratio. The Minimum Inhibitor Concentration (MIC) for a given SI is taken as the scaling induction time which corresponds to at least 5 times

the blank value (Bazin et al., 2004). The graphs in Figure 8 and Figure 9 summarise the effects of injecting inhibitors to the system.

A similar trend is observed with respect to scale inhibition for both the conventional tube blocking and the adapted short capillary systems. For SI 2.1, no scale formation was observed with the addition of 0.5ppm concentration of PPCA while for S.I value of 2.8, the formation of scale in the capillaries was prevented with the injection of 4ppm concentration of PPCA inhibitor.

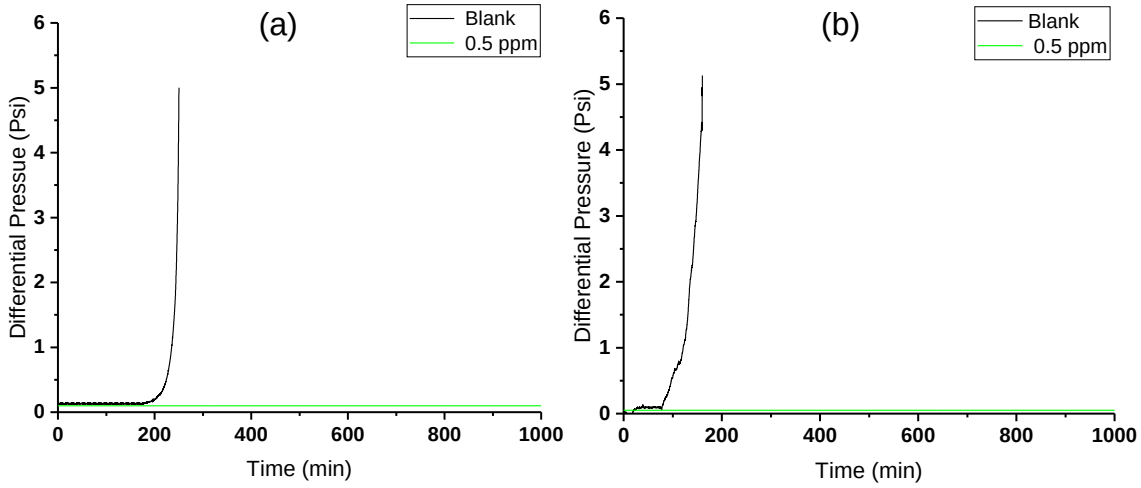


Figure 8: Scaling in capillary rig at SI = 2.1 (a) Short capillary (b) Long capillary

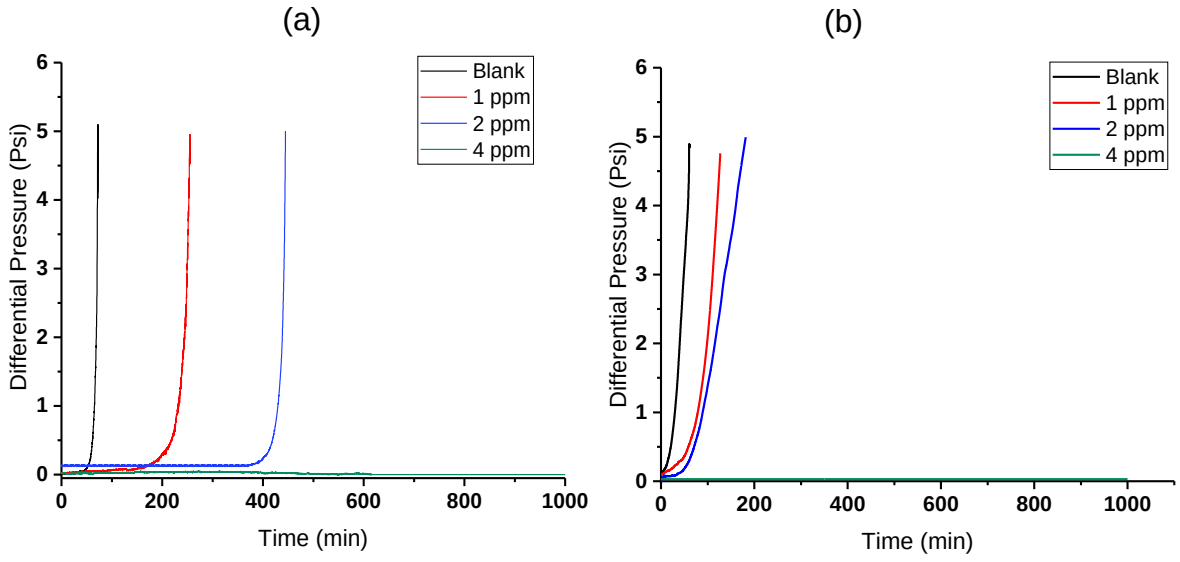


Figure 9: Scaling in capillary rig at SI = 2.8 (a) Short capillary (b) Long capillary

Results of the inhibition tests from the capillary rig show the concentration of the inhibitor needed to prevent surface scale formation to be lower compared to the static bottle test for bulk. A previous study at 50^{o}C by Graham et al (Graham et al., 2005) reported that the reaction kinetics are moderately fast in the bulk solutions and larger amount of inhibitors were required to control the bulk reaction. The interplay of two or

more factors is responsible for the discrepancies between low value of $MIC_{surface}$ obtained from tube blocking test and the high MIC_{bulk} obtained with static bottle test. Firstly, the residence time (0.025s) for the brine solution to travel through the capillary cell after mixing is very short compared to the long residence times (2 hours, 22 hours) used for the standard bottle test (Graham and Sorbie, 1997). The longer residence time of bottle test would promotes growth of crystals at later stages. It is erroneous to make a direct comparison of MIC between the two systems as the parameters may vary and the residence times differ. Secondly, the chemistry of inhibitors which make them efficient in stopping either nucleation or growth of crystals with PPCA regarded as being more effective nucleation inhibitors (Reddy and Hoch, 2001; Yuan et al., 1998). The short residence time of brine solution in the capillary cell and long coil coupled with the effective nucleation inhibiting mechanisms of PPCA, the nucleation sites are reduced significantly, the differential pressure would be held at zero or rise slowly depending on the SI and concentrations of inhibitors.

Employing the MIC determined from the tube blocking rig may pose a potential problem both with regards to scaling in bulk and surface facilities as surface growth of nucleated crystals can still take place at a slow rate. Previous studies have shown surface MIC ($MIC_{surface}$) to be higher than MIC_{bulk} (Bukuaghangin et al., 2015; Chen et al., 2004; Graham and Sorbie, 1997; Graham et al., 2005; Setta and Neville, 2011). Surface deposition is usually initiated by heterogeneous nucleation which requires a lower energy barrier than the homogenous nucleation in bulk precipitation (Myerson, 2001; Setta and Neville, 2011). The growth of scale on metal surfaces is clearly a much more serious problem than precipitation within the bulk solution.

3.5 Surface scaling and inhibition using in-situ visualization

The in-situ flow visualization set up has been used to assess surface deposition and inhibition under the same set of conditions in the capillary rig. The range of inhibitor concentration, SI values, flow rates and temperature are maintained as in the capillary rig test.

3.5.1 In-situ surface images

The in-situ images for each set of experimental condition were recorded every 5 minutes for 4 hours. Figure 10 shows surface crystals formed after 10 minutes and 240 minutes at SI value of 2.1 without inhibitor. The constant SI means that the thermodynamic condition is constant across the cell, as such, surface growth and bulk precipitation can be observed to continue over the duration of the experiment with larger crystals and more surface coverage at 240 minutes.

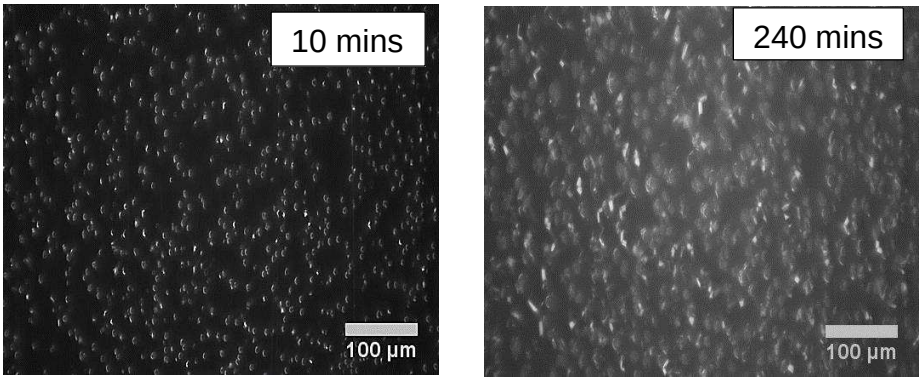


Figure 10: In-situ surface images for Blank test at SR = 2.1

The number of crystals formed on the surface is reduced with the injection of 1ppm inhibitor. This is the MIC_{bulk} determined from the bottle test and also effective to control the in-situ bulk precipitation in the visualization rig. However, contrary to assessment of surface inhibition using the capillary rig, it is shown with the in-situ surface images in Figure 11 that the active surface nucleation sites are only reduced but the growth of already nucleated crystals continued. Real time visualization test in contrast to the capillary tests shows that complete inhibition of surface scaling was not achieved at 1ppm concentration. At this concentration, the inhibitor molecules are not completely adsorbed and block all the active growth sites to prevent growth of the crystals (Bukuaghangin et al., 2016; Graham and Sorbie, 1997; Graham et al., 2004) .

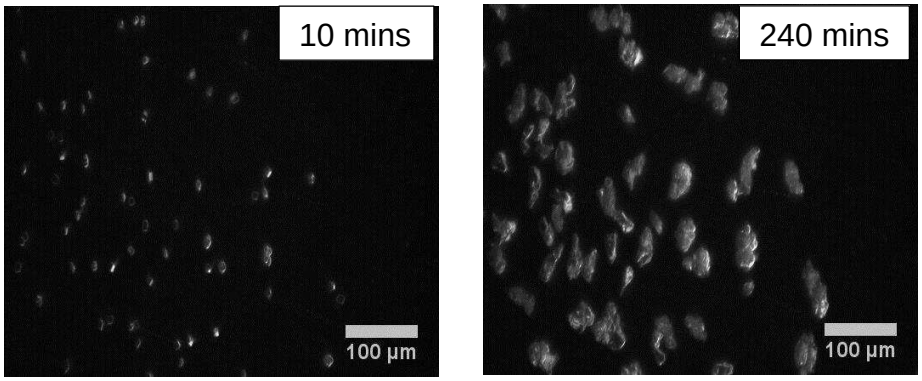


Figure 11: In-situ surface images at SR = 2.1 and 1ppm PPCA

Further increase in the concentration of PPCA to 2ppm resulted in greater reduction in the number of crystals as shown in Figure 12. Here, more crystals growth's sites are blocked compared to 1ppm concentration of PPCA concentration. The scale formation at the surface is significantly diminished but not entirely controlled at concentration slightly above the MIC_{bulk}. The overall surface coverage was significantly reduced and could be accountable for the inability of the capillary rig to detect the surface scaling at the same concentration of PPCA.

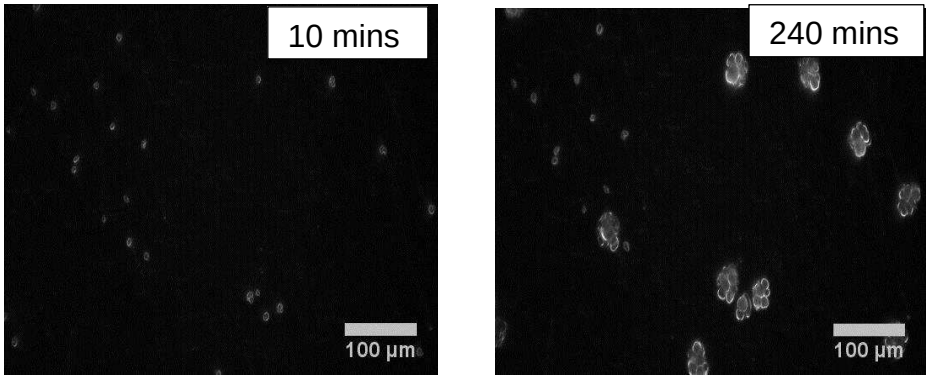


Figure 12: In-situ surface images at SR = 2.1 and 2ppm PPCA

Scanning Electron Microscope (SEM) images were taken to assess the morphology of the surface crystals formed on the samples in the in-situ cell after 4 hours. Figure 13 and Figure 14 show the SEM images for SI = 2.1 and 2.8 respectively at flow rate of 20 ml/min. For the uninhibited test, the crystals are distributed uniformly across the metal surfaces. The crystals are composed of mainly leaf-like vaterite and a few sparsely distributed cubic calcite crystals which is consistent with previous works on $CaCO_3$ deposition at 50^oC (Euvrard et al., 2000; Kjellin, 2003; Sanni et al., 2017). However, injection of inhibitors at MIC_{bulk} resulted in distorted growth of the surface crystals because the inhibitor molecules are not completely adsorbed on all faces resulting in preferential growth of faces (Bukuaghangin et al., 2016; Mavredaki, 2009).

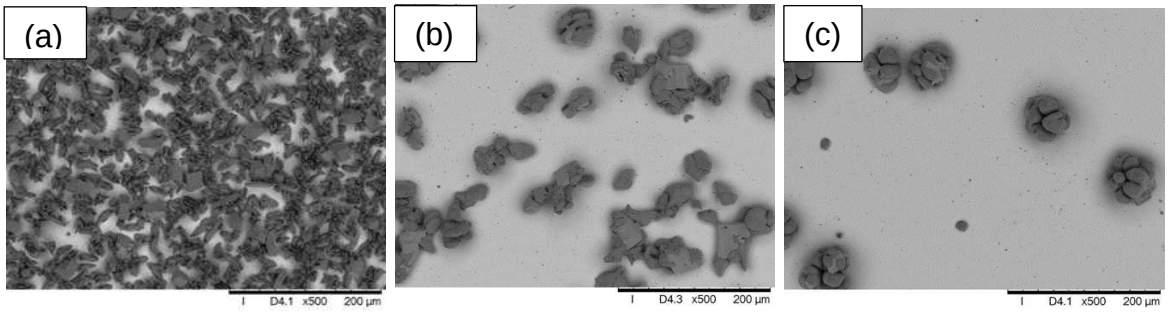


Figure 13:SEM images of the CaCO3 scale deposited on the surface for SI = 2.1 at 50C; (a) blank (b) 1ppm PPCA (c) 2ppm PPCA

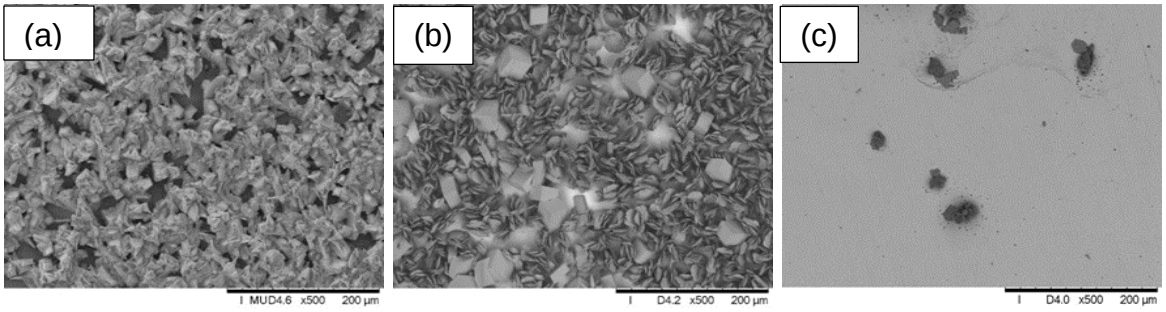


Figure 14: SEM images of the CaCO3 scale deposited on the surface for SI = 2.8 at 50C; (a) blank (b) 4ppm PPCA (c) 8ppm PPCA

3.5.2 Crystal nucleation and surface coverage

The in-situ images from the visualization rig were analysed to assess the number and the surface coverage of crystals. In all cases, the crystals could be quantified as soon as their sizes reached 1µm. Figure 15 presents the reduction in surface nucleation and total surface coverage of scale as PPCA concentration is increased from 1ppm, 2ppm to 4ppm for SI of 2.1.

Generally, the number of crystals decreases with increase in the concentration of PPCA inhibitor. The PPCA acts to block active nucleation sites and consequently inhibits scale formation to various degrees depending on its concentration and brine solution SI.

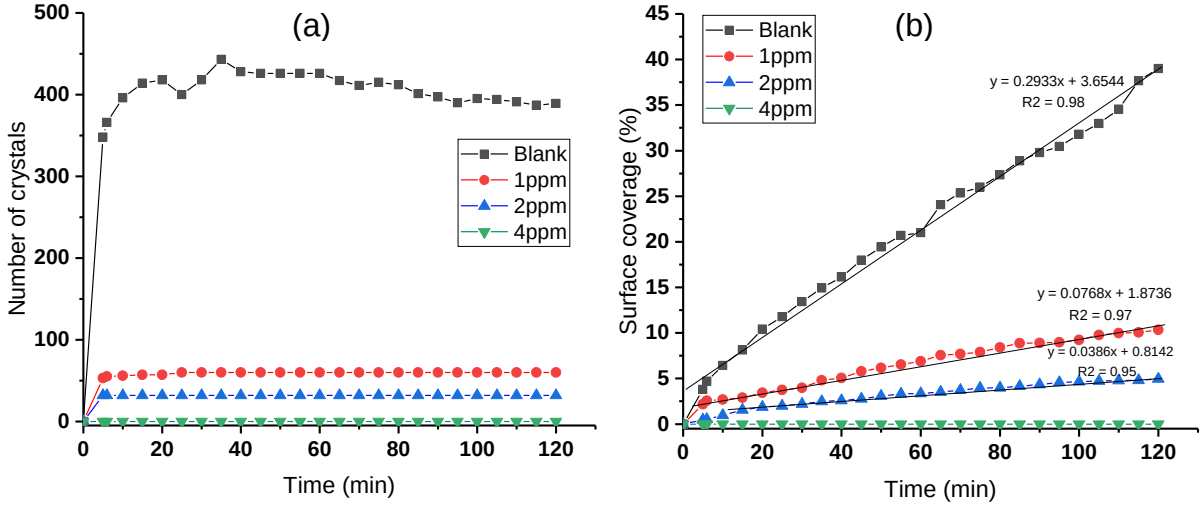


Figure 15: (a) Number of crystals and (b) Surface coverage at SR = 2.1 for blank and with PPCA inhibitor at different concentrations

For SI value of 2.1 (Figure 15), the inhibitor concentration required to effectively inhibit scaling is 4ppm compared to the capillary rig test where the concentration is 1ppm for the same SI. The visualization rig technique shows that nucleation of crystals is only partially inhibited with the injection of 1ppm and 2ppm of PPCA inhibitor, and the rates of surface coverage are only significantly reduced with respect to the non-inhibited test as shown in Figure 15b. Nucleation of crystals is completely inhibited when 4ppm of PPCA was added as no crystals are detected, therefore the surface coverage remains at zero. At this concentration, heterogeneous surface nucleation was totally controlled with complete adsorption of inhibitor molecules on the nucleation sites.

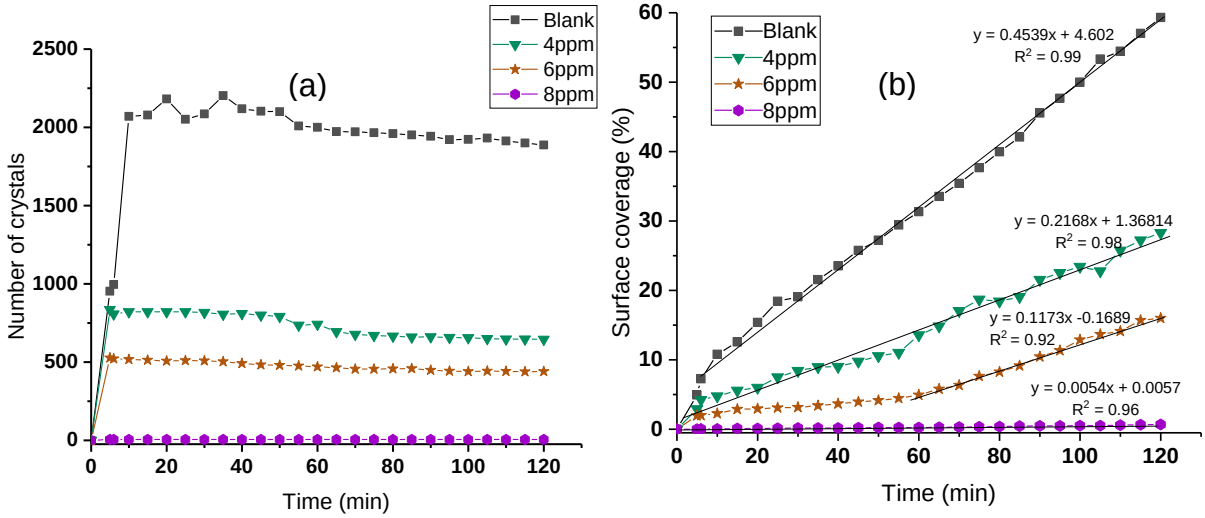


Figure 16: (a) Number of crystals and (b) Surface coverage at SR = 2.8 for blank and with PPCA inhibitor at different concentrations

For higher SI of 2.8 (Figure 16a), the inhibitor concentration of 4ppm was not sufficient to block all the nucleation sites. The number of active nucleation sites is a function of SI, therefore, a function of the ionic concentration of the brine solutions. Here, higher PPCA inhibitor concentration of 8ppm is required to completely inhibit crystal growth. This is in contrast to the capillary rig test where no increase in differential pressure was observed with the addition of PPCA at 4ppm. The results from the visualization rig in Figure 16 shows that at this concentration (4ppm), the number of crystals was only reduced while the rate of surface coverage of scale significantly dropped from 0.29 μm^2/min to 0.04 μm^2/min. PPCA partially inhibits calcium carbonate nucleation by decreasing the number of nuclei and also the number of active sites on the metal (Martinod, 2008).

Thus, MIC levels depend on the sensitivity that can be achieved in the different rigs. The visualization set up could be used to evaluate the minimum inhibitor concentration at which complete inhibition of scaling on surface equipment is achievable. This is usually higher than the MIC require to delay the surface induction or scaling time as determined by the dynamic tube blocking rig. The concentration requires to completely inhibit further growth is a function of percentage surface coverage of crystals and the number of active growth sites. With greater surface coverage, it requires higher concentration of the inhibitor to be completely adsorbed on the crystals.

The effects of injecting the PPCA inhibitor on the kinetics is summarised in Table 4. The rate of scale formation is the slope of the linear fit on the surface coverage area (Figure 15 and Figure 16) as a function of time.

Table 4: Rate of surface coverage with inhibitor injection at S.I = 2.1 and 2.8

SR	Inhibitor Concentration	Linear Equation	Rate ($\mu m^2/s$)
2.1	Blank	y = 0.293x + 3.654	0.293
	1 ppm	y = 0.077x + 1.874	0.077
	2 ppm	y = 0.038x + 0.814	0.038
	4 ppm	y = 0.000	0.000
2.8	Blank	y = 0.454x + 4.602	0.454
	1 ppm	y= 0.216x + 1.368	0.216
	2 ppm	y= 0.112x – 0.1698	0 .112
	4 ppm	y = 0.005x + 0.005	0.005

Higher SR shows higher rates of surface scale coverage while a decrease in rate of formation is clearly observed with an increase in the concentration of inhibitors. This shows that the adsorption rate of inhibitors is a function of its concentration. The in-situ technique allows to know the concentration that completely inhibit surface scaling, in this case, 4ppm was able to block all the active sites at S.I value of 2.1 and prevent nucleation of crystals.

In regards to the crystallization mechanisms, it can be observed from Figures 15a and 16a that nucleation takes place very fast with no measurable induction period (Karabelas, 2002) and the number of crystals stabilizes very quickly. The nucleation mechanisms is instantaneous nucleation as all active nucleation sites are assumed to be converted into nuclei at the early stage of crystallization (Beaunier et al., 2001; Euvrard et al., 2006). The nucleation process did not proceed for the entire duration of the test. The number of crystals reaches a maximum, as such, the later stages of crystallization process would be dominated by the growth or agglomeration of existing crystals as indicated by the increase in surface coverage with time (Figure 15b and Figure 16b). It shows that a scaling surface consists of a finite number of active nucleation sites (Beaunier et al., 2001).

As stated in equation (1), for instantaneous nucleation:

$$\boldsymbol{S(t) = \frac{MK_1N_o t}{\rho}}$$

Therefore, plotting the actual surface coverage, $\boldsymbol{S(t)}$ against time, t for SI values of 2.1 and 2.8 gives a linear relationship as shown in Figure 15b and Figure 16b.

The $CaCO_3$ crystals are formed in a short time and grow progressively as a result of constant supersaturation as shown in Figure 17. The early stage of crystallization is dominated by rapid nucleation with all available active sites generating nuclei in a relatively short period (Sanni et al., 2016). This is similar to the observations by

Beaunier et al (Beaunier et al., 2001) for high concentrations of calcium ions where it was assumed that difusion controls the process.

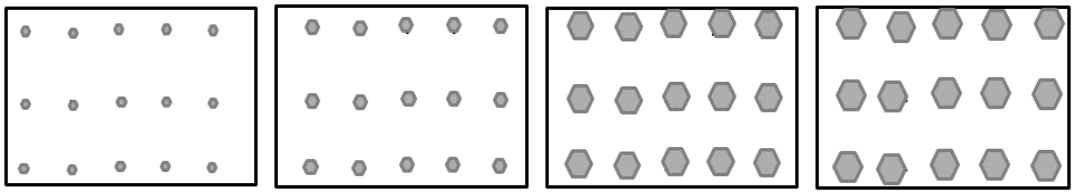


Figure 17: Schematic illustration of instantaneous crystallization mechanisms

There are different mechanisms to control the process of scale formation at different ionic concentrations. The ability to understand and determine the surface crystallization mechanisms allows for the correct type and dosage of inhibitor to be selected. It could also help to assess how efficient inhibitors would be in controlling either the nucleation or growth of scale on surfaces. Inhibition strategy should be able to accommodate the possibility of surface scaling without bulk precipitation and the use of either nucleation or growth inhibitors.

3.6 Minimum Inhibition Concentration from the different test methods

The minimum inhibitor concentrations obtained for each technique is summarised in Table 5.

Table 5: Minimum inhibition concentration (MIC) values from different techniques

	Bulk Precipitation		Surface crystallization	
Technique	SI 2.1	SI 2.8	SI 2.1	SI 2.8
Bottle jar test	1	8	-	-
TBT Long	-	-	0.5	4
TBT Short	-	-	0.5	4
Visualization test (VR)	1	8	4	>8

The MIC_{bulk} determined from bottle test and supported with the in-situ turbidity MIC_{bulk} for SI of 2.1 and SI of 2.8 are 1ppm and 8pmm respectively. It requires a considerably lower concentration of PPCA for the surface inhibition test using the capillary rig. The method for assessing the efficiency of scale inhibitor varies in the two systems. Scale inhibition efficiency is measured in terms of the reduction of scaling ion concentrations for static bottle test while it is expressed in terms of delaying the induction time up to 5 times of the blank scaling time in the capillary rigs. By comparison, the longer residence time in static bottle test could result in further growth of nucleated crystals which invariably require higher concentration of inhibitor for maximum efficiency than the capillary rig (Graham and Sorbie, 1997). The consumption of inhibitor by adsorption within the lattice of growing crystals leads to a reduction in its concentration

and consequently restricts its ability to prevent further growth. The dynamic condition in the tube blocking rig can also magnify a possible dispersion mechanisms in addition to nucleation inhibiting mechanisms, since the scale inhibition and differential pressure rise is determined by the build-up of scales on the wall of the tubing (Graham and Sorbie, 1997).

The surface visualization methods enables the range of concentration of inhibitors at which both bulk and surface scaling are completely controlled to be determined. MIC in the visualization cell is defined as the concentration of inhibitors which prevent surface crystallization completely by blocking all the active nucleation sites. The surface inhibition from the in-situ visualization rig shows the surface MIC at SI values of 2.1 and 2.8 is 4ppm and 8ppm respectively. The visualization rig as compared with the capillary rig shows that surface inhibition requires higher concentrations to reach PPCA inhibition efficiency. In agreement with previous study, the calcium carbonate inhibition requires higher concentrations for surface scaling than for bulk scale precipitation. The formation of surface scale is as a result of heterogeneous process compared to scale precipitation which originally starts as a homogeneous reaction in a bulk free of suspended particles (Setta and Neville, 2011). The inhibitor concentrations needed to suppress $CaCO_3$ scale precipitation are generally not enough to prevent $CaCO_3$ deposition on a stainless steel surface due to the different mechanisms and kinetics involved in these two processes (Cheong et al., 2012; Morizot and Neville, 2001; Sanni et al., 2017).

MIC cannot be viewed in isolation. It depends on whether scale formation is to be completely prevented as in the case of downstream safety control valves or controlled/reduced as in pipelines. It is important to ascertain whether the application of inhibitor is actually meant to achieve a delay of induction period or to effectively stop the growth of crystals. For this, there needs to be an understanding of the tolerable level of scale and often this is very difficult to determine.

The $MIC_{surface}$ from capillary test which effectively delayed the induction time throughout the experiment is considerably lower than the $MIC_{surface}$ from the visualization test. At the $MIC_{surface}$ from the capillary test, the visualization cell shows that surface growth continues, albeit at a lower rate. The difference in $MIC_{surface}$ between the capillary rig and the in-situ visualization rig can be due to the sensitivity and capabilities of the two techniques. It emphasises the need to understand each technique and their limitations in order to predict scale formation and evaluate its control using inhibitor.

3.7 In-situ visualization versus capillary tests - Thickness of scale deposits

The surface scale deposition were further analysed by profilometry technique to assess the thickness of scale formed with time on the surface. Estimating the scaling kinetics would be difficult using the Hagen-Poiseuille flow equation (Jianxin wang, 2004; Kazeem A. Lawal, 2012; Zhang et al., 2001) especially for the longer coil where there is a drop in the saturation ratio across the capillary cell due to longer residence

time. The scale layer is not uniform, and as such to link the deposition thickness to the pressure drop along the capillary tube based on Hagen-Poiseuille equation will not be valid. Figure 18 shows the surface thickness, which is a measure of the vertical characteristics of the surface deviation as a function of time. It distinguished the stages of growth clearly detected by both the in-situ visualization and capillary cells.

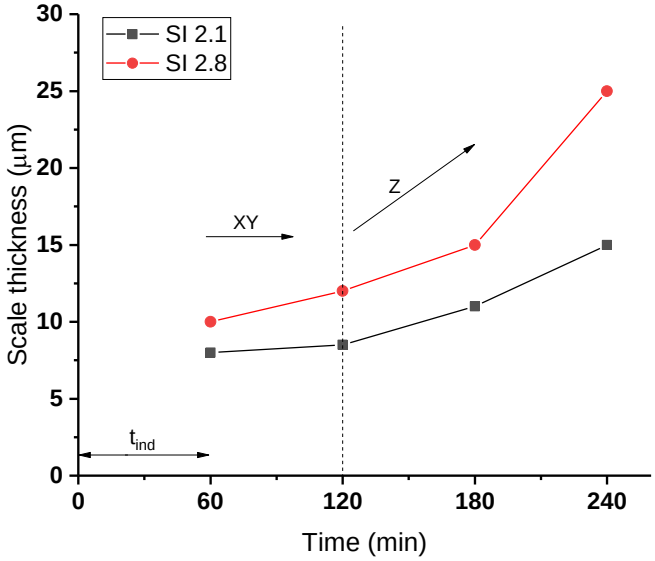
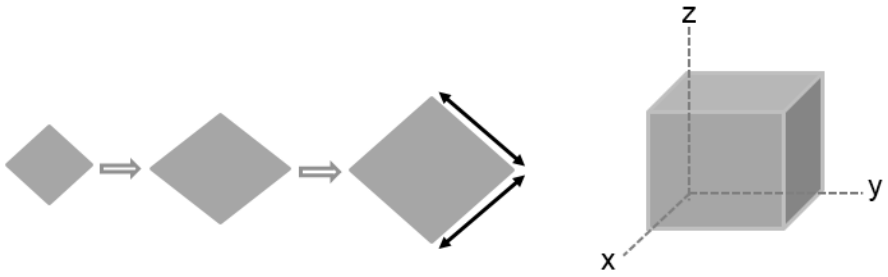


Figure 18: Surface thickness of deposits

The induction period is followed by an early stage of crystallization up to about 120 minutes where the growth is parallel to the surface and increasing the scale coverage. The growth of the crystals at the initial stage is basically on the XY plane as depicted in Figure 19a.



(a) (b)

Figure 19: Schematic representation of the growth of scale during (a) Initial (b) later stages of crystallization process.

This is the region where the in-situ visualization is more practically suitable to detect and analyse crystallization processes comprising of induction, nucleation and the early stages of growth. For the capillary rig, this initial stage corresponds to the surface induction period (Figure 7) where the differential pressure remains at zero. However, the surface induction time from the capillary test is different when compared to the in-situ visualization test. The surface induction time for the visualization test is taken as the time for the first crystal to be detected on the surface. Scale crystals are already

detected with the in-situ visualization cell for the period of induction indicated in the capillary test. The critical nuclei are not detected when formed upon nucleation in the capillary test until after growing to a size large enough to occupy a significant volume fraction of the cell.

At the later stages of crystallization, the scale start to grow in the z-direction which increases the scale thickness as depicted in Figure 18b.This second stage is observed to coincide with the time or point where there is a rise in differential pressure in the capillary test (Figure 7). At the later stage of growth, the scale deposition could not be easily analysed with the visualization rig as the crystals begin to cluster and grow out of focus. The visualization rig would therefore be best for detecting and assessing early stages of surface crystallization. The analysis shows that the scaling or induction time for the dynamic tube blocking rig could actually be the onset of growth in the z-direction.

A good understanding of the mechanisms of bulk and surface scaling processes can enable reliable strategies for mitigating its formation in the field to be developed. A knowledge of the mechanisms is required to predict scale formation and its control using inhibitor, therefore, scale inhibitor selection and ranking for a proposed field application can be made more effective by employing laboratory test techniques that will better simulate and reflect the real field scaling environment that the inhibitor will encounter on application.

4 Conclusions

The work has shown the uniqueness and suitability of the various techniques including a recently developed in-situ visualization rig to distinctively quantify the inhibition of both nucleation and growth of surface scaling. The use of shorter capillary length instead of the more conventional long coil of the tube blocking system allows to keep the experimental conditions constant across the working section.

The determination of the correct dosage or minimum inhibition concentration (MIC) to effectively combat scale problems relies amongst other factors, on the accuracy, sensitivity or effectiveness of the techniques employed. It points to a potential problems if viewed in isolation. Each technique has its merits and contributes specific performance data that could provide the basis for scale mitigation when viewed together. There is no single test design which can successfully stimulate all possible field scenarios. Bottle test, capillary test (dynamic tube blocking test) and the new in-situ visualization method offer complementary information to study crystallization and inhibition of sparingly soluble salts.

- The standard bottle test provides useful data regarding the threshold below which scale precipitation is likely to occur. It also emphasises the efficiencies of chemical inhibitors to prevent homogeneous bulk crystallization.

- The capillary and dynamic tube blocking tests provide more insight on the kinetics of crystal growth in Z direction, relating to the later stages of crystallization.
- The in-situ visualization cell is effective to study early stage surface crystallization, when the growth is in the XY plane. The scale is typically single layer of crystals and can offer a good evaluation of nucleation inhibitors. It also offers a close assessment of both bulk and surface scaling inhibition

A good understanding of the mechanisms of bulk and surface scaling processes could enable reliable strategies for mitigating its formation in the field to be developed. Information needed to ascertain the performance of scale inhibitors should not be based only on their performance under various environmental conditions such as temperature, pH, hydrodynamic conditions and brine composition but also where possible on data from two or more techniques.

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