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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 crystallization 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.

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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. (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, 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. (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

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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 (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 25 ppm of PPCA was applied, bulk scaling was greatly reduced; but enhanced surface deposition occurred.

A similar study by Bukuaghangin et al. (2005) and 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, 10 mm 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 μm). 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 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.

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

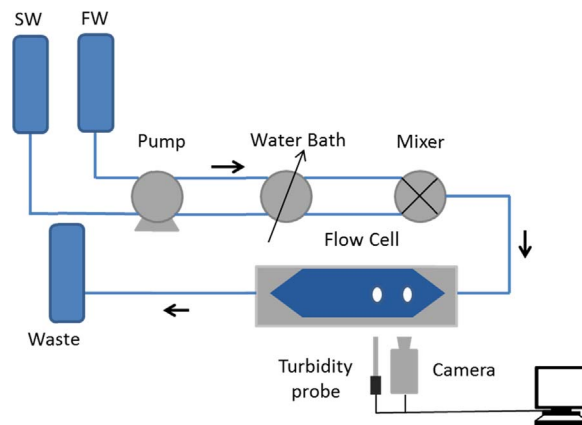


Fig. 1. Schematic of Experimental Set-up.

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.

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 Tables 1, 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.

2.3. Growth and nucleation model

The nucleation/growth model used during this study was developed by 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:

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

Beaunier et al. (2001) 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.

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