

Impact of Surface Conditions on Calcium Carbonate (CaCO_3) Scaling Kinetics in a Once-Through Capillary Flow Rig

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ABSTRACT

Mineral scale formation is one of the most common deleterious challenges in oil and gas production, restricting the steady flow of fluids. It poses major safety & operational issues and results in significant costs due to loss of production and remediation when not properly managed. Recent studies have shown that scaling processes on the surface are not necessarily a result of precipitation of crystals in the bulk solution and that they do not often share the same trends with regards to crystal growth kinetics and inhibition. Most of the past studies on scale deposition have focused on the static bulk data, some attention has been paid to surface conditions and hydrodynamic parameters. However, there is still no reconciliation between bulk precipitation and surface deposition. This study investigates the kinetics of CaCO_3 fouling by assessing the interplay between surface feature/condition and scale growth during heterogeneous nucleation processes, to better understand what characteristics of a surface promotes or reduces the likelihood of scale formation.

To study the effect of surface “history” on fouling kinetics, scaling tests were performed on pre-scaled samples using brines of two saturation ratios (SR) at a flow rate of 10ml/min up to a previously determined induction time. Surface wettability effects were investigated by the application of silane on stainless steel to increase hydrophobicity, at three SR values and flow rates ranging from 10-30 ml/min at 70°C. CaCO_3 surface scaling kinetics was assessed from differential pressure change in a novel capillary flow rig designed to study heterogeneous scale formation under hydrodynamic conditions by keeping SR constant and ensuring that there is no bulk precipitate in the solution. The results show a non-water wet surface having improved scale performance by delaying the onset of nucleation and reducing the amount of surface fouling, while pre-scaled surfaces enable faster scale growth in comparison to non-seeded surfaces.

Keywords: CaCO_3 , surface precipitation, heterogeneous nucleation, kinetics, pre-scale, capillary cell, dynamic tube, wettability, flow rate.

INTRODUCTION

The formation of sparingly soluble inorganic salts also known as mineral scale is one of the old but pertinent challenges encountered in the recovery, refining, and transportation of oil & gas.¹ The formation of calcium carbonate (CaCO_3) has been extensively studied, most of the work has been focused on the bulk solution with some more recent work focused on surface precipitation. The question to be answered has been to determine whether the mechanisms that dominate precipitation in bulk and on surfaces are the same.²⁻⁴ Recent investigations,^{5,6} have shown that crystals present on the surface are not always the result of a secondary deposition process occurring after the precipitation of scale in the bulk solution. Scale management is often a complex mixture of prediction, inhibition, and sometimes removal strategies, therefore in terms of practical importance, surface fouling phenomena are as important as bulk scaling. Thus, scale formation on surfaces is one of the criteria to take into account before implementing new scale management strategies.^{6,7}

Two classes of factors can influence the formation of calcium carbonate scale both in bulk solution and on surfaces: *physiochemical* variables (related to the solution from which the deposit is formed - supersaturation, temperature, flow, chemical composition) and *surface* variables (related to substrate material on which deposit is attached - nucleation, adhesion process, and crystal growth mechanisms)⁸. Any of the above factors can influence nucleation, growth of nuclei (or both simultaneously), the morphology of particle, and polymorphism.^{9,10} The essential driving force of all crystallization conditions is known as supersaturation, it plays a significant role in mechanisms that occur during the crystallization process (nucleation and growth). In addition to the bulk solution chemistry, the nature of the substrate has been shown to have a significant influence on the deposition, adhesion, form, and structure of scale deposit.¹¹ Competing interactions between an inorganic foulant, a solid surface, and a medium can promote or prevent adhesion. It is important to understand and quantify these interactions influenced by the substrate properties such as wettability and roughness (inherent or induced by pre-existing scale or corrosion product) and their effects on heterogeneous crystallization.¹²

Wettability is an important attribute associated with a solid surface and is governed by surface chemical composition and the roughness of the solid surface; it also gives an indication of the surface energy of the substrate¹³ as described by Wenzel,¹⁴ and Cassie.¹⁵ Primarily, wetting is characterized by a static contact angle defined as the angle a liquid makes with a solid surface. The contact angle depends on other substrate properties such as roughness, surface preparation, and cleanliness.¹⁶ Surfaces with low wettability and hence low surface energy have been shown to perform better regarding scaling, while high surface energy substrate due to an increase in surface area (resulting from roughness) leads to greater adhesion. It has been shown that the adhesion of fouling is lower and induction times longer in systems with low surface energies.¹⁷

The field of biofouling has seen major advancement being made towards developing substrates to prevent adhesion or attachment of deposits on surfaces, where low energy surfaces (i.e. hydrophobic surfaces) have shown great efficiency in terms of reducing biofouling. As reported in most of the studies from the bio-fouling industry where this application has been adopted to mitigate or reduce marine biological species on surfaces, reduction in induction time for heat transfer through a system and lower fouling adhesion is shown in systems that exhibit lower surface energy.^{6,17,18} Research works in inorganic fouling have applied modified surfaces as a result of similarities with the bio-fouling industry,⁶ this has been focused on reducing the surface energy because of the perceived similarity to the biofouling process where particles from the bulk move and adhere on the surface but inorganic fouling in some cases has been shown to have different mechanisms to biofouling.¹⁹

CaCO₃ scale formation is affected by the nature of a surface, different materials have been used to modify surfaces of different substrates by using coatings.²¹⁻²⁵ Neville and Morizot,²⁶ investigated scale formation on a stainless steel surface coated with polycarboxylic acid and showed that the coating was very effective in reducing scale formation. Jahouari *et al.*,¹¹ used an electrochemical technique to deposit calcium carbonate scale on different samples of stainless steel, bronze, and gold. The study showed that the nature and state of the substrates influence the kinetics of deposition and hence the crystal morphology. Advances in biofouling studies appear to have made obvious contributions to the understanding of the influence of surface properties on this kind of fouling. In mineral scaling the situation is different and there are still some substantial gaps in our understanding of what surface properties really influence scaling.

A commonly used method to induce crystallization in supersaturated solutions is known as seeding. It primarily occurs in bulk precipitation where there has been an addition of tiny particles that favor crystal nucleation. Secondary nucleation is a process that takes place as a result of the presence of pre-existing crystals of the material being crystallized, implying a prior presence of the new phase being formed.²⁰ The presence of seed particles in the bulk can enhance scale precipitation or inhibit the growth of calcite.^{27,28} Furthermore, seed crystals can result in lower interfacial tension to favour nucleation, thereby acting as a template for nuclei formation.²⁹ There are different kinetic study approaches in seeded media, most of them were performed in bulk.³⁰⁻³³ However, it is not only in the bulk solution that seeding can be undertaken but also on the surface in a dynamic process. Graham *et al.*,^{34,35} utilised the dynamic tube blocking (DTB) methodology for the deposition of scale with low sulphate and carbonate brines, in their work nucleation was indicated by measurement of differential pressure up to 0.5 and 1 psi to produce the desired surface nucleation. They referred to this surface as pre-scaling and can be an important parameter in the evaluation of scaling kinetic on nucleated and non-nucleated surfaces. The effect of pre-existing crystals on the mechanism of surface scaling is a vital part of this study, pre-scaling a surface with deposited crystals from the same composition is implemented to better mimic real field scenarios where it is likely that some pre-existing scale is present on components' surfaces. By pre-scaling the surface, the important questions were; how do pre-existing scale crystals influence surface scale kinetics? Will surface scaling time increase or decrease? And how will it enhance the scale growth rate?

This work evaluates a range of surface conditions with the aim to better understand surface characteristics that can act as driving forces in controlling or promoting surface scale formation. The design of scaling tests that reduce variations in experimental conditions and suitably simulate actual field conditions is key to understanding how surface features affect mineral scale formation and is essential for the improvement of current thermodynamic prediction models to incorporate kinetic considerations. The DTB technique has been used to examine and investigate mineral scale formation within a long micro-bore tube or coil under flowing conditions with or without scale inhibitors, it has been used extensively to determine the minimum inhibitor concentration (MIC).^{34,36,37} Scale formation is evaluated by measuring the differential pressure between the inlet and outlet of a tube (in the magnitude of millimeters in diameter) with time when a supersaturated solution flows through and there is a build-up of scale on the tube surface.³⁸

A lot of the studies using the DTB technique for scale formation relies on the change in differential pressure across a long coil, however, a quick change in differential pressure in a long coil/tube could be misleading regarding kinetic assessment as the scales formed are scattered along the long capillary. Besides, observation of scale crystals in terms of shape, surface coverage, growth, and morphology is much difficult in long coils. Another drawback is that the saturation ratio drops with time along the coil,

length in a long capillary, making it challenging when experimental conditions are required to remain constant. A novel capillary flow rig was developed that eliminates the shortfalls of the DTB, replicate field conditions and provide an improved understanding of surface scaling kinetics. The capillary flow rig allows the reliable determination of the actual deposit amount, ensures that there are no pre-precipitated crystals in the bulk solution, and keeps SR constant in the cell. The build-up of scale in the capillary cell monitored from the differential pressure change as a function of time provides a mechanistic understanding of scale nucleation and growth kinetics on surfaces.

EXPERIMENTAL PROCEDURE

In this study, the main test methods and materials used for investigating precipitation of CaCO_3 scale, surface properties, and their influence on scaling in the capillary flow rig are described below:

Capillary Flow Rig

The capillary rig is designed to simulate aspects of flow in a typical industrial system, this technique by the nature of its setup allows scale deposits on the wall of the flow cell offering complementary information on scaling kinetics. The rig is equipped with a pressure transducer which measures the pressure change across the capillary cell. During a typical experiment, the brines are kept in separate reservoirs supplied by two reciprocating pumps driving the cation and anion species at the desired flow rate in separate steel coils immersed in a heated water bath. The water bath raises the solution temperature to the required experimental temperature. After leaving the water bath, the heated brines enter the mixing section “E” as shown in **Figure 1**, and combine to flow through the capillary cell “F” where scale deposition occurs on the capillary surface. The pressure is maintained by a pressure gauge regulator that leads to the effluent. Pressure relief valves are located before and after the compartment that holds the cell sample for safety reasons. The increase in pressure during experiments is measured and logged continuously throughout. When the stainless steel capillary cell is blocked at the system threshold of 2.5 psi, the automatic pumps shut-down, while the differential pressure and solution temperature as a function of time are automatically recorded by the LabVIEW data acquisition system on a computer.

A schematic illustration of the capillary cell flow rig assembly is presented in **Figure 1**. The rig is designed for both laminar and turbulent flow regimes. At the end of each experiment, the scaled capillary cell & flat coupon downstream of the rig are retrieved and dried in the oven for 30-45 minutes. The rig is cleaned with a cleaning solution of sodium hydroxide (NaOH) and ethylene-diamine-tetra-acetic acid (EDTA) in a 50:50 ratio at a pH of 10 for 30-40 minutes depending on the severity of scaling followed by distilled water for two hours. The location of the capillary cell (sample) can be adjusted to vary the time it takes the mixed solution to arrive at the working section. This can either result in a solution having pre-formed colloidal particles in the bulk solution as it flows through the cell and hence “surface deposition” (if the sample is far away from the mixing section), or can allow precipitation on the surface without any pre-precipitated crystals in the bulk solution when the sample is close to the mixing zone as shown in **Figure 2**.

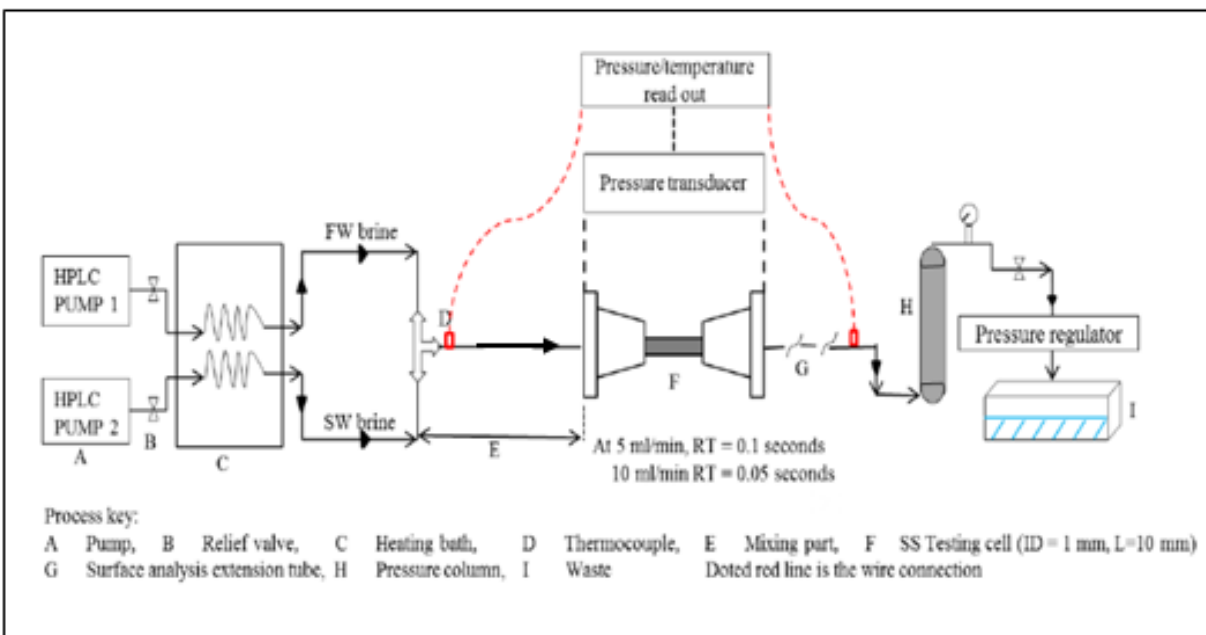


Figure 1: Schematic of capillary cell flow rig incorporating surface coupon.

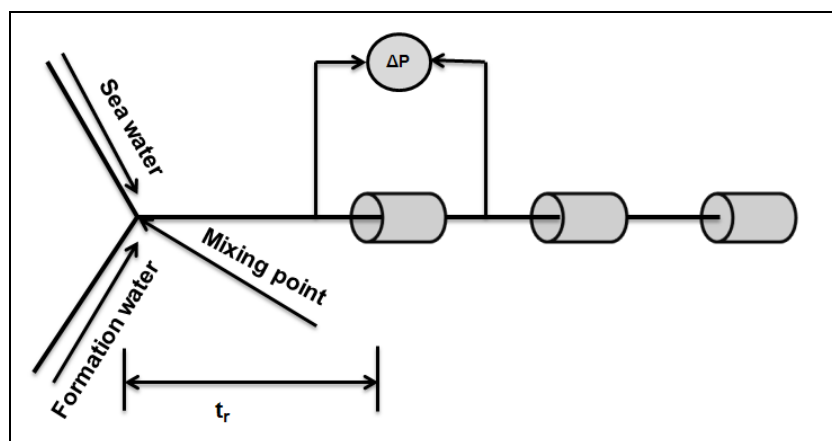


Figure 2: Schematic of capillary rig mixing section with varying locations of the sample cell.

This study focuses on “surface precipitation”. To enable the study of CaCO_3 scale formation using the capillary flow rig, it is important to ensure that when the mixed solution is flowing through the capillary cell, there is no precipitation or crystals already formed in the bulk solution i.e. $t_{ind} > t_r$. Where t_{ind} is induction time and t_r is residence time. In this case, the scaling mechanism is likely to be a crystallization process on the capillary cell surface rather than deposition and adhesion of already precipitated crystals from the bulk solution. When scale formation occurs, there is the possibility of CaCO_3 scaling in the bulk solution and at the pipe wall surface; scaling is favoured on pipe wall surfaces depending on surface energy and wettability.⁴¹

Hydrodynamic Parameters

The flow rig conditions in the study of surface scale kinetics aim to mimic part of an oil field flow mixing condition. It is important to accurately understand the nature of flow condition either laminar or turbulent flow. Assessment of the surface scale precipitation is essential to determine the time and at what rate scale forms. In the design of the capillary rig, the pipe flow parameters such as entrance length, Reynolds number, and residence times of the solution in the rig were considered. An increase in flow

velocity should result in an increase in the differential pressure according to the Hagen Poiseuille (HP) flow equation expressed in **Equation 1**.

$$Q = \frac{\pi D^4 \Delta P}{128 \mu L} \quad (1)$$

Where Q is flow velocity (m^3/s), D is the internal diameter (m), ΔP is pressure drop (psi), μ is viscosity (NS/m^2) and L is the capillary length (m).

One parameter that requires consideration for the HP assumption is the determination of the entrance length. To ensure a fully developed flow, the length of the capillary after mixing section “**E**” must be greater than the entrance length and the internal diameter before the capillary is the same as the sample cell. The entrance length (L_e) for different flow rates from 5–30ml/min at 70°C, for fluid viscosity of $4.06 \times 10^{-4} \text{ mPa}\cdot\text{s}$ was calculated to be between 15.66 – 93.96 mm using the relationship between Reynold’s number (R_e) and internal diameter (D). The Reynolds number (R_e) at different flow rates and the temperature was calculated and this allows the determination of the flow regime of the fluids entering the capillary cell from the mixing section, and the residence times (sec) of the mixed brines inside the capillary cell. **Table 1** presents a summary of the hydrodynamic parameters for the flow rig, the flow regime in all test conditions in this study is laminar flow.

Table 1
Hydrodynamic Parameters of the Capillary Flow Rig

Flow rate		Reynolds number	Residence time (sec)	Capillary cell shear stress N/m^2	Regime
ml/min	m^3/s	70°C			
10	1.67×10^{-7}	523	0.05	1.4	Laminar
15	2.5×10^{-7}	784	0.031	2.1	
20	3.33×10^{-7}	1045	0.024	2.8	
25	4.17×10^{-7}	1307	0.019	3.4	
30	5×10^{-7}	1560	0.016	4.1	

Metal Substrate

The metal substrates (capillary cell and flat coupon) used for surface scaling studies are made from stainless steel UNS S31603. The composition is given in **Table 2**. Due to the confined nature of the capillary cell, it is challenging to investigate the scale deposit using ex-situ surface analytical techniques. A suitable flat coupon that eliminates the need for destruction of the capillary cell is designed and incorporated into the rig to enable the characterization of the scale deposited. Its dimensions are set to be able to get into the ¼ inch spool extension casing, the coupon is 25 mm length, 1 mm thick, and 4.4 mm in diameter. **Figure 3 (a)** and **(b)** show the schematic diagram of the capillary cell and coupon samples with dimensions respectively, the capillary cell is located in position “**F**” while the surface analysis coupon is in position “**G**” in **Figure 1**.