

Surface Precipitation and Growth Kinetics of Calcium Carbonate (CaCO₃) Scale Using a Novel Capillary Flow Rig

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ABSTRACT

The oil and gas industry is plagued with various flow assurance challenges including the formation of inorganic scale on component surfaces. Much research into scaling and inhibition is now being directed towards surface deposition as fouling on surfaces often causes operational problems and the rates cannot be predicted by consideration of bulk precipitation processes. However, achieving a mechanistic understanding of surface kinetics requires laboratory techniques that offer the ability to control thermodynamic parameters. A novel once-through capillary flow rig design based on the conventional tube blocking methodology was used to evaluate the surface formation of CaCO₃ under dynamic flowing conditions; an important attribute of this set-up is that saturation ratio (SR) remains constant in the capillary cell due to the short residence time of the flowing brine, and conditions can be such that there is no bulk (pre-precipitated) crystals in the solution when it flows through the cell. This allows the decoupling of bulk and surface scaling, enabling the reliable assessment of the kinetics of scale deposits present in the capillaries and provides an improved mechanistic understanding of mineral scaling on surfaces. CaCO₃ surface scaling kinetics was investigated by evaluating the induction times and gravimetric measurements of mass gain in the capillary cell.

Scale precipitation tests were carried out on as-received (plain) and functionalized stainless steel substrates at three saturation ratios and flow rates ranging from 10-30 ml/min. Analyses of the induction times and deposition of scale show the significant influence of flow velocity and surface wettability on heterogeneous crystallization processes, and that scale growth on surfaces is not necessarily due to the deposition of bulk precipitated crystals.

Keywords: CaCO₃, surface deposition, bulk precipitation, kinetics, capillary cell, dynamic tube, wettability.

INTRODUCTION

The formation of scale and oil & gas go hand in hand, it is a natural consequence of handling water associated with crude oil production.¹ Scales can build-up anywhere from clogging wellbore area to surface facilities such as production tubings, valves (subsurface control valves, SSCV), fouling pumps (electrical submersible pumps, EPSs) amongst many others; thereby restricting fluid flow and posing significant operational costs.² Dealing with damage as a result of inorganic scale formation is one of the major oil and gas industry challenges costing hundreds of millions of dollars per year in lost production in emergency shutdown, equipment failures or maintenance costs, and reduction in production.^{1, 3} The inability to properly predict the severity ensures the industry spends millions of dollars in preventing and removing scale formation.^{4, 5} There are various studies on the precipitation and deposition of inorganic scales, particularly calcium carbonate (CaCO_3). Most of these past studies on scale deposition and predictive models are mainly focused on the thermodynamic parameters in the bulk with little attention paid to scaling on surfaces, hence there is little reconciliation between bulk precipitation and surface deposition.

Scaling process can be broadly separated into two: bulk precipitation and surface deposition. Scale formation in the bulk solution and surface deposition have been described as interlinked processes with potentially very different kinetics.⁶ However, from a fundamental perspective, there is not much understood on the mechanism of surface deposition. Engineering the physical and/or chemical nature of a substrate potentially can be a good method in the reduction of surface scale formation. The importance of some parameters in reducing scaling has been studied such as induction time,⁷⁻⁹ saturation ratio,¹⁰ surface roughness,^{11, 12} surface wettability,¹²⁻¹⁵ crystallization kinetics, and surface deposition,^{2, 3} and scale formation influenced by flow regime.^{16, 17} Scale formation on a surface is driven by heterogeneous nucleation requiring a lower energy barrier compared to bulk homogenous precipitation, hence scale growth on component surfaces is a bigger challenge.¹⁸ Advancements in the biofouling industry in the development of hydrophobic surfaces have shown significant improvement towards preventing adhesion or attachment of deposits on surfaces and appear to have made obvious the influence of surface properties for this kind of fouling. In mineral scaling the situation is different as there are still some substantial gaps in our understanding of what surface properties influence scaling. Research studies in inorganic fouling have applied modified surfaces due to the perceived similarities with the biofouling industry,¹² where particles migrate from the bulk solution to the surface but inorganic fouling has been shown to have different mechanisms to biofouling.^{19, 20} Although scale formation is a crystallization process, it is not immediately obvious if hydrophobicity is a key surface parameter in controlling scaling.

CaCO_3 scale precipitation is dependent on the nature of a surface. The effects of different substrates on the formation of scale have been investigated by many researchers and others have attempted to modify surfaces of different substrates by using coatings. Neville and Morizot,²¹ investigated scale formation on stainless steel surface coated with polycarboxylic acid and showed that the coating was very effective in reducing scaling. Jahouari *et al.*,⁷ used an electrochemical technique to deposit calcium carbonate scale on different samples of stainless steel, bronze and gold showed that the nature and state of the substrate influence the kinetics of deposition and hence the crystal morphology. Charpentier *et al.*,²² studied chemically and morphologically modified coatings in the prevention of mineral scale formation under both laminar and turbulent dynamic conditions using a rotating cylinder electrode in a complex scaling condition, the authors observed that coatings with anti-fouling properties show the most promise with regard to reduction in mass gain. Müller-Steinhagen and Zhao,²³ reported

that CaSO_4 scale on an implanted stainless steel surface was comparably looser and porous making it easy to break up and wash away in comparison to the same scale formed on bare stainless steel. Other researchers have used modified surfaces in the study of scaling.^{14, 24-26}

The Dynamic Tube Blocking (DTB) methodology has been used in the ranking of scale inhibitor efficiency under various environmental conditions by investigating the ability of such inhibitors to prevent the growth of scale and its adherence to the wall of the tubing coil.^{27, 28} The rig operates under laminar flow condition. It examines growth kinetics of scale and inhibition mechanisms within a long micro-bore tube or a coil under dynamic flow conditions with the use of an applied back pressure, giving the DTB a unique advantage over conventional bulk jar tests which are static.²⁹ Scale formation is evaluated by measuring the differential pressure between the inlet and outlet of a tube (in the magnitude of millimetres in diameter) with time when a supersaturated solution flows through and there is a build-up of scale on the tube surface.¹ A lot of the studies using the DTB technique on scale formation rely 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 capillary length. Besides, surface observation of scale crystals in terms of shape, surface coverage, growth, and morphology is much difficult in 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 to eliminate the shortfalls of the DTB, replicate field conditions, and provide an optimum understanding of surface scaling kinetics. The capillary flow rig allows the accurate determination of scale 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. This paper assesses the effect of wettability and flow hydrodynamics on relative scaling tendencies of modified and plain (as-received) stainless steel surfaces.

EXPERIMENTAL PROCEDURE

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 set-up allows scale deposition 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 (formation and seawater) are kept in two separate reservoirs is supplied by 2 reciprocating pumps driving the cation and anion species at the desired flow rate in two separate steel coils immersed in a heated water bath which 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 flowing through the capillary cell “**F**” where scale deposition occurs on the capillary cell surface. 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 every test is measured and logged continuously throughout the experiment. When the stainless steel capillary cell is blocked or the device threshold of 2.5 psi is reached, 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 the computer.

A schematic representation of the capillary flow rig assembly is presented in **Figure 1**. The rig is designed for both laminar and turbulent flow regimes. After every experiment is completed, the scaled capillary cell & flat coupon downstream of it 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.

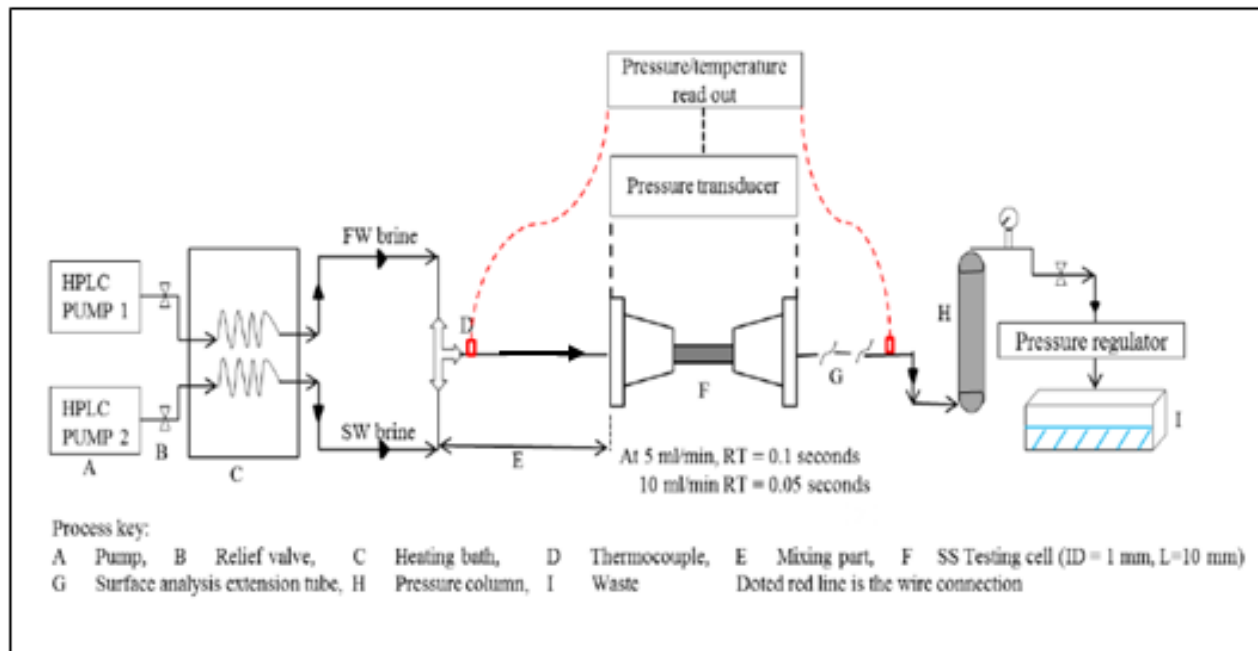


Figure 1: Schematic of capillary cell flow rig incorporating surface coupon.

The location of the capillary cell 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 “deposition” on the surface (if the sample is far away from the mixing section) or can allow precipitation on a surface without any pre-precipitated crystals in the bulk solution when the sample is close to the mixing zone as shown in **Figure 2**.

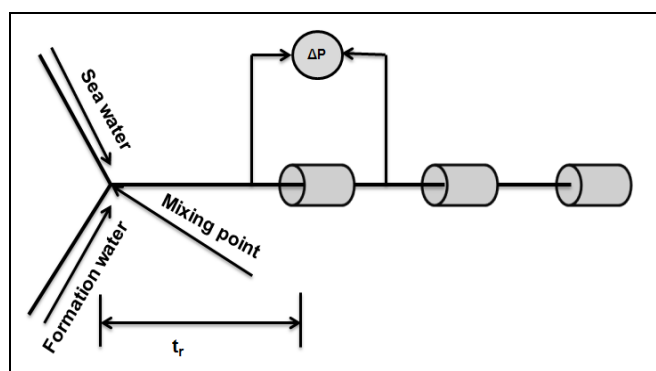


Figure 2: Schematic of capillary rig mixing section with varying locations of the sample cell.

The focus of this study is “surface precipitation”, to enable a surface 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 direct crystallization on the capillary surface rather than deposition and adhesion of already pre-precipitated crystals from the bulk solution.

Hydrodynamic Parameters

The flow rig conditions in the study of surface scale kinetics aim to mimic part of an oil field flow mixing scenario, it is important to accurately understand the nature of flow condition either laminar or turbulent. Assessment of the surface scale precipitation kinetics 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 in making the Hagen-Poiseuille 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) at different flow velocities from 10–30ml/min at 70°C, for fluid viscosity of $4.06 \times 10^{-4} \text{ mPa.s}$ was calculated to be between 15.66 – 93.96 mm using the relationship between Reynold’s number (R_e) and internal diameter (D). Reynolds number (R_e) at different flow rates was also calculated, this allows the determination of the flow regime of the fluids entering the capillary cell from the mixing section, the residence times (sec) of the mixed brine inside the capillary cell was also derived. A summary of the hydrodynamic parameters of the capillary flow rig is presented in **Table 1**, the flow regime in all test conditions for 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
12	2×10^{-7}	628	0.04	1.7	
14	2.33×10^{-7}	732	0.034	1.9	
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	