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Following the formation of $CaCO_3$ scale formation by *in-situ* WAXS

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The aim of this paper is to further the understanding of calcium carbonate scale formation by *in-situ* probing of crystal growth by synchrotron radiation Wide Angle X-Ray Scattering (WAXS). This novel technique enables *in-situ* study of mineral scale formation and inhibition and information on the nucleation and growth processes is accessible. This technique studies *bulk precipitation* and *surface deposition* in the same system and has great benefit to understand an industrial scaling system. It has been shown that WAXS has been successfully used for the study of calcareous formation and enables crystallization mechanisms to be investigated. This paper discusses how surface scale evolves – exploring the power of the synchrotron *in-situ* methodology.

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1. Introduction

Calcium carbonate scaling on metallic or insulating walls in contact with hard water may create technical problems in oil and gas production, water-piping systems, power generator and batch precipitation, including impedance of heat transfer, increase of energy consumption, under-deposit corrosion, pipe or valve blockage and, even more, unscheduled equipment shutdown 0 0. Calcium carbonate scale formation occurs according to the reaction given in Equation 1.

$$Ca^{2+} + CO_3^{\ 2-} \rightarrow CaCO_3 \qquad (1)$$

Calcium and carbonate ions form scale that has very little solubility and are likely to precipitate in water, even if only small amounts of dissolved calcium and carbonate ions are present. One of the driving forces for scale formation is supersaturation and the formula for supersaturation ratio is given in Equation 2.

$$S_a = (a_1 \times a_2) / K_{(P.T)} \qquad (2)$$

$$a = \gamma \times C$$

where S_α is the supersaturation ratio and α is the activity of the separate species. α_1 and α_2 are the activity of calcium ion and bicarbonate ion in the solution respectively. K is normally called the solubility product, which depends on the pressure P and the temperature T. C is concentration of the ions in the solution. γ is the ionic activity coefficient.

Three possibilities exist in terms of scale formation from the solution with thermodynamics. (1) S_α <1: the solution is undersaturated and scale formation is not thermodynamically feasible; (2) S_α =1: the solution is saturated. The scale formation and dissolution rate in the solution is the same and no scale is formed in the solution; (3) S_α >1: the solution is supersaturated and scale formation is thermodynamically possible.

The precipitation of calcium carbonate has been widely studied over the past few decades. Traditionally, studies of scale formation have concentrated on bulk scale formation using laboratory beaker tests 0; turbidity probes, pH measurement or bulk chemical analysis have been used to analyse kinetics of precipitation. The primary focus has been the assessment of the kinetics of homogenous and heterogeneous precipitation in the bulk solution 0. It has been demonstrated that there are often wide anomalies between actual deposition and rates estimated by predictive models based on scaling indices and thermodynamics 0.

Much effort has been turned to the aspect of scaling on surfaces to attempt to overcome some of the shortfalls of beaker tests. Hasson *et al*. studied calcium carbonate scale formation in a pipe flow system 0. The thickness of scale deposited on a surface was measured and monitored by the differential pressure between the inlet and outlet of the pipe. Sullivan *et al.* studied scale formation by monitoring the change in heat transfer 0. The heat resistance of a scaled pipe is higher than when the same surface is clean. Abdel-All 0 studied the initial stages of calcium carbonate surface adhesion with the quartz crystal microbalance (QCMB). The change in oscillating frequency of the quartz crystal is directly proportional to the change of mass of deposit on the surface. Teng 0 studied the kinetics of calcite growth using atomic force microscopy (AFM) and an attached fluid cell. The relationship between the microscopic surface processes of calcite and supersaturation of scaling solutions was observed.

Another means of achieving $CaCO_3$ surface scaling alone is to apply cathodic protection (CP) where the surface conditions, through production of hydroxyl ions, trigger a sequence of reactions, which result in the deposition of ‘calcareous deposits’ 0. This method provides a way to accelerate scale formation and can give information on the mechanisms of scale formation. However, scale generated by electrodeposition forms by a different set of processes and the interpreting mechanistic information should be treated with caution.

Traditional studies on scale formation have been focused on the precipitation formed in the bulk solution or deposition formed on the metal surface. However, few studies have been concerned with the difference between bulk precipitation and surface deposition. In this paper, synchrotron radiation Wide Angle X-Ray Scattering (WAXS) was used to further the understanding of $CaCO_3$ scale formation in the laboratory by *in-situ* probing of crystal growth at micron level, including induction time, nucleation and growth on the substrate and the surface of scale crystals. The crystallization of mineral scale has been followed *in-situ* and information on the nucleation and growth processes of both bulk precipitation and surface deposition are accessible simultaneously in the same scaling system. The nucleation and growth of various calcareous polymorphs and their individual crystal planes can be followed in real time.

2. Experiment procedure

Dynamic flow cell tests in conjunction with WAXS measurement

A novel silicon reaction cell was specifically designed for the *in-situ* observation of scaling processes under non-ambient conditions. This cell, shown schematically in Fig. 1, allows *in-situ* collection of XRD data with the ability to mix brines and form scale under non-ambient (up to 200 °C and 34 MPa), flowing conditions.

The experiments were carried out at 80 °C. Calcium carbonate was precipitated spontaneously by mixing brine 1 and brine 2 in the *in-situ* cell for WAXS measurements, as shown in Fig. 1. The composition of brine 1 and brine 2 are given in Table 1. The pH of brine 2 was buffered to 6.8 by acetic acid at the start of experiment. A line pressure of 3.4 MPa and a flow rate of 10 ml/min (5 ml/min brine 1 and 5 ml/min brine 2) were used. An oven was set up between the pumps and the mixing chamber to heat the brine 1 and brine 2 and the temperature was controlled at 80 °C in the mixing chamber. The supersaturation ratio of the mixture of brine 1 and brine 2 is 78 calculated with ScaleSoftPitzer^{TM} software 0, a typical severe scaling solution in the oil and gas industry. Synchrotron X-ray data were collected at 2 minutes intervals.

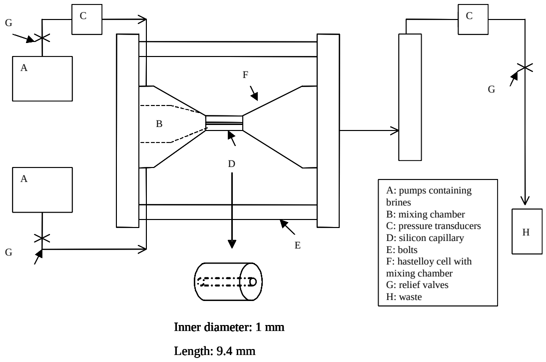

Fig. 1. In-situ cell for WAXS measurements at high temperature and pressure.

Table 1. Composition of brine 1 and brine 2.

	Brine 1 (mg/l)	Brine 2 (mg/l)
NaCl	15367	15367
$CaCl_2.6H_2O$	15743	-
$NaHCO_3$	-	6046

Calcium carbonate crystals deposit on the surface of silicon capillary cell (as was shown in Figure 1) and precipitate in the bulk solution. The silicon capillary cell is a single crystal silicon cell with 9.4 mm length and 1 mm inner diameter tube. Scaling system is cleaned by pumping 10% acetic acid, 5% Decon 90 (detergent) and distilled water respectively to remove the scale deposition.

The X17B1 beamline with a X-ray energy of 67 keV, at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory in USA, was used for the experiments. In contrast to conventional XRD, the synchrotron XRD with high energy takes about 10 second to analyse a calcium carbonate sample and as such real time data can be collected *in situ*. A Siemens CCD detector allows effective two-dimensional data collection 0. The raw data, from each frame in each WAXS run, are integrated and converted to appropriate file formats by an in-house program at X17B1 in Brookhaven National laboratory. The combination of the FullProf suite 0 and Chekcell software 0 covers all the analysis required. The FullProf suite is used for the initial data analysis, peak fitting, indexing etc., as well as quantitative analysis in the form of peak integrations. The LMGR suite is used for unit cell refinement.

3. Results and discussion

Hennessy and co-workers 0 previously demonstrated the potential of *in-situ* synchrotron XRD for the study of crystallization mechanisms relevant to oilfield scaling in their work on $BaSO_4$. A key element in this work is a pressure flow cell, which is integrated into the beamline. The cell enables high pressure, temperature and various flow regimes to be set to more closely approximate field conditions in the oil field. Both the evolution of surface deposit and bulk precipitate can be observed. Only preliminary studies were carried out on $BaSO_4$ and in this paper the comprehensive results on $CaCO_3$ are reported.

The growth of calcium carbonate crystals at 80 ^{o}C is shown in Fig. 2. The initial phase of crystallization is characterized by instability up to 6 minutes with individual planes from various polymorphs emerging and subsequently disappearing under the hydrodynamic conditions. A peak being present then disappearing in the next frame is attributed to crystals forming as bulk precipitate. The majority of these planes can be assigned to the aragonite polymorphs. For example, the peak appearing after 4 minutes at 2 theta 5.697 ^{o} is the aragonite (110) plane.

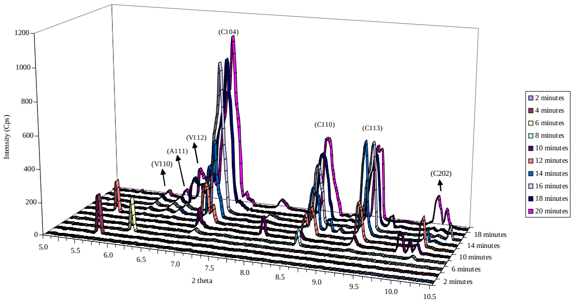

Fig. 2. The growth of $CaCO_3$ crystals at 80 ^{o}C detected by synchrotron radiation (WAXS).

After the initial unstable phase where aragonite is the principal crystal morphology, the crystals then attach to the surface and grow on the surface. Stable (104) and (110) planes of calcite are present after 8 minutes (i.e. a peak is present then the intensity and integrated area of this peak increase in subsequent frames due to growth of a surface deposit). The next plane to emerge is the (113) plane of calcite after 10 minutes. Another three crystal planes are present and grow on the surface after 14 minutes, which represent the (110) and (112) planes of vaterite and the (111) plane of aragonite.

As the experiment progresses, the growth of calcite (104), (110) and (113) planes is apparent. In addition, various planes from the vaterite and aragonite polymorphs start appearing again, as in the initial stage of the experiment from bulk precipitate. However, after 14 minutes the first stable vaterite (110) and (112) planes and aragonite (111) planes emerge. This time they are derived from crystals adhering to the surface.

One of the achievements in this study has been to demonstrate that the nucleation and growth of various calcium carbonate polymorphs and their individual crystal planes can be observed. The growth process of calcium carbonate scale can be divided into two phases: (1) the initial phase of unstable crystallization and (2) the growth of crystals on the surface. The initial phase of unstable crystallization is characterized by instability and individual planes from various polymorphs emerge and subsequently disappear under the hydrodynamic conditions. The majority of these planes can be assigned to the aragonite polymorphs. The crystals formed in this stage are mainly from precipitate formed in bulk solution. After the initial unstable phase, the crystals attach to the surface and then grow on the surface and at this point the intensity and the integration area of the peaks increase as time elapses, which is the main contribution to scale problems in industry.

In this study, it is clear that the process of bulk precipitation and surface deposition are two different processes. It gives the explanation that there are often wide anomalies between actual deposition and rates estimated by predictive models based on scaling indices and thermodynamics by beaker test, which focus on the study of bulk precipitation 0. The scale crystals form in the bulk precipitation are unstable and do not contribute to the tube blockage. However, surface deposit crystals are the main contribution to tube blockage. Sometimes, using the results from bulk study cannot reflect the surface deposition formed on the surface which causes the main contribution to tube blockage. It is shown that both of the bulk precipitation and surface deposition processes should be studied in order to fully understand the mechanisms of scale formation in industry.

The integrated intensity of X-ray diffraction is in proportion to the crystal volume 0 and the growth rate can be measured by integrated intensity analysis. The integrated intensity peaks of calcite crystals are shown in Fig. 3, which is shown the growth processes of scale formation and can be divided into three stages: (1) Induction time. Before 6 minutes, the integrated intensities for calcite crystal planes is zero, which means that there are no stable planes observed during this period. The induction time for surface deposition at 80°C in the absence of inhibitor is 6 minutes; (2) Initial stage of nucleation and growth on the surface of substrate. After 8 minutes, the integrated intensity is above zero and increases slowly as time elapses until 12 minutes. It represents the first layer of nucleation and growth of scale crystal on the surface of silicon; (3) Nucleation and growth on the pre-scale surface. After 12 minutes, the integrated intensity increases fast as time elapses. This represents the nucleation and growth of scale crystals on the pre-scaled surface.

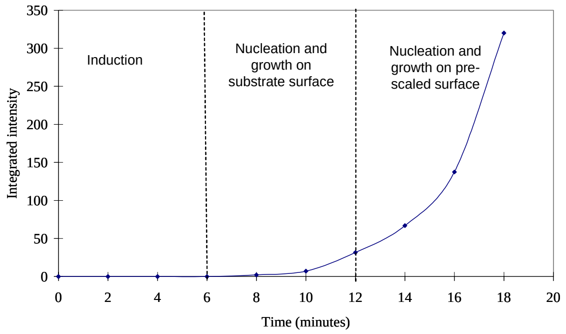

Fig. 3. Evolution of X-ray diffraction integrated intensity peaks of calcite crystals at 80 °C.

The crystal structure of a material is often discussed in terms of its unit cell. The unit cell is given by its lattice parameters, the length of the cell edges and the angles between them, while the positions of the atoms inside the unit cell are described by the set of atomic positions (a, b and c) measured from a lattice point 0. The lattice parameters (a, b and c), calculated by Chekcell software 0, for the hexagonal calcite unit cell at 80 °C are 4.9978 Å, 4.9978 Å and 17.0119 Å respectively. These parameters provide information of crystal structure of calcite crystals in the absence of scale inhibitor. This can be explored to study the scale formation in the presence of inhibitors and help understand the effect of scale inhibitors on the crystal structure of calcium carbonate crystals.

In summary, this study has provided an insight into the mechanism of calcium carbonate scale formation. In particular, it achieved the *in-situ* observation of growth of each plane of scale crystals, invaluable for the understanding of the mechanisms of growth and inhibition at the micro level, including induction, nucleation, growth, morphology and lattice parameter of $CaCO_3$ crystals. It is a promising technique to understand the mechanisms of scale inhibition in the presence of inhibitors.

4. Conclusions

- ❖ WAXS has been successfully used for the study of calcareous formation and enables crystallization mechanisms at engineered surfaces, under realistic conditions, to be investigated.
- ❖ Two stages of scale formation have been identified: *unstable* and *stable* stages. The initial $CaCO_3$ crystallization phase is characterized by individual unstable planes. They arise from vaterite and aragonite polymorphs emerging and subsequently disappearing under the hydrodynamic conditions. After the initial unstable phase, various calcium carbonate crystal planes attach to the surface of substrate and then growth.
- ❖ *In-situ* synchrotron XRD can be used to study the scale formation at micron level, including induction, nucleation and growth process of each face of scale crystals. In addition, it provides the lattice parameter of scale crystals.

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