113 Determining calcium carbonate scale kinetics by online technique

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ABSTRACT

The deposition of calcium carbonate on the surface is well known problem. The deposition of calcium carbonate which is often termed as scale costs billions of dollars to the worldwide economy. The present paper is the extended work on the understanding of calcium carbonate crystal formation and deposition. It shows the application of online technique to determine the rate of calcium carbonate scale formation. The online technique is based on the Focused beam reflectance method. The effect of calcium ion concentration and temperature on the scale rate is determined. The online result was compared with the offline scale measurement technique.

The present technique not only determines scale rate but has proven to be sensitive technique to monitor the initial stage of the scale formation process.

Keywords: scaling rate, online, calcium carbonate, FBRM.

1 INTRODUCTION

Scale is a major concern in different areas of industrial processes and domestic equipments. It can be referred to as undesirable hard, adherent deposit that usually precipitates from solution and grow on surfaces. Calcium carbonate is the most common scale component found in industry and nature.

Excessive scale create problems like lowering of heat transfer coefficient in heat exchangers by coating the heat transfer surfaces, In the United Kingdom alone the formation of scales in industrial process plant where water is heated or used as a coolant is estimated to cost 0.5 billion dollar per year (Qui Tai-qui 1999) Hence there is a considerable interest to find methods that effectively prevent the formation of this deposit. The knowledge of scale kinetics on the scaling conditions is thus important as it controls the efficiency of the process equipments.

Few studies has been performed pertaining to scale deposition on surface such as (Hasson et al 1968) and (Zhang et al 2001), studied calcium carbonate scale formation in a pipe flow system in oil and gas and desalination industry. (Sullivan et al 1996) studied scale formation by monitoring the heat transfer change. These methods were developed primarily to assess efficiency of scale inhibitors and give only a relative estimate of the thickness of scale. They are usually not sensitive enough to study the primary layer of scale.

Other online techniques those have been reported to measure the extent of scale deposition e.g RDE technique, image analysis. In RDE technique the extent of scale deposition at an electrode surface can be followed by calculating the change of surface area of the electrode. The validation of the technique has been demonstrated in accompanying work, by comparing the coverage determined by image analysis (Morizot and Hodgkiess1999). The RDE can only measure the deposition of crystals but to obtain information on the precipitation offline sample analysis has to perform.

The measurement instrument used in the present work is able to provide online data for precipitation and scaling simultaneously in real time. Unlike previous methods which measure the mass of crystals deposited the present technique monitors the scale by measuring the number of chord sizes of the crystals, which makes its sensitive to measurement of initial stages of scaling process. Effect of calcium ion concentration and temperature on scale rate measurement is studied. The online results obtained were compared by performing offline measurements.

2 EXPERIMENT SETUP AND PROCEDURE

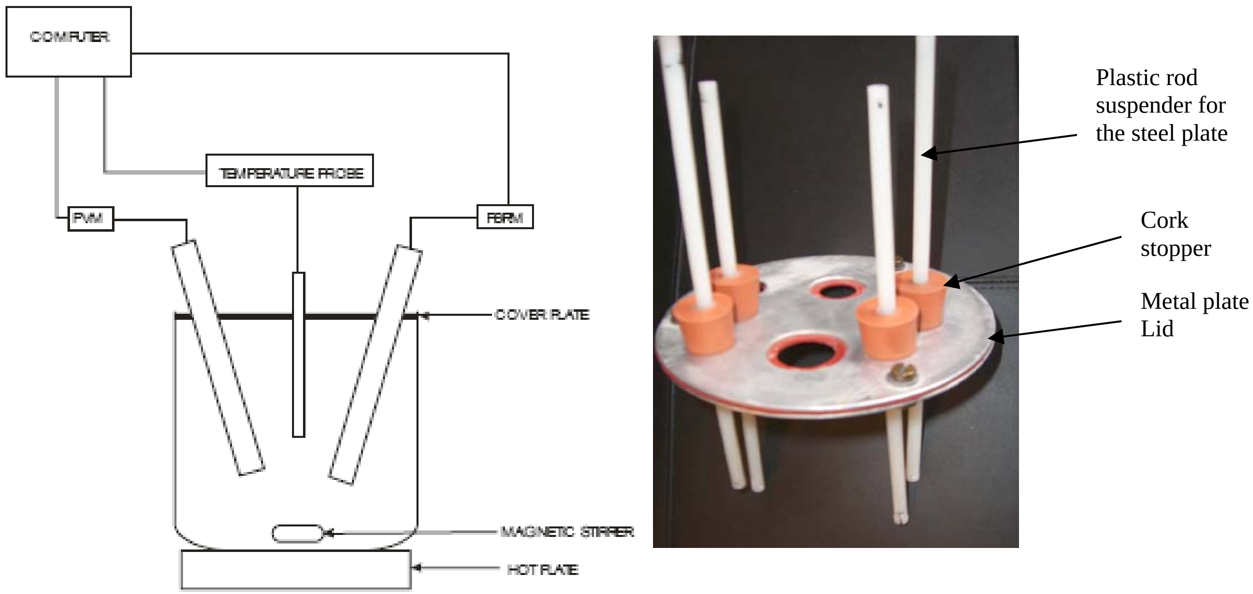

Figure 2a, b: Experimental setup for online and offline measurement

The experimental procedure is as follows: Firstly, solutions required for precipitation of calcium carbonate were prepared. The sources of calcium ions and carbonate ions were *(*$CaCl_2 \cdot 2H_2O$*)* and *(*$NaHCO_3$*)*. The chemicals were provided by Analar and the purity was>99%. One Litre solution of each chemical was prepared using distilled water. The two solutions poured into the 3L beaker placed on a hot plate as shown in Fig. 1 and set at the required solution temperature, at this moment the FBRM and temperature measurements were started simultaneously. The numbers of particles within the solution were recorded after every two seconds by FBRM (Mettler Toledo). Mixing was brought about by a magnetic stirrer at a speed sufficient to give good mixing in order to keep all the crystals in suspension without settling. The experiments were conducted at various calcium ion concentrations from 0.01 - 0.05 mol/L at 25˚C and 60˚C temperature.

For offline scale measurement four steel plates were used, the dimension of the plate is (6cm x 2cm x 0.1cm). These rectangular plates were weighed using sartorius weigh balance up to four decimal point accuracy before immersing in the scale forming solution. Each steel plate was suspended with rods at fixed depth of 10 cm from the cover plate and removed after 30, 60, 120 and 180 minutes from the start of the measurement. The removed plates were air dried and reweighed. The difference in weights of plate thus gives mass of caco3 deposited. This technique is used here to compare with online scale measurements.

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3. DETERMINING SCALING RATE FROM FBRM DATA

The mixing of two solutions as described in experimental procedure resulted in spontaneous precipitation of calcium carbonate. The calcium carbonate formed readily deposits on the sapphire window of the FBRM probe. The continuous deposition of calcium carbonate crystals lead to coating of the probe window resulting in measurement of high number of chord counts. In order to measure actual number of crystals in the solution the FBRM probe was removed from the solution and the probe tip was cleaned. The number of counts measured by FBRM to zero indicates probe tip to be thoroughly cleaned.

The deposition of calcium carbonate crystals on the probe tip of FBRM has significance in determining the kinetics of deposition on the sapphire surface. This gives online information of the rate of deposition of calcium carbonate.

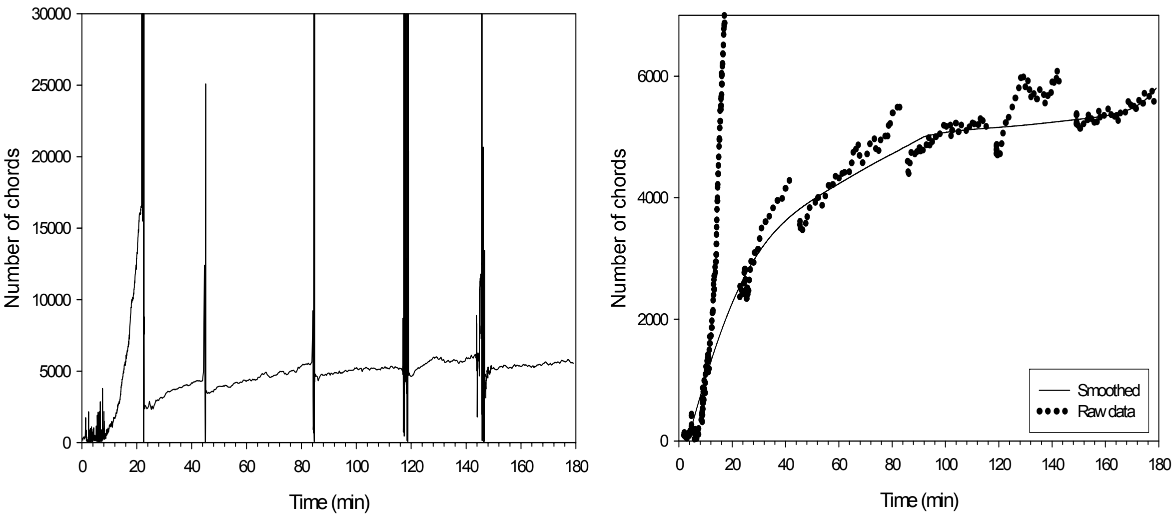

Figure 3a,b: Typical raw and smoothed data obtain for calcium carbonate precipitation experiment.

Figure 3a shows the typical raw data obtain from FBRM showing number of chords measured vs time. In this the cleaning time as indicated by the peaks is at 20 minute interval. The 20 minute interval was kept so that sufficient deposition of calcium carbonate is formed on the sapphire window of FBRM probe for low calcium ion solutions. For high calcium ion solution in some cases the cleaning time is as short as up to 4 minutes.

As calcium carbonate deposits on the surface of FBRM probe there is increase in number of chord counts. It can be seen in Figure 3 for initial 20 minutes of experiment the number of counts increase to 15000. After following the cleaning procedure as explained earlier, the number of counts measured is approximately 2500. This indicates that the rise in number is the result of deposition of crystals on the surface. Figure 3b shows the raw data without peaks. The discontinuous curve shows the effect of cleaning on the number of chord counts of calcium carbonate crystals measured by FBRM.

In Figure 3b it can be seen that as the time progress the difference in the number of chord counts before and after cleaning is reduced. If the increase in chord counts due to deposition of calcium carbonate is neglected and only number of counts in the solution is considered, above data can be traced as a continuous curve as shown in figure 3b.

Figure 3b thus shows chord counts in absence of deposition as continuous curve and the presence of deposition as the discontinuous curve. The calcium carbonate deposit can be quantified by simple relationship as shown below.

Hence the number of crystals deposit on the surface could be measured by following equation.

$$\text{Total number of particles deposit} = \Delta N = \frac{\sum_{t_{sc}}^{t_{ec}} m_0 t - \sum_{t_{sc}}^{t_{ec}} m_0^{'} t}{\Delta t} \qquad (1)$$

The rate of deposition on the surface based on number chords measured is calculated as follows.

$$\text{Scale rate} = \frac{\Delta N}{T} \qquad (2)$$

Where m_0 is number of chord before cleaning, $m_0^{'}$ number of chords after cleaning t_{ec} is the time before cleaning , t_{sc} is the time after cleaning, Δt difference in the time between m_0 and $m_0^{'}$ and T is total time of scaling period.

4. RESULTS

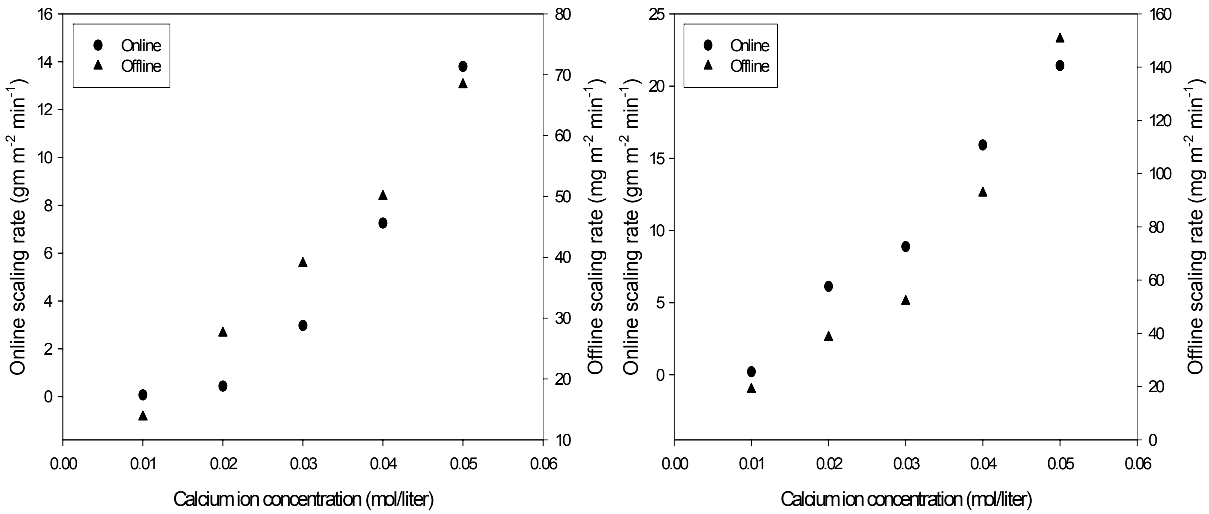

Figure 4a-b: Online and Offline measurement of maximum scale rate with relative supersaturation at 25^{o}C and 60^{o}C temperature.

Figure 4a-b shows the plot of scale rate vs supersaturation at 25 and 60^{o}C for online and offline measurement. The scale rate values shown here are obtained for first 30 minutes of the process.

An attempt has been made to obtain the scale rate values for online measurement in terms of mass rather number. The estimated mass deposition from the number of crystals is calculated as shown below.

$$m_c = V_c \cdot \rho_c \qquad (3)$$

$$M_{est} = \Delta N \cdot m_c \qquad (4)$$

$$\text{Estimated scale rate (mass based)} = \frac{M_{est}}{T} \qquad (5)$$

Where, m_c is mass of a crystal, V_c is volume of a crystal, ρ_c is density of a crystal, M_{est} is total estimated mass of crystals.

At present precipitation condition calcite is the principle precipitate, calcite has the cubic shape hence the volume of the single crystal is calculated from the mean chord size measured by FBRM.

The estimated scale rate based on the mass for online measurement show increase in scale rate values with solution concentration and solution temperature. The scale rate values for offline measurement shows similar trend. Interestingly comparing the scaling rate values at 25 and 60^{o}C temperatures as against the effect of solution concentration, it is evident that solution concentration has higher influence on the scaling rates than solution temperature.

The estimated scale rate measured by online method is 3 orders of magnitude higher than the offline measurement. The area of measurement for online is 5 orders of magnitude lower than offline, in addition the surface of deposition of online measurement is sapphire while for offline method the scale deposition is measured on stainless steel plate.

The difference in estimated mass deposition could be attributed to the surface material (P.C. Rieke). However it is most likely that the orientation of crystals on the scanning surface may play major role in the estimated mass, since the FBRM measurement does not measure the number of crystal but the number of chords.

However the purpose of the present research was not to obtain the absolute measurement of mass deposition using online technique but to monitor the scale formation process.

The experimental results from online and offline measurements are in accordance with the observations reported in literature. The increase in scale with high concentrated scale formation solution was attributed to supersaturation of the scale forming solution by (Chen et al 2005; Zhang et al 2001). Amor et al 2004 reported that degree of supersaturation affects the deposition of calcium carbonate. The increase in scale at high temperature is in agreement with (Hasson 1968; Khan M. 1996). The effect of temperature may be explained by the degree of supersaturation. At high temperature the supersaturation of scale forming solution is high hence result in increase in scale.

5. CONCLUSION

The scaling rate measured by online technique based on FBRM principle shows that the scale rate of the calcium carbonate increase with increase in calcium ion solution concentration and solution temperature. The supersaturation of scale forming solution is attributed to the increase in scaling rate. The online result is in agreement with the offline scale rate measurements. The estimated mass based scale rate calculated from online measurement show similar trend as in offline scale rate values. Although the absolute values are order of magnitude higher than offline measurement which may be due to measuring of chord counts rather particle count.

Finally the online measurement is found to be sensitive technique useful in monitoring the initial stage of scale formation and hence increase the understanding of scaling mechanism.

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