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New insight into the relation between bulk precipitation and surface deposition of calcium carbonate mineral scale

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ABSTRACT

The formation of calcium carbonate mineral scale is a major issue in desalination. Understanding the precipitation and deposition of such scale is a necessity in order to prevent fouling of components and also under deposit corrosion. Research has mainly focused on either bulk scale precipitation or surface deposition. However, understanding both together is of great interest to predict and therefore prevent the formation of such inorganic deposits. This study presents an assessment of the kinetics of calcium carbonate formation in the bulk and on a stainless steel surface. The objective of the study is to improve the knowledge of the relationship between bulk precipitation and surface deposition. Both the processes (bulk precipitation and surface deposition) have been assessed together *in situ* and in real time. The procedure enabled the assessment of bulk precipitation by measuring the turbidity while the surface coverage of the surface scale was assessed by analysing images of the surface at different time intervals. Four brines were tested under three different temperatures to give a combination of 12 different supersaturation ratio values. From the results, the rate constants for both the processes and their relation have been assessed. It has been confirmed that both the processes are different and show different kinetics. The study therefore suggests that the relation between both processes has to be taken into account when developing a kinetic model or preventing the formation. However, the paper highlights the need for more investigation before the relationship between both the processes is fully understood.

Keywords: Scale; Crystallization; Calcium carbonate; Surface; Bulk

1. Introduction

The formation of inorganic scale within installations such as membranes or pipe surface is a real challenge for desalination or oil and gas industries. The scaling process can be divided into bulk precipitation and surface deposition which have been found to be different processes resulting in different rates of formation and in the case of calcium carbonate different polymorphs [1–3]. Both surface deposition and bulk precipitation have been widely studied separately; however, although recently a few authors have tried to link both, the relation between these has received little attention. In addition, literature shows that prediction of scaling is mainly based on thermodynamics and lack of knowledge regarding the kinetics for both bulk and surface deposition is evident. Many authors noticed the gap in understanding the kinetics compared to the thermodynamics, and have

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reiterated the fact that both are important to fully understand the scaling process [4–6].

Calcium carbonate crystallization from the liquid phase involves three different steps: supersaturation, nucleation, and crystal growth. The period necessary to form the first nucleus, as measured from the beginning of the supersaturation, is called induction time [7]. From a supersaturated solution and after the induction period, calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}) start to join as a cluster to form stable nuclei that are the centre of crystallization; this is known as the nucleation process. Nucleation induced by the influence of external stimuli is known as heterogeneous nucleation, as opposed to homogeneous nucleation which occurs in the absence of external stimuli [7]. Many parameters can influence the rate at which crystallization in the bulk or on surfaces occurs. The influence of temperature on calcium carbonate was studied under different conditions, Feng et al. [8], for example, observed that as temperature increases, the crystallization process was faster. Indeed, the precipitation kinetics is largely influenced by temperature. Amor et al. [9] showed that low temperature increases heterogeneous precipitation whereas high temperature supports homogeneous precipitation. Temperature also plays a role in determining the tendency to form deposits and the degree of supersaturation. Dyer and Graham [10] used a model to predict supersaturation and confirmed it by experimentation. They showed that the tendency to produce deposits increases with the temperature. It was also noticed that under the conditions applied and at 50°C, no calcium carbonate was formed. The possible explanation for this was that at low temperature the kinetics rate is also low.

Various models and techniques have been developed in order for the rate of calcium carbonate crystallization to be assessed. In general, kinetics studies have involved measuring the solution properties or the amount of scale formed *ex-situ* after experimentation. However, as mentioned previously, it has been noticed that both bulk precipitation and surface deposition are different processes and that their kinetics and mechanisms are different [1,2]. Al Nasser et al. [6] noticed a lack of real-time measurements and therefore developed a technique to study the kinetics of precipitation using an *in-line* technique. Regarding surfaces, Dawe et al. [4] studied the kinetics of calcium carbonate by observing its formation through glass micromodels. They assessed the increase in particle size as a function of time under various temperature and ionic strength conditions. However, both the processes have not been assessed together *in-line* and in real time.

The present study uses a new method, for studying scale formation in real time. It is generally assumed that if the induction time of a solution is longer that the residence time (i.e. corresponds to the time the solution stays in contact with the component), no scale will occur [11]. Therefore, most models to predict scale on a surface have been based on bulk measurements of the induction time.

In order to improve inhibition methods and strategies, it is necessary to get a better understanding of the two processes (bulk precipitation and surface deposition). The purpose of this study is to examine the kinetics and the link between scale formation in the bulk and on surfaces in a flowing system. The final aim, in the future, being to predict the formation of scale on a surface with time.

2. Experimental details

2.1. Chemical reagents

In total, four different brine compositions labelled A, B, C and D were used. Each of them was generated by mixing two stable solutions in a 1:1 ratio. Both solutions (Brine 1 and 2) were prepared separately, the beginning of an experiment corresponding to the time at which the brines were mixed.

The composition of Brine 1 for the solutions A, B, C, and D is presented in Table 1; Brine 2 is presented in Table 2. Table 3 presents the concentration of different ions for the different brines tested.

Each solution (A–D) shows a simple composition to minimize the effect of impurities as they are known to influence the formation of calcium carbonate [1,2, 12–14]. The composition was chosen to have a saturation ratio to induce scale formation but also to allow visualization of deposition onto the surface through the flow. The different compositions were determined to show a large range of different supersaturation ratios (SRs) under various temperature conditions; these are presented in Table 4. When a high temperature was applied, both brines were heated prior to mixing.

Table 1
Composition of brine 1 for each solution (A, B, C and D)

	Brine 1A	Brine 1B	Brine 1C	Brine 1D
NaCl (mg/L)	17,119	17,498	17,798	18,043
$CaCl_2.6H_2O$ (mg/L)	7,871	3,826	2,710	1,890

Table 2
Composition of brine 2 for each solution (A, B, C and D)

	Brine 2A	Brine 2B	Brine 2C	Brine 2D
NaCl (mg/L)	17,119	17,498	17,798	18,043
$NaHCO_3$ (mg/L)	2,560	1,469	600	260

Table 3
Concentration of the different ions (mol/L) for each brine (A, B, C and D)

	Brine A	Brine B	Brine C	Brine D
Na^+ (mol/L)	0.31	0.31	0.31	0.31
Cl^- (mol/L)	0.33	0.32	0.32	0.32
Ca^{2+} (mol/L)	0.036	0.017	0.012	0.009
HCO_3^- (mol/L)	0.03	0.017	0.007	0.003

Table 4
SR calculated for the different brines tested (A, B, C and D)

	20℃	50℃	80℃
Brine A	34	45	68
Brine B	11	15	25
Brine L	4	5	9
Brine F	1	2	3

2.2. Set up for deposition

Fig. 1 presents the apparatus used for the study. It consists of a recirculating system including an *in situ* flow cell containing the surface to study, an *in-line* turbidity meter, a jacketed beaker connected to a bath, a pump and a video camera linked to a computer. It permits accurate measurement of both the surface and bulk scaling processes. The turbidity meter allows assessment of bulk precipitation whereas the observation of the surface through a window with the video camera permits visualization of scale deposition. To avoid settling of the particles, the brine solution is stirred in the jacketed beaker and the surface is oriented vertically. The temperature was controlled at 20, 50 and 80℃. From the beaker the solution is pumped into the cell at a flow rate of 1 L/min.

2.3. Experimental procedure and image analysis

In order to study the kinetics, precipitation in the bulk solution and scale deposition onto the surface were assessed *in situ* and in real time using the rig presented above. The tests were performed for an hour with four brines and three temperatures giving a combination of 12 different supersaturation conditions.

For each experiment the turbidity was assessed as a function of time and images of the surface recorded at different time intervals. The images were then analysed by segmentation to assess the surface coverage as a percentage. No physical quantity of scale has been measured, as only the initial rate of coverage was to be assessed, gravimetric measurements on this system would not be accurate. A schematic diagram of the experimental overview is presented in Fig. 2.

3. Results

3.1. Bulk precipitation assessed by turbidimetry

The turbidity curves obtained for each brine at 20, 50 and 80℃ are presented in Figs. 3–5, respectively.

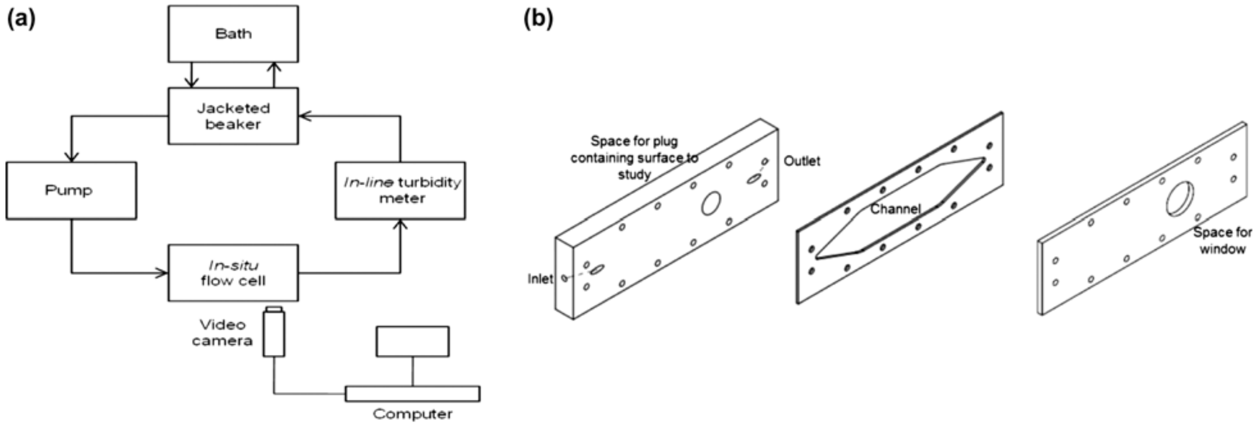

Fig. 1. Experimental assembly (a) and *in situ* flow cell (b).

A typical turbidity curve (crystallization curve) consists of an induction time, followed by an increase corresponding to the formation of calcium carbonate and a plateau suggesting the end of the reaction [15]. It is observed in the figures (Figs. 3–5) that after reaching the maximum value, a decrease is sometimes observed. This is due to the fact that once the particles reach a certain size, the influence of the gravity forces becomes greater than the buoyancy and hydrodynamic forces leading to a settling of the particles in the system. As it is a recirculating system, the supersaturation decreases with time as calcium carbonate is forming. For these reasons, only the initial rate of the crystallization process has been assessed. For each curve, a tangent is drawn allowing the induction time to be determined and to evaluate the kinetics of crystallization. The equation of the tangent is also used to assess the rate of crystallization where the gradient of the slope is assimilated to the rate constant of bulk precipitation.

As expected, for a given brine, the higher the temperature, the faster the kinetics. At 20°C, no precipitation is observed for brine C and brine D (low SR values) whereas both brine A and brine B (higher SR

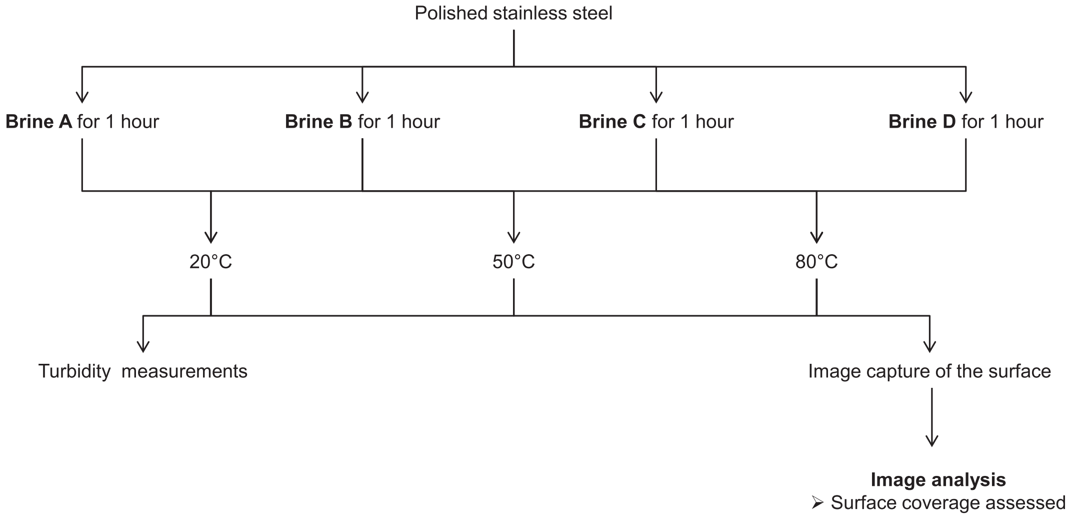

Fig. 2. Experimental overview of the precipitation and deposition kinetics tests.

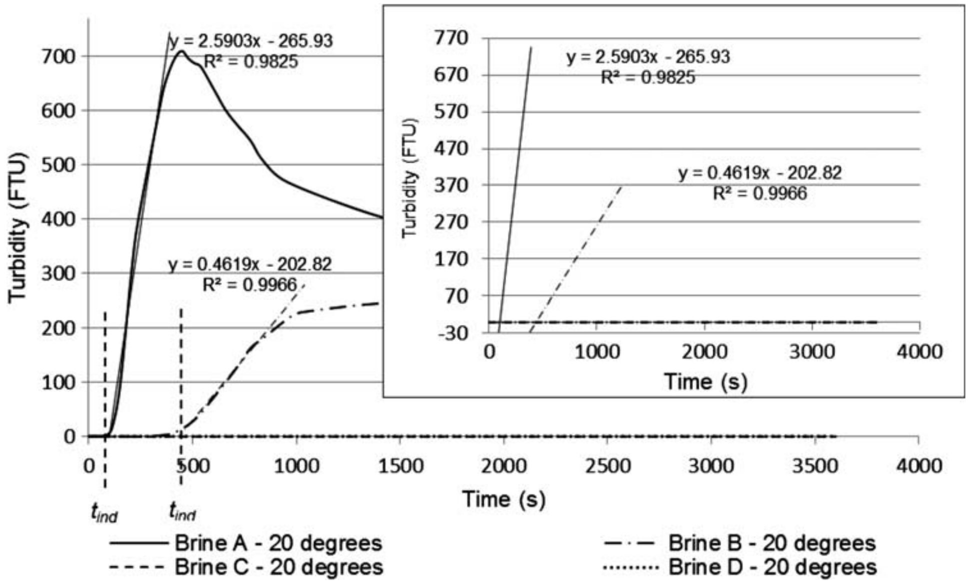

Fig. 3. Comparison of the turbidity measured with time for the four different brines (A, B, C and D) at 20°C for a 1-h experiment.

values) show an induction time of 100 s and 450 s respectively before crystallization starts. The kinetics being faster for brine A than for brine B is expected due to the composition of the solution. At 50˚C, all brine mixtures show precipitation, however only brine C and brine D show an induction time (of 90 s and 1200 s) whereas spontaneous nucleation occurs for both brines A and B. Once initiated, the kinetics can be ranked from slow to fast: brine D, brine C, brine B and brine A. Regarding tests performed at 80˚C, induction times of a few seconds to a minute are observed for both brines C and D whereas the reaction starts immediately after mixing for brine A and brine B. It can be noticed that both brine A and brine B show a similar rate of crystallization; the same observation is made for brine C and brine D.

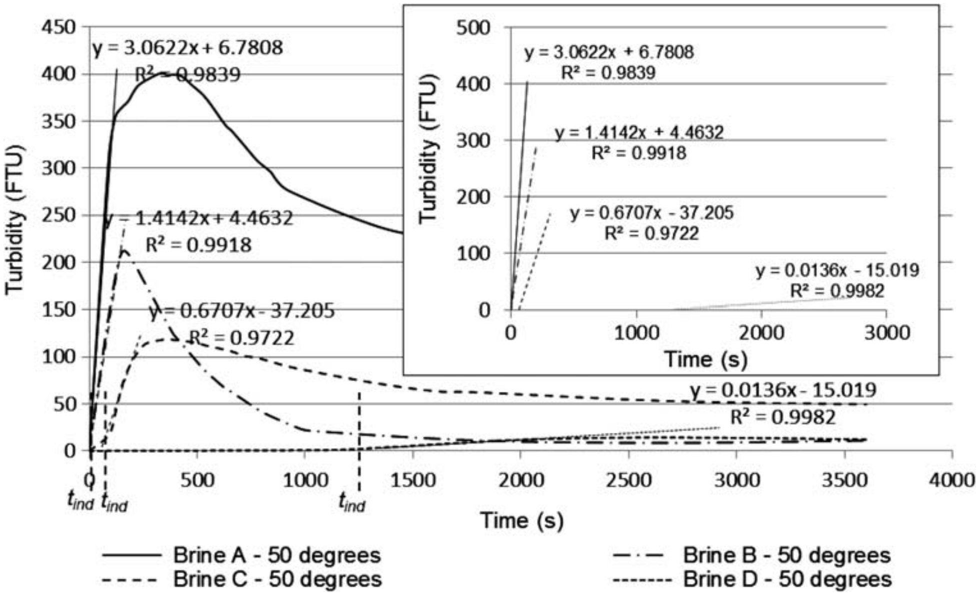

Fig. 4. Comparison of the turbidity measured with time for the four different brines (A, B, C and D) at 50˚C for a 1-h experiment.

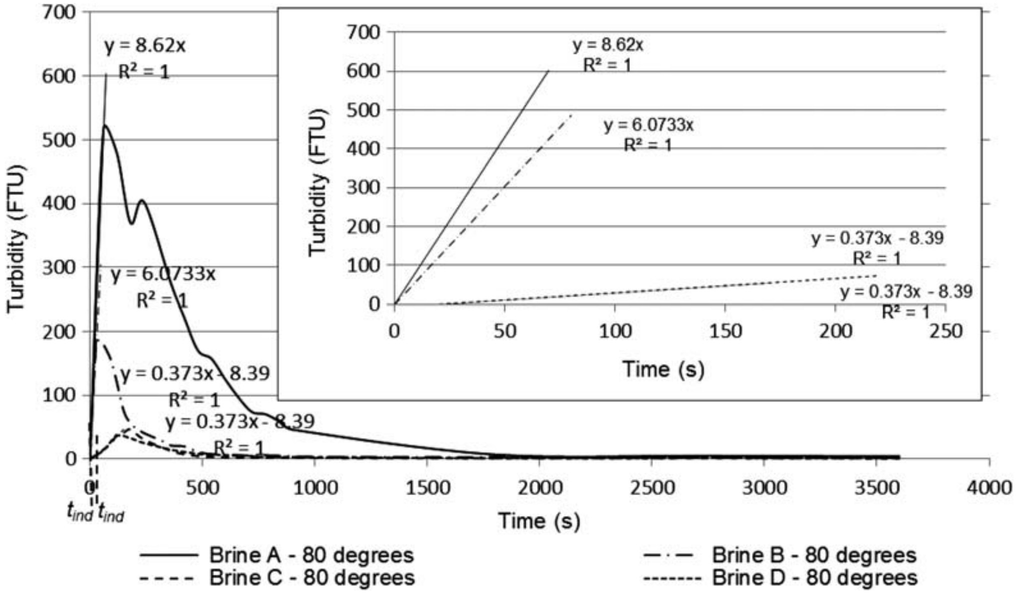

Fig. 5. Comparison of the turbidity measured with time for the four different brines (A, B, C and D) at 80˚C for a 1-h experiment.

This paper aims at getting a better understanding of the relation between bulk precipitation and surface deposition. The results regarding surface deposition are presented in the next part of the paper as shown in Figs. 6–8.

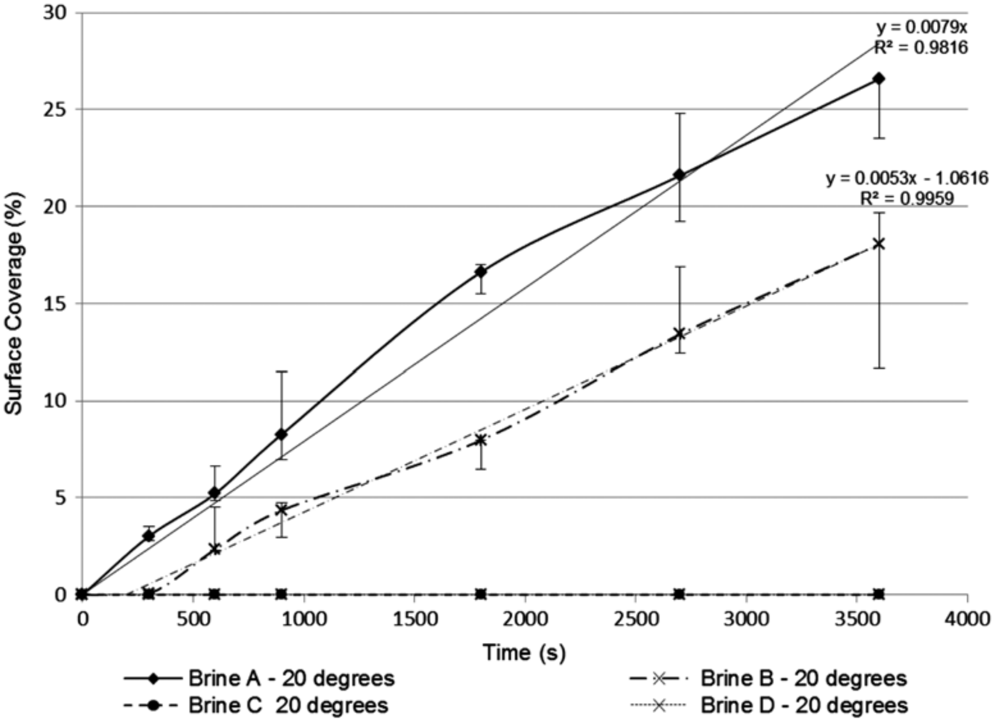

Fig. 6. Comparison of the surface coverage with time for the four different brines (A, B, C and D) at 20°C for a 1-h experiment.

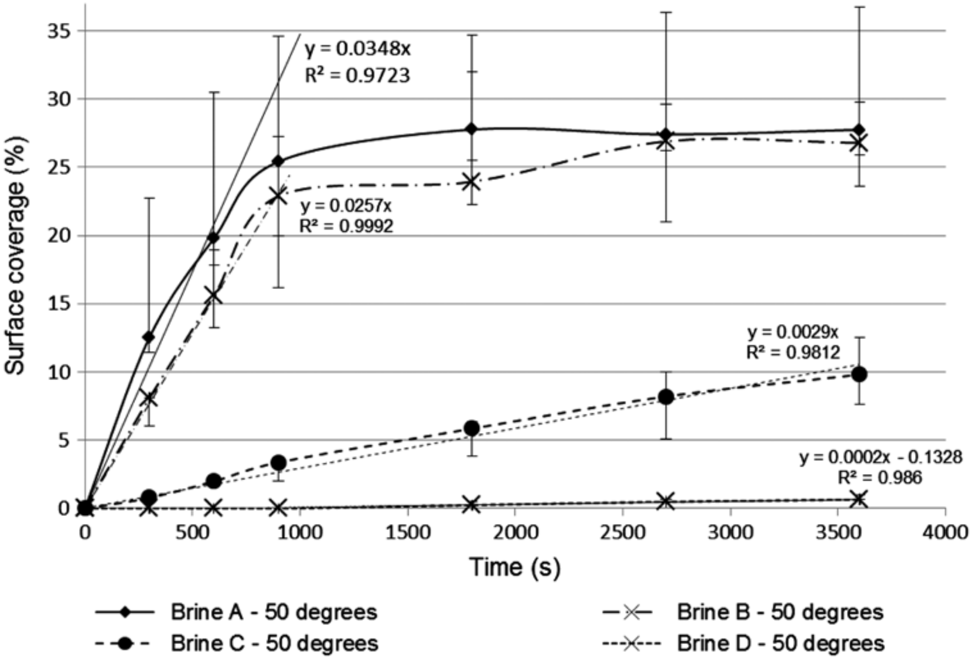

Fig. 7. Comparison of the surface coverage with time for the four different brines (A, B, C and D) at 50°C for a 1-h experiment.

3.2. Surface deposition assessed by surface coverage

Surface coverage (%) has been assessed for the different brines and temperatures. As for bulk precipitation, the increase corresponding to the crystallization of calcium carbonate has been analysed and a tangent to the curve is drawn in order to determine the rate constant of surface deposition to be assessed. Fig. 9 summarizes the results obtained. At 20°C, as for bulk precipitation, brine C and brine D show no deposition during the hour of experimentation. Both brine A and

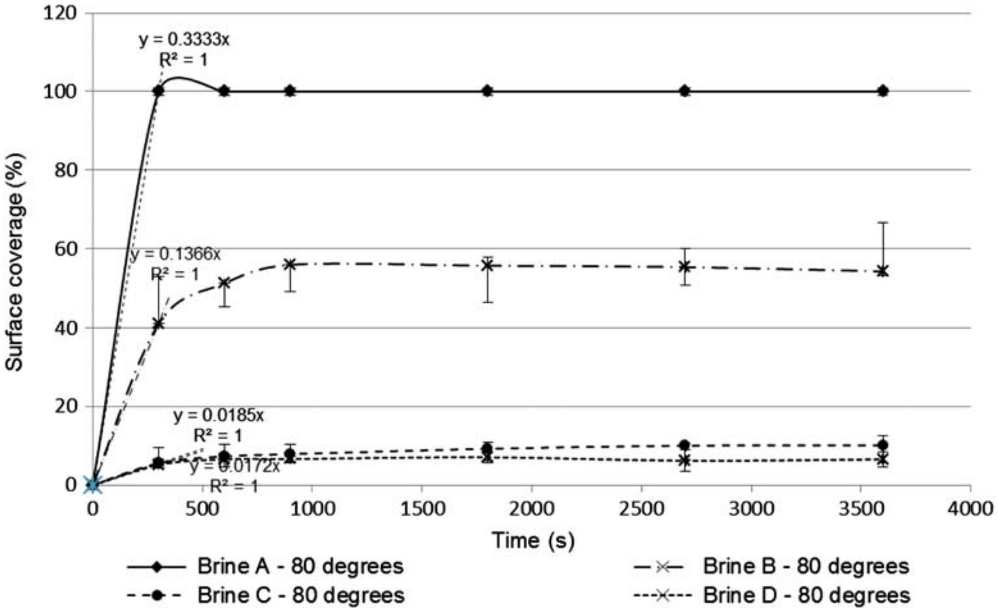

Fig. 8. Comparison of the surface coverage with time for the four different brines (A, B, C and D) at 80°C for a 1-h experiment.

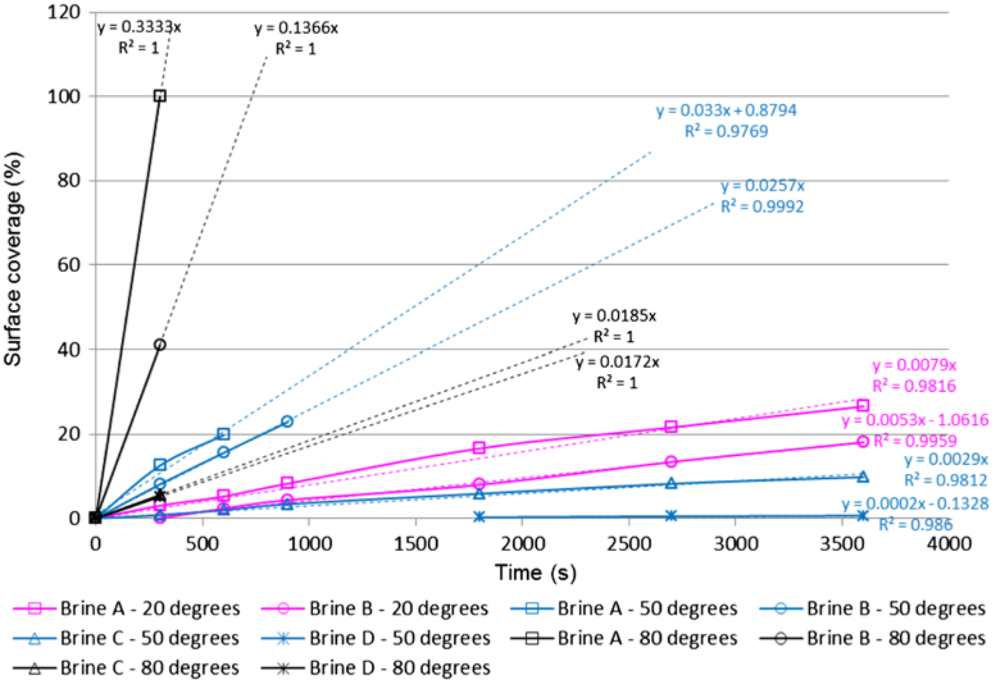

Fig. 9. Trendlines presenting the initial kinetics of the reactions for the different conditions tested.

B show a continuous increase once deposition has begun. Compared with bulk precipitation where different stages were observed, the surface deposition at 20˚C does not appear to show any difference in the shape of the curve. A relatively linear trend is observed for both brines for the duration of an experiment.

At 50˚C, calcium carbonate deposition on the surface occurs for all brines. However, only brine D shows a significant induction time. For both brines C and D, once crystallization starts on the surface, a linear trend is observed that continues up to the end of the experiment. However, brine A and brine B show two different stages. First an increase in the surface coverage is observed which follows a linear trend and then a maximum value is reached and a plateau is observed. As described, the supersaturation in the system decreases, therefore it is expected that a maximum coverage value would be reached.

Regarding the experiment performed at 80˚C, all curves show an increase in the surface coverage followed by a plateau. The kinetics for brine C and brine D shows a very similar trend. Brine A shows the fastest kinetics with the surface being completely covered after 5 min.

4. Discussion

Many authors have noticed a gap in the understanding of kinetics compared to thermodynamics, and related the fact that both are important to fully understand the scaling process.

Zhang et al. [16], developed a model to predict down-hole scaling. They performed tube-blocking tests and correlated the thickness of scale observed at the end of the experiments with bulk measurements recorded as a function of time. In general, kinetics studies have involved measuring the solution properties or the amount of scale formed *ex-situ* after experimentation. However, it has been noticed that both bulk precipitation and surface deposition are different processes and that their kinetics and mechanisms are different [1–3]. In this study, the scale formation has been studied in real time. In comparison to Zhang et al. [16], who measured the thickness of the scale after experiments, the present work assesses the surface coverage with time. As the model developed by Zhang et al. [16] showed good consistency with carbonate scaling profile measured in a real oilfield, a combination of both the models could be promising in developing a scaling rate model.

Research is still on-going, to improve the calculation of scale indices and kinetic scaling rates in order to predict the fouling rate more accurately and apply the most suitable inhibition methods and strategy. However, only few prediction models exist in literature regarding the time for scale to form on a surface with time. Most of them have been derived from core flooding [17] or tube blocking test [16] experiments, associated with bulk solution measurements, but real time measurements of surface deposition appear to be lacking. In fact, measurements of the scale thickness in the tube after testing were correlated to the curves of the bulk measurements obtained with time expressing the bulk precipitation rate but there is no evidence that both rates (precipitation and deposition) are the same.

In this study, it is intended to get a better understanding of the kinetics for both bulk precipitation and surface deposition and assess if there is any correlation between the crystallization rates. The rate constants for both bulk precipitation and surface deposition have been evaluated in the previous part; the results obtained are compared in Table 5 which summarizes the results.

Table 5 shows very different results between the gradient of the slope obtained for the bulk precipitation and that of surface deposition suggesting different crystallization rates. It is also interesting to notice that higher SR does not necessarily correspond to

Table 5
Summary of the results obtained; comparison of the gradient of the slope (rate constant) for bulk precipitation and surface deposition

Brine label	Temperature	SR	Gradient of the slope (rate constant bulk)	Gradient of the slope (rate constant surface)
A	20˚C	34	2.59	0.0079
	50˚C	45	3.06	0.0348
	80˚C	68	8.62	0.3333
B	20˚C	11	0.46	0.053
	50˚C	15	1.41	0.0257
	80˚C	25	6.07	0.1366
C	20˚C	4	–	–
	50˚C	5	0.67	0.0029
	80˚C	9	0.37	0.0185
D	20˚C	1	–	–
	50˚C	2	0.01	0.0002
	80˚C	3	0.37	0.0172

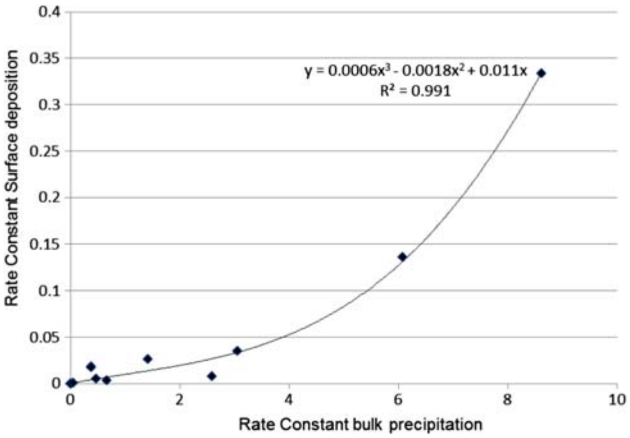

Fig. 10. Assessment of the correlation between the bulk precipitation rate constant and the surface deposition rate constant.

faster kinetics. This will be discussed in more detail in future papers.

From the results obtained and in order to assess any correlation between both rates and therefore to improve the knowledge regarding the relation between both the processes the rate constant values of bulk precipitation for each point has been plotted against the rate constant values obtained for the surface coverage rate. This is presented in Fig. 10.

The plot presented in Fig. 10 shows that even if both bulk precipitation and surface deposition showed different rates of calcium carbonate formation, there is a relation between both rate constants. The equation fitted to the relation between bulk and surface is a polynomial of third order with a coefficient of determination equal to 0.99 suggesting very good accuracy. It therefore confirms that both the processes have different kinetics (i.e. understand here, different rate constants) but also that the relation between both does not follow a linear correlation. It suggests that developing a kinetic model of scale surface deposition using bulk precipitation data is feasible and can be improved by understanding the relation between both the processes.

5. Conclusion and future work

It has been confirmed that bulk precipitation and surface deposition are two different processes with their own kinetics. It has been shown that the kinetics (constant rate) of bulk precipitation and surface deposition is different but that a physical relation exists between both rates. The equation describing the relation between both was found to be a polynomial of third order. It could therefore be taken into account when deriving an expression to predict the formation of the scale as a function of time.

This work does not present a new theoretical model with a derived expression allowing quantification of the scaling rate. However, it gives new insight into the physical relation existing between bulk precipitation and surface deposition. This will help derive a physical expression to allow the scaling rate to be quantified for a set of conditions.

Prediction of the scale rate would help in using adequate strategies to prevent deposition. However, it has been shown that many parameters can influence the kinetics of calcium carbonate scale formation (temperature, flow rate, substrates, SR, presence of foreign ions …). It is therefore important to remember when developing a kinetic model that these parameters may also modify the kinetics. Once a scale layer is formed the kinetics may change, as formation of scale onto scale can be different than on the surface. It therefore appears difficult to develop one single model that could be applied to every case. This therefore suggests that developing a model of scaling rate onto scale in addition to the initial kinetics would permit the entire process to be encompassed.

The present work used adequately with other prediction models where the scale thickness and weight have been assessed could be of real interest in order to derive an expression giving the amount of scale in centimeter per year.

Acknowledgments

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