Microscopic Study of CaCO_3 Scaling on Heat Transfer Surfaces*

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For the purpose of obtaining essential information on scaling in heat exchangers, microscopic observations were made for CaCO_3 deposition from a flowing solution onto initially clean heat transfer surfaces. The growth rates of CaCO_3 crystals were measured by changing the Reynolds number and supersaturation degree of the bulk solution, materials and temperature of the heat transfer surface. The growth rate was found to be relatively well correlated with the supersaturation degree of the solution adjacent to the surface, deduced from the equilibrium relationships between the species in the calcium carbonate solution. The nucleation rate was also estimated by measuring the change of the cumulative number density of deposited crystals against time. The crystals were formed on the surface at a constant nucleation rate over time, but the factors which dominate the nucleation rate could not be determined.

Key Words: Heat Exchanger, Forced Convection, Mass Transfer, Fouling, Scaling, Experiment, Microscopic Observation, Calcium Carbonate, Crystal Growth, Nucleation

1. Introduction

Control of fouling is very important for maintaining good performance of heat exchangers. Among the various ways in which fouling occurs, scaling, the deposition of soluble matter on heat transfer surfaces, is one of the major causes. Numerous studies regarding scaling have, therefore, been carried out and are reviewed by Hasson⁽¹⁾ and Tabolek et al.^{(2),(3)}. Most of these studies have been carried out in order to derive empirical relationships estimating scaling behavior, based on measurements of thermal resistance caused by scaling on heat transfer surfaces. Although these studies offered valuable results for practical use, the fundamental mechanisms of scaling have not been sufficiently understood. Few studies have been conducted for the purpose of clarifying the scaling mechanism essentially, and these efforts have met with little success. The primary cause is a lack of information of

direct observations of a heat transfer surface on which scaling is occurring.

We thought that in order to elucidate the essence of this problem, it would be of vital importance to observe the scaling process in detail with a microscope. As a first step we planned an experiment for direct observation of scaling on a heat transfer surface and reported the results in a previous paper⁽⁴⁾. In the experiment, calcium carbonate (CaCO_3) was chosen as a scaling material, because it has been widely used in past experiments and is a representative material for scaling in practical equipment. An experimental system for this purpose has been developed to establish a specified degree of supersaturation of a solution dissolving CaCO_3 and to maintain that state for a long period of time. The observations clearly demonstrated that CaCO_3 scaling begins with deposition of nuclei on a surface, followed by growth and coalescence of these nuclei. It was also found that several kinds of crystals were deposited on a surface, and each of them seemed to have a different growth rate. The previous paper was, however, less quantitative and did not include the estimation of numerical values of factors to determine scaling rate.

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The present study measured the growth and nucleation behaviors under various supersaturation degrees of the solution, Reynolds numbers, temperatures and materials of deposited surface, and the effects of these parameters on the scaling behaviors are discussed quantitatively.

2. Nomenclature

- $[Ca]_{tot}$: concentration of total calcium species, Eq. (2)
 f_D : activity factor for divalent ions
 $[H_2CO_3]_{tot}$: concentration of total carbonic species, Eq. (4)
 K_s : solubility product of $CaCO_3$
 $K_{s,w}$: solubility product of $CaCO_3$ adjacent to the deposited surface
 l : length of crystal projected on the deposited surface
 $\dot{l}$: crystal growth rate
 n : number of crystals per unit area
 R : thermal resistance
 Re : Reynolds number at the inlet of the test section defined with twice the height of the flow channel
 S_{in} : supersaturation degree of solution at the inlet of the test section
 S_w : supersaturation degree of solution adjacent to the deposited surface
 T_{in} : solution temperature at the inlet of the test section
 t : time
 ΔT_w : temperature difference between the deposited surface and bulk solution
 $[]$: mol concentration
 $[]_w$: mol concentration adjacent to the deposited surface

3. Experiment

3.1 Experimental system

Figure 1 shows the experimental system, which was essentially the same as that described earlier in the previous paper. It utilizes the dependency of $CaCO_3$ solubility on the concentration of CO_2 dissolved in solution, permits achievement of a specified degree of supersaturation, and maintains that state over a long period of time. In the previous system, a flow line was formed, as the solution was allowed to flow through the test section during the waiting time (1 or 1.5 hours) required for the temperature of the deposited surface to rise to the desired value of the final state. This introduced uncertainty into the determination of the initial temperature corresponding to the deposit-free surface. To avoid this disadvantage, the present system has a bypass line which allows

pure water to flow into the test section during the waiting time and then turn from water to solution after the surface temperature reaches a steady state. (This bypass line is not shown in the figure for the sake of simplicity.)

The solution was prepared in the following manner: deionized water with a conductivity of less than $0.2 \mu S/cm$ was filtered with a $0.45 \mu m$ mesh filter; then calcium chloride ($CaCl_2$) and sodium bicarbonate ($NaHCO_3$) were dissolved in the water. To test for impurities, the concentrations of metals such as Fe, Mg, Cu, which are known to be the impurities affecting the shapes of deposited crystals, were measured by atomic absorption analysis, and it was confirmed that they were not present in the solution. To avoid contamination by nonmetallic impurities and identify the experimental condition of the solution, a fresh solution was prepared in the same way for each run.

3.2 Test section

Figure 2 shows a cross-sectional view of the test

Fig. 1 Experimental system

Fig. 2 Test section

section for CaCO_3 deposition. It was the same as the previous one except for the materials of the deposited surfaces. The flow channel had a rectangular cross section of 16 mm in width and 5 mm in height. The upper end of a copper block 10 mm in width provided the deposition surface. However, exposure of the copper surface to the solution causes corrosion, and the dissolved copper ions inhibit measurement of calcium concentration. To prevent such problems, the copper surface must be covered with metals that are not corroded by the solution. In the previous experiment gold was plated on the copper surface. In this experiment two types of deposited surfaces, nickel plating and stainless steel foil stuck to the surface, were prepared. After each run the surface was immersed in sufficiently dilute hydrochloric acid to dissolve deposited CaCO_3 and was reused after washing with water and ethanol.

Thermocouples for measuring the surface temperature were placed in 1-mm-dia. holes drilled from the bottom of the copper block to 1 mm below its surface. They were located 50 mm apart along the flow direction. The heating surface had a length of 500 mm, and a microscope with a maximum magnification of 128 was placed at a location 350 mm downstream from the starting point of the heating section. A camera was mounted on the microscope to photograph the surface during CaCO_3 deposition.

Analyses of the deposition phenomena were mostly performed through use of the photographs, but some were done with an image analyzer in the later stages of the experiments.

3.3 Calculation of supersaturation degree of a solution

The supersaturation degree of the solution at the inlet of the test section was determined in the same way as that reported by Wiechers et al.⁽⁶⁾ The procedure can be outlined as follows. The solution of CaCl_2 and NaHCO_3 used here contains 9 species, Ca^{2+} , CO_3^{2-} , HCO_3^- , CaCO_3^0 , CaOH^+ , CaHCO_3^+ , H_2CO_3^* , H^+ , and OH^- , where H_2CO_3^* represents $\text{CO}_2 + \text{H}_2\text{CO}_3$, because CO_2 and H_2CO_3 are in their equilibrium state in water and are difficult to treat individually. CaCO_3^0 is an ion pair of Ca^{2+} and CO_3^{2-} formed in the solution without precipitation. These 9 species are related by an electroneutrality condition and 6 equilibrium relationships expressed by 6 equilibrium constants (K_1 to K_6). An example of the relationships is

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} f_b = K_1. \quad (1)$$

The 6 equilibrium constants are given as functions of solution temperature by Wiechers et al. The concentration of total calcium species in the solution is given by

$$[\text{Ca}]_{\text{tot}} = [\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{CaHCO}_3^+] + [\text{CaCO}_3^0]. \quad (2)$$

The unknown variables contained in the solution are the 9 species described above, and $[\text{Ca}]_{\text{tot}}$ given in Eq. (2). These 10 variables are interrelated by 8 independent relationships, which are 6 equilibrium relationships, an electroneutrality condition and Eq. (2). Concentrations of two variables must, therefore, be measured to determine the concentrations of all unknown variables. In this study $[\text{Ca}]_{\text{tot}}$ and $[\text{H}^+]$ were measured by the EDTA titration method and pH meter, respectively, and then the concentrations of all variables in the solution flowing into the test section were calculated. This allows the calculation of the supersaturation degree of the solution at the inlet of the test section by means of the following equation:

$$S_{\text{in}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_s} f_b^2. \quad (3)$$

4. Experimental Results

4.1 Change in thermal resistance with time and observed results of deposition behavior

Experimental runs were performed using a solution under the conditions of $S_{\text{in}} = 4.1 \sim 8.5$, $\Delta T_w = 19 \sim 33$ K and $Re = 5200 \sim 12000$ at the inlet of the test section. The temperature and calcium concentration of the solution flowing into the test section were fixed at the same values of $T_{\text{in}} = 25^\circ\text{C}$ and $[\text{Ca}]_{\text{tot}} = 5 \times 10^{-3}$ mol/l in all experimental runs.

Figure 3 shows examples of the change in thermal resistance with time caused by the deposition of CaCO_3 on the heat transfer surface. The thermal resistance was calculated by measuring the temperature difference between the wall and bulk solution and dividing it by the wall heat flux. In the previous experiment a superficial increase of thermal resistance appeared for 1 or 2 hours after a run start-up, and was attributed to the temperature rise of the heating surface before the surface temperature reached a steady state. This superficial increase was

Fig. 3 Change in thermal resistance with time

avoided in the present experiment due to the improvement of the experimental apparatus mentioned earlier. Thermal resistance keeps its initial value for a certain time interval, and then increases linearly with time. This tendency of thermal resistance is similar to those observed in earlier studies and is the general feature of thermal resistance behavior caused by scaling.

The period of time during which thermal resistance maintains its initial value after starting from a clean surface is called the 'waiting time' or 'induction time'. From the viewpoint of practical use it is important to evaluate the waiting time during which heat exchangers maintain the initial good performance, as well as the linear increase rate of thermal resistance.

Figure 4 shows photomicrographs of the heat transfer surface which were taken at the same location as the measurements made for Fig. 3. The figure is the result given by the stainless steel surface. It can be seen that fine crystals formed on the clean surface and grew to cover the surface. Within the range of the experimental conditions used here, most of the deposited crystals were of the type called 'aragonite' (the authors refer to it as the A-type here). This type of crystal has a needle shape initially and changes to a dendritic shape with a complicated three-dimensional structure. Another type of crystal, which grows thinly along the surface, was also observed, but the frequency of the appearance was low. This type of crystal could not be identified and was termed the B-type. In this experiment the above results for the stainless steel surface were similar to those for the nickel-plated surface, and the differences in surface materials had no identifiable effects on the types of crystals deposited.

In the previous study using the gold-plated surface, crystals of the third type, 'calcite', were observable; these have a cubic shape and grow in a cubic pattern (the authors refer to it here as the C-type). The crystals deposited in the present study were, however, limited to the A and B types. There are several factors affecting the deposition behavior of crystals, such as solution temperature, surface temperature, flow rate of solution, material and condi-

tions of the surface, solution composition and impurities in a solution. Although we have controlled these factors with great care to assure the reproducibility of the experimental results, we may not have been fully successful in controlling all of the factors. Further studies will be needed to clarify the cause of the difference of crystal shape between the previous and present experiments.

Comparing the thermal resistance measurements and the microscopic observations made in the previous and the present studies, we find that the 'waiting time' corresponds to the period in which the heating surface is fully covered with deposited crystals due to their growth and coalescence. The region of linear increase in thermal resistance following the 'waiting time' is interpreted as indicating that the deposited layer increases in thickness monotonously with the further crystal deposition. Therefore, quantitative predictions of the 'waiting time' and increasing rate of thermal resistance require knowledge of both the crystal growth rate and crystal nucleation rate. This also means that the formerly reported general approaches to scaling, which are based solely on measurement of the change in thermal resistance, are not able to reach the final goal of clarifying the essential mechanism of scaling.

The following sections will describe the experimental results on both the crystal growth rate and crystal nucleation rate.

4.2 Crystal growth rate

To demonstrate the growth rate of the crystals quantitatively, the change in crystal size over time was recorded with photomicrographs at a magnification of 64. A-type crystals have a complicated three-dimensional structure, and their shape varies with time. This study assumed that A-type crystals have almost the same growth rate in each of the three dimensional directions, and the maximum length of a crystal projected onto the heating surface was used as a measure of crystal size. Since the dimensions of B-type crystals were difficult to determine and the frequency of their appearance was low, this crystal type was excluded from the measurement of growth rate. For the C-type crystals observed in

Fig. 4 Deposition behavior of CaCO_3 crystals (Stainless steel, $\Delta T_w = 29.0 \text{ K}$, $S_{in} = 6.0$, $S_w = 21.3$, $Re = 7200$)

the previous paper, the length of one side was used as a measure of crystal size for cube-shaped crystals.

Figure 5 shows the results of the change in crystal size over time. The plotted data are representative data selected from a number of crystals for which the change in size with time was measured. The crystals not shown in the figure had inherent growth curves similar to those in Fig. 5. Furthermore, the growth curves for the crystals deposited under the same experimental conditions were confirmed to agree with each other by correcting for the initial time deviations of nucleation. The growth rate of C-type crystals tends to decrease slightly over time. On the other hand, the growth rate of A-type crystals is constant over time and varies with the experimental conditions.

It has been generally recognized that degree of supersaturation is one of the important factors controlling phase change phenomena such as melt solidification, mist formation, crystal nucleation and growth in solution. As shown in Fig. 4, scaling is a phenomenon accompanying crystal formation on a solid surface, and therefore can be categorized as a phase change phenomenon. This suggests that the supersaturation degree of solution adjacent to the deposited surface can be an important factor. In order to examine this point, the supersaturation degree of the solution adjacent to the deposited surface, S_w , was estimated, and the dependence of this factor on the crystal growth rate was investigated.

In the present experiment, solution temperature increases very sharply in the thin thermal boundary layer formed in the vicinity of the deposited surface. The equilibrium constants K_1 to K_6 and solubility product K_s , which are functions of solution temperature, therefore also change steeply in the vicinity of

Fig. 5 Change in crystal size with time

the deposited surface, as in the solution temperature profile. We, therefore, need local values of $[Ca]_{tot}$ and pH in the vicinity of the surface to determine the value of S_w in the same way as mentioned in section 3.3. As such measurement is quite difficult, this study estimated the value of S_w in the following manner. In this experiment calcium species depositing on the surface is very small compared with those dissolved in the solution flowing in the test section. This allows us to assume that $[Ca]_{tot}$ given by Eq. (2) is constant at any location inside the test section. In addition there is no CO_2 gas released to outside of the test section, because the solution in the test section does not come into contact with the atmosphere. Therefore, neglecting gasification of dissolved CO_2 in the solution, the total carbonate given by

$$[H_2CO_3]_{tot} = [HCO_3^-] + [CO_3^{2-}] + [CaHCO_3^+] + [H_2CO_3^*] + [CaCO_3^0] \quad (4)$$

can be assumed to be constant, as is $[Ca]_{tot}$. Therefore, if each species in the solution is always in the equilibrium state and the change in concentration distribution of each species caused by mass transfer due to $CaCO_3$ deposition on the surface is negligible, then the solution composition adjacent to the surface can be estimated from $[Ca]_{tot}$ and $[H_2CO_3]_{tot}$, with Eq. (2), Eq. (4), the electroneutrality condition, and equilibrium constants K_1 to K_6 corresponding to the surface temperature. In the present experiment $[Ca]_{tot}$ was measured in the inlet of the test section by the EDTA titration method, and $[H_2CO_3]_{tot}$ was calculated from the species in the solution, which were determined in the inlet of the test section in the way described in section 3.3. Then the supersaturation degree of the solution adjacent to the deposited surface was estimated by

$$S_w = \frac{[Ca^{2+}]_w [CO_3^{2-}]_w}{K_{s,w}} f_D^2 \quad (5)$$

Figure 6 shows the results for crystal growth rate. The data are plotted as a function of S_w estimated in the manner mentioned above. The growth rate of the A-type crystals was calculated from the gradient of the straight line through the data points, as shown in Fig. 5. For C-type crystals, of which the growth rate decreases with time, the average growth rate over experimental time was plotted in the figure. The growth rates for both A and C-type crystals are well correlated with S_w , and the reproducibility of the data is also fairly good. The present data obtained using the stainless steel and the nickel plated surfaces increase linearly with S_w , and the data of the previous paper, obtained using a gold plated surface, lie on the line extrapolated from the present data. Furthermore, the data for three different Reynolds numbers do not exhibit notable discrepancies. From these results it

Fig. 6 Crystal growth rate arranged by S_w

Fig. 7 Cumulative number density of crystals

seems that the growth rate of A-type crystals once deposited is not affected by surface materials but is controlled by a single parameter, S_w . Furthermore, in the Reynolds number range of this experiment, the limiting process determining the growth rate of A-type crystals may not be the diffusion resistance of the species in the solution but some other mechanism occurring on the crystal surface.

The growth rates of C-type crystals observable in the previous work are considerably lower than those of A-type crystals for the same Re and S_w conditions, and indicate little dependence on S_w . This may reflect the differences in crystal shapes between A and C-type crystals. A-type crystals have a complicated

three-dimensional dendritic shape and may allow the arbitrary growth of each dendrite branch. C-type crystals have a cubic shape and each side of a cube may grow uniformly. This may lead to the difference in growth rate between A and C-type crystals.

4.3 Crystal nucleation behavior

Figure 7 shows the measured results for the cumulative density of crystals deposited on the surface. These results were obtained by selecting fixed rectangular areas of $1.5 \text{ mm} \times 1 \text{ mm}$ from the photomicrographs taken at the same intervals and by carefully counting the total number of crystals present in each area. The lower limit of detected crystal size is about $5 \mu\text{m}$. The cumulative densities for any experimental conditions increase linearly with time. In the Reynolds number range of this experiment, once the crystals were deposited on the surface they remained at the same location and never re-entered the flow. The results in Fig. 7, therefore, indicate that crystals deposit on the surface at the same nucleation rate. However, the nucleation rate given by the gradient of the interpolation line through the data does not show any dependence on S_w and scatters over a wide range. For example, the nucleation rates calculated from two sets of data (denoted by the symbols $\circ$ and $\blacktriangle$) obtained under almost the same S_w conditions show an approximately 50-fold discrepancy. As can be seen from the figure, the nucleation rates did not indicate reproducibility of the kind seen in the growth rate shown in Fig. 6.

By analogy with heterogeneous nucleation theory in the vapor phase, the crystal nucleation rate on a solid surface from a solution may be affected by the free energy of crystal nuclei formation and its reduction ratio caused by heterogeneous nucleation on a solid substance. Therefore, undetectable slight changes in solution composition or surface conditions such as finish, wettability, and cleanliness may cause marked change in the nucleation rate. The authors have not been able to offer a good explanation for the results in Fig. 7. Further studies will be needed in order to advance discussion on this point.

5. Conclusions

As the first step in clarifying the scaling mechanism, microscopic observations were made for CaCO_3 deposition from a flowing solution on a heating surface. The conclusions reached in the present study are as follows.

(1) The growth rate of CaCO_3 crystals does not depend on the surface material or Reynolds number, and is correlated well with the supersaturation degree of the solution adjacent to the deposited surface, S_w , which was approximately estimated from the equilib-

rium relationships between the species in the solution under the assumption that total calcium and total carbonate are constant at any location in the flow channel.

(2) The growth rate of A-type crystals (aragonite) is considerably greater than that of C-type crystals (calcite) and increases linearly with the increase of S_w . This means that the scaling process depends strongly upon the types of crystals having been deposited on a surface.

(3) Under any experimental conditions, the nucleation rate of CaCO_3 crystals on the surface is maintained as a constant rate over time.

(4) C-type crystals (calcite) observable in the previous study did not appear, and the nucleation rate did not show reproducibility. Further studies will be needed in order to discuss the causes of these problems.

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