Experimental Investigation of CaSO$_4$ Crystallization on a Flat Plate

M. G. Mwaba $^a$; C. C. M. Rindt $^a$; A. A. Van Steenhoven $^a$; M. A. G. Vorstman $^a$

$^a$ Department of Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

To link to this article: DOI: 10.1080/01457630500458187
URL: http://dx.doi.org/10.1080/01457630500458187
Experimental Investigation of CaSO₄ Crystallization on a Flat Plate

M. G. MWABA, C. C. M. RINDT, and A. A. VAN STEENHOVEN
Eindhoven University of Technology, Department of Mechanical Engineering, Eindhoven, The Netherlands

M. A. G. VORSTMAN
Eindhoven University of Technology, Department of Chemical Engineering, Eindhoven, The Netherlands

The scaling of calcium sulfate was studied by performing laboratory experiments under controlled conditions. The experiments were aimed at measuring the rate of deposition at different positions on a heated surface. The overall thermal resistance was determined from temperatures measured using thermocouples positioned in the bulk fluid and the wall of the heated plate. Calcium sulfate was used as the experimental fluid. It was observed that nucleation started forming on the downstream side. A nucleation front was formed, and it was seen to move from the downstream to the upstream side. The rate of growth as a function of position was observed to increase with the initial wall temperature distribution, resulting in a final thickness of the scale layer that increases accordingly. While the rate of growth was found to be independent of flow velocity for Reynolds numbers of 11,000 and 23,000, the results showed that the rate of growth decreased by about 20% for Re = 34,000. Further, the induction period is reduced by increasing the flow velocity. An increase in the degree of supersaturation also reduces the induction period. It is concluded that scaling due to CaSO₄ results in a non-uniform porous scale layer with a profile that mimics the initial surface temperature.

INTRODUCTION

Fouling of heat transfer surfaces is a problem that permeates the life cycle of heat exchangers. At the design stage, a commonly used remedy is to increase the heat transfer surface area. Garrett-Price et al. [1] reported that in practice heat exchangers are designed with an average oversize of about 35%. While this strategy is widely accepted, it has some economic penalties associated with it. Heat exchangers designed with excess surface area tend to be larger and heavier, which evidently results in extra costs to cover additional material, transportation, and installation. During the operational stage of a heat exchanger, operators resort to periodic cleaning as a way of managing fouling. Periodic cleaning results in additional costs arising from the loss of production and additional maintenance activities. Steinhagen et al. [2] have shown that fouling-related costs constitute a significant portion of the industry’s running costs.

Scaling, or crystallization fouling, occurs when inverse solubility salts that are originally dissolved in the process fluid deposit on heat transfer surfaces. A characteristic feature of inverse solubility salts is that their solubilities decrease with an increase in temperature. Salts that normally lead to scaling are usually sulfates, phosphates, and carbonates of calcium. Calcium sulfate is one of the commonly encountered scale forming materials. It is found in nanofiltration technology [3], the desalination of seawater by reverse osmosis, the handling of geothermal brines for energy production, and water distillation [4]. Consequently, work aimed at understanding the underlying mechanisms in calcium sulfate scaling has received a lot of attention [5–13]. Investigations of calcium sulfate deposition mechanisms using a saturated calcium sulfate solution flowing in a double-pipe heat exchanger with the inner tube heated electrically can be found in the literature [5, 8, 12]. In the experiments reported in [5], the bulk temperature was maintained at 55°C with the Reynolds number set at Re = 400; it was observed that the surface nucleation along a heated tube occurred at a non-uniform rate, being highest at the downstream side. A correspondingly non-uniform scale layer was observed that was thickest at the downstream edge. These results were presented as a series of photographs, showing the position of the scale front at different times. It was further...
observed that rates of nucleate front propagation and scale layer growth increased with the surface temperature and decreased with the flow velocity. With filtration of the bulk solution, a decrease in the rate of nucleation and crystal growth was observed. It was concluded that the movement of the nucleation front was a predominant mechanism in calcium sulfate scale formation, and based on this mechanism, the authors presented a kinetic model of which the nucleate front propagation was shown to be a function of axial distance.

Working from the first principles and assuming that the fouling layer growth would be arrested after a certain time by deposit removal arising from fluid shear stresses, Bohnet [8] developed a physical model to describe fouling caused by crystallization and sedimentation. He conducted experiments with constant heat flux, fluid velocity, bulk concentration, and bulk temperature. The range of the Reynolds number was between 12,000 and 32,000. The bulk temperature ranged from 42°C to 88°C, while the surface temperature was between 75°C and 88°C. He deduced that the fouling resistance, as a function of time, approached an asymptotic limit that depended on the rate of fluid flow. It was concluded that fluid shear stress was essentially responsible for removal. Further, it was concluded that the strength of the scale was reduced by thermal stresses, which assisted the removal process. With Reynolds numbers ranging from 30,000 to 40,000 and surface temperatures between 62°C and 70°C, Mori et al. [12] obtained asymptotic fouling curves and observed that asymptotic values were influenced by surface temperature and fluid velocity. They concluded that calcium sulfate scale formation was a surface reaction-controlled mechanism.

In the studies cited earlier, fouling rates were determined from temperatures measured at a single point. In the scaling experiments reported in this paper, the fouling rates were calculated from temperatures measured at five different points distributed axially on a flat plate. With five thermocouples, the movement of the scale can be shown by the differences in the fouling resistances. Besides, the differences in the growth rate due to a developing thermal boundary layer can also be seen. The experiments were performed with the Reynolds number ranging from 11,000 to 34,000, corresponding to flow velocities in the test section of between 0.3 and 1.0 m/s. The calcium sulfate solution used was supersaturated, the degree of supersaturation ranging from 40–70%.

**BACKGROUND THEORY**

As already stated, scaling occurs when salts dissolved in the process fluid crystallize on a heat transfer surface. Three basic steps are necessary for crystallization to occur: the attainment of supersaturation, formation of nuclei, and growth of crystals.

**Supersaturation**

The degree of supersaturation, $S$, is often used as a measure of supersaturation and is expressed as a ratio of the bulk concentration, $C_b$, to the saturation concentration, $C_s$. In heat transfer equipment, supersaturation may be achieved by either evaporating a solution beyond the solubility limit of a dissolved salt or heating a solution that contains a dissolved salt of inverse solubility nature to a level above its solubility temperature. The latter is responsible for supersaturation conditions in most sensible heat exchangers and is of interest in this work.

**Nucleation**

Nucleation refers to the process by which the smallest stable aggregates of a crystalline phase are formed in a crystallizing system. These minute particles then act as centers of crystallization. The process of nucleation may either occur spontaneously or be induced artificially; that is, the energy required to form new surfaces is reduced by external factors, such as the presence of impurities. When nucleates form without being aided, the process is called *homogeneous nucleation*; nucleation that is induced by foreign bodies is known as *heterogeneous nucleation*. It is this type of nucleation that is expected to occur in heat exchangers. The inducement may come from the presence of a surface, such as that provided by foreign particles. The rate of heterogeneous nucleation is given as [9]:

$$J = A' \exp \left( - \frac{16\pi N S^2 \sigma^3}{3R_g T_i^3 (ln \beta)^2} \right)$$

(1)

where $A'$ is the pre-exponential factor, $N$ is the Avogadro’s constant, $V_m$ is the molar volume, $\sigma$ is the interfacial tension between the foreign surface and the nucleating substance, $R_g$ is the gas constant, and $T_i$ is the interface temperature. It is evident from Eq. (1) that the rate of nucleation is governed by three variables: degree of supersaturation, $S$, interface temperature, $T_i$, and interfacial tension, $\sigma$. The interfacial tension is a material-dependent property that is strongly dependent on the condition of the surface. Hence, some surfaces may enhance nucleation, while others would offer resistance. In this study, efforts were made to keep the condition of the surface constant between experiments.

**Crystal Growth**

Minute crystal particles that are formed during nucleation subsequently grow into crystals of visible sizes. For growth to occur, a series of processes have to take place. Mullin [14] has identified six processes that may be taking place simultaneously when an electrolyte crystallizes from an aqueous solution. The six stages can be compounded into two main mechanisms: the transport of ions from the bulk to the liquid-crystal interface, and, at the surface, the integration of ions into the crystal lattice.

The transport of ions is normally modeled as:

$$\frac{dm'}{dt} = \beta (C_b - C_i)$$

(2)
where \( m' \) is the mass deposited per unit area, \( C_b \) is the concentration of the ions in the bulk, and \( C_i \) is the concentration of the ions at the solid-liquid interface. In the case of calcium sulfate, \( Ca^{2+} \) and \( SO_4^{2-} \) ions are transported from the bulk to the solid-liquid interface. Once at the interface, the \( Ca^{2+} \) and \( SO_4^{2-} \) ions are built into the crystal lattice to form crystals of calcium sulfate. The accumulation of mass resulting from this reaction is given by:

\[
\frac{dm'}{dt} = k_r (C_i - C_f)^n \tag{3}
\]

where \( k_r \) is the crystal growth rate constant and \( n \) is an index, usually determined empirically. From a theoretical analysis, Kono [15] showed that this index depends on the number of types of ions taking part in the reaction. Using the logic presented in [15], \( n \) can be taken as two for CaSO₄ crystallization. However, several researchers have reported that for CaSO₄ crystallization \( n \) can range from two to four, depending on experimental conditions [9]. For the experiments reported here, it will be shown later that \( n = 2 \).

The rate constant, \( k_r \), depends on temperature, and this dependency is described by the Arrhenius expression [16]:

\[
k_r = k_{re} \exp \left( \frac{-\Delta E}{R_f T_i} \right) \tag{4}
\]

where \( k_{re} \) is the pre-exponential constant, \( \Delta E \) is the activation energy, and \( T_i \) is the temperature at the solid-liquid interface. Bohnet [8] obtained \( k_{re} \) as 22.15 m⁴/kg s and \( \Delta E = 40.4 \times 10^4 \) J/mol. Krause [17] reported a value of 7.07 m⁴/kg s for \( k_{re} \) and 37.1 \times 10^4 J/mol for \( \Delta E \). When the values obtained in [8] and [17] are used in Eq. (4), the difference in \( k_r \) is zero at 74°C. Mori et al. [12] obtained the activation energy as 62.0 kJ/mol. The above values represent average values for a cluster of crystals. Linnikov [9] determined the activation energy for one of the faces of a single face of calcium sulfate crystal as 61.1 kJ/mol. This value compares well with that obtained by Mori et al. [12].

In experiments, the species concentration at the solid-liquid interface is not known, and it is usually convenient to eliminate it from the analysis. This is normally done by assuming that steady-state conditions exist at the solid-liquid interface, resulting in Eqs. (2) and (3) being equal. With the index \( n = 2 \), it can be shown that eliminating \( C_i \) from these equations results in the rate of mass accumulation per unit area taking the form [17]:

\[
\frac{dm'}{dt} = \beta \left[ \frac{1}{2} \left( \frac{\beta}{k_r} \right) \right] (C_b - C_f) - \sqrt{\frac{1}{4} \left( \frac{\beta}{k_r} \right)^2 + \left( \frac{\beta}{k_r} \right) (C_b - C_f)} \tag{5}
\]

In terms of the thickness of the scale layer, the mass deposited per unit area is:

\[
m'(x, t) = \rho_f \delta_f (x, t) \tag{6}
\]

where \( \rho_f \) and \( \delta_f \) are the density and thickness of the layer, respectively. Further, the resistance of the scale layer is given by:

\[
R_f (x, t) = \frac{\delta_f (x, t)}{\lambda_f} \tag{7}
\]

with \( \lambda_f \) being the thermal conductivity of the scale.

Deposit formation in crystallization is controlled by two parameters: \( \beta \) and \( k_r (C_b - C_f) \). When \( \beta \gg k_r (C_b - C_f) \), the surface reaction is the controlling mechanism, and the mass flux is given by Eq. (3), with \( C_i = C_b \). On the other hand, when \( k_r (C_b - C_f) \gg \beta \), mass transfer will control the process, and the mass flux will be given by Eq. (2), with \( C_i = C_f \). The mass transfer coefficient depends on the flow conditions and geometry, and it can be obtained from published correlations. For a fully turbulent pipe flow, the Sherwood number is given as [18]:

\[
Sh = 0.023 Re^{0.8} Sc^{0.33} \tag{8}
\]

with the Sherwood number, \( Sh = \frac{\delta_b}{D_l} \), and the Schmidt number, \( Sc = \frac{\mu}{\rho D_l} \). In the Sherwood and Schmidt number expressions, \( D_l \) is the hydraulic diameter of the test section, \( D_l \) is the solution diffusion coefficient, and \( \mu \) is the fluid dynamic viscosity. Entrainment effects are accounted for by following guidelines similar to those for estimating the heat transfer coefficient, as given in [18]. Two equations are given in [18] depending on the dimensions of the tube. For the conditions existing in the problem under consideration, the type of equation to use has been selected on the basis of the initial surface temperature, as explained in [19]. Therefore, Eq. (8) can be expressed as:

\[
Sh = 0.023 Re^{0.8} Sc^{0.33} \left( 1 + \frac{6 \delta_b}{x} \right) \tag{9}
\]

for \( 20 < \frac{x}{\delta_b} < 60 \). To use these relationships, knowledge of the physical properties of calcium sulfate solution and diffusivity of CaSO₄ in water is needed. These values (taken from [8]) are diffusivity \( D_l = 1.057 \times 10^{-9} \) m²/s, density \( \rho_1 = 991 \) kg/m³, and dynamic viscosity \( \mu_1 = 614 \times 10^{-6} \) Pa s.

**EXPERIMENTS**

**Experimental Setup**

The process of scaling is very sensitive to external factors, and thus puts strenuous demands on the design of a test apparatus for scaling experiments. It is imperative that the walls of the experimental setup be made of materials inert to the scaling species being investigated. In this regard, the material selected for the piping was poly vinyl chloride (PVC), and for the same reason, the pump chosen had all of its components made of plastic. A closed system was opted for to prevent impurity contamination and evaporation of water from the system. Another important consideration is the thorough cleaning of the experimental setup at the end of each experiment. The apparatus was...
made of a series of short pipes connected together by threaded couplings. This made it possible for the pipes to be dismantled and cleaned using a high-pressure pump.

A test apparatus meeting the above requirements was designed and constructed (see Figure 1). The main parts of the apparatus are a centrifugal pump, a rotameter, a double pipe heat exchanger, and the measuring section. The double pipe heat exchanger was used to cool the solution after being heated in the test section. In the next subsection, a detailed description of the measuring section is given.

**Measuring Section**

The measuring section consisted of a stainless steel rectangular channel with internal dimensions of 620 mm \(	imes\) 46 mm \(	imes\) 16 mm. Provisions were made to have the channel optically accessible so that progress of the scale development could be observed. The channel had windows of perspex glass on the sides and top. A section of the steel, 600 mm \(	imes\) 14 mm, was removed from the bottom of the channel to accommodate the heated surface. A copper plate provided the heated surface and was fastened to the bottom of the channel. The plate was heated by a cylindrical WATLOW heater, which was inserted in the plate 20 mm below the surface. The heater was 600 mm long and had an outer diameter of 10 mm. There was an unheated section on either side of the heater, 60 mm on the upstream side and 5 mm on the downstream side. The heater was able to supply up to a maximum heat density of 220 kW per m\(^2\) of rod. The bottom and the sides of the copper plate were insulated with glass wool. Five thermocouples were placed at different axial positions in the center of the plate. Each thermocouple was located 2 mm below the surface. Another five thermocouples were positioned in the bulk at axial positions corresponding to those in the plate, as shown in Figure 2. A cross-section at one of the measuring points is shown in Figure 3. This figure also shows how the copper plate was thermally isolated from the steel housing by PTFE (Teflon) of 5 mm thickness.

The length of the measuring section was selected to ensure that a part of the section would have hydrodynamic and thermal conditions that are fully developed. The experiments were conducted under turbulent flow conditions, turbulence being the flow regime in industrial heat exchangers. For turbulent flow, fully developed conditions are attained after approximately ten diameters [20]. This means that fully developed conditions in the measuring section is attained after about 250 mm.

**Experimental Methods**

A supersaturated solution of calcium sulfate was continuously pumped in the loop. The solution was made by mixing calcium nitrate tetrahydrate \([\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}]\) and sodium sulfate \([\text{Na}_2\text{SO}_4]\). These chemicals (obtained from Merck), were chosen because of the ease with which they dissolve in water. When these two chemicals are separately dissolved in water and...
then mixed, the following balanced equation results:

\[
\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 \leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaNO}_3 + 2\text{H}_2\text{O} \quad (10)
\]

Calcium sulfate is an inverse solubility salt, while sodium nitrate is a normal solubility salt. Under the stated conditions, the solubility of calcium sulfate would decrease toward the heated plate, and that of sodium nitrate would increase. Therefore, only calcium sulfate is expected to crystallize and form deposits on the plate. Calcium sulfate is known to crystallize in three phases: anhydrite (CaSO_4), hemihydrate (CaSO_4 · 1/2H_2O), and dehydrate or gypsum (CaSO_4 · 2H_2O) [21]. It is important to point out that the formation of gypsum according to Eq. (10) depends on operational conditions. The formation of gypsum may be affected by impurities, other salts, and temperature range. Gypsum is the usual precipitating phase in the temperature range 40°C to 98°C, while anhydrite and hemihydrate are the species likely to precipitate above 98°C. Under the conditions of the reported experiments, gypsum is the phase that is most likely to form crystals on the heated plate.

**Preparation of Solution**

Calcium sulfate solution was prepared by mixing the sodium sulfate and calcium nitrate solutions. The sodium sulfate and calcium nitrate solutions were prepared from the respective solids. For a given concentration of calcium sulfate, Eq. (10) was used to calculate the required moles of solute of Na_2SO_4 and Ca(NO_3)_2 · 4H_2O. The calculated mass of each chemical was then weighed using a Sauter scale. Thereafter, the chemicals were separately dissolved in one liter of demineralized water. The demineralized water used had an electrical conductivity of 100 µS/cm at 40°C, which is the temperature of the solution at entry to the test section. First, the Na_2SO_4 solution was poured in a tank containing demineralized water weighing approximately 35 kg. After thorough mixing with a stirrer, the Ca(NO_3)_2 · 4H_2O solution was added to the tank. The solution was stirred thoroughly for about one minute to ensure good mixing. Enough water was then added to the tank until the scale reading was 50 kg. The density of the solution, at operating temperature, is 991 kg/m^3, making the volume of the solution approximately equal to fifty liters.

The prepared solution was examined for spontaneous crystallization. Spontaneous crystallization takes place when the solution is highly supersaturated and is likely to affect the scaling process by reducing the induction time and changing the morphology of the crystal layer. At high supersaturation of CaSO_4, Sheikholeslami and Ong [22] obtained crystals that formed with no induction period and appeared to look like a “flaky and flowery” fine powder. For the experiments reported in this paper, it will be shown that at low supersaturation (40%), spontaneous crystallization did not take place during the runs. At higher supersaturation levels, however, the possibility of spontaneous crystallization was manifested by the reduction in induction times.

The setup was filled with the solution and the pump switched on. The solution was circulated for about 30 mins with the heater off. This was done so that dissolved and trapped air could find their way to the deaerators and leave the system. Next, the desired flow rate was set by regulating the flow using a bypass line and a valve placed at the outlet of the pump. Power for the heater was switched on by setting the voltage regulator (variac) to the required voltage. Next, the valve for the cooling water was opened, and the desired cooling water flow rate set. Finally, the computer-based data acquisition system was started.

For each experiment, the variables measured were the bulk and wall temperatures, solution conductivity, voltage, and current of the heater. All of the temperatures were measured using the THERMOCOAX TK105/25/D thermocouple of type K. The thermocouples were connected to a terminal block and then to a personal computer. Workbench software by National Instruments was used as the acquisition software.

The change in concentration of the solution was monitored by measuring the electrical conductivity of the solution. Electrical conductivity is a measure of the total amount of ions present in a solution. Besides the water ions, the solution used had four different ions: Ca^{2+}, SO_4^{2-}, Na^+, and NO_3^-.

During the process of scaling, the amount of Ca^{2+} and SO_4^{2-} ions decreased, while those of Na^+ and NO_3^- remained constant. To determine CaSO_4 concentration from conductivity measurements, a calibration was performed at different supersaturation levels. The procedure involved making a solution at a certain supersaturation and then gradually reducing the Ca^{2+} and SO_4^{2-} ions while keeping the concentration of Na^+ and NO_3^- constant. At each step, the solution conductivity and its temperature were measured. The conductivity was measured with a conductance cell, which had a cell constant of 0.110 µS/cm. The conductance cell was connected to a C832 conductivity meter. The conductivity meter was connected to a computer for data logging. LabView was used for data acquisition.

Electrical conductivity is a temperature-dependent parameter. It increases with an increase in temperature due to the resulting increase in the ionic movement. This would result in conductivity values changing with temperature, even though the actual ion concentration had not changed. To account for these changes, a thermocouple was attached to the conductance cell, and the temperature measured was used to make corrections in the conductivity values.

At the end of each experiment, samples of scales were collected and examined microscopically. The morphology was studied using a scanning electron microscope (SEM), while X-ray diffraction (XRD) was used to establish the phase of the calcium sulfate.

**Data Reduction**

The rate of deposition is determined by following the changes in the local overall thermal resistance. With an increase in time, a layer of deposit starts forming on top of the heat transfer surface.
As a result, the thermal resistance of the system is changed. The overall thermal resistance increases strongly with an increase in the amount of scale deposited. An equivalent thermal circuit is set up between a point in the wall of the plate and a corresponding point in the bulk fluid. The change in the overall thermal resistance is determined from time-dependent temperature measurements. In reducing the data, it is assumed that the problem is one-dimensional. At any measuring point the following relationship holds:

\[ R_f = \frac{\left( T_w - T_b \right)}{q''} - \frac{\left( T_w - T_b \right)}{q''(t)} \]  

(11)

where \( T_w \) and \( T_b \) are the copper wall and bulk liquid temperatures, respectively, and \( q'' \) is the heat flux. The subscript \( t \) and 0 denote conditions at any time = \( t \) and at time = 0, respectively. The terms on the right hand side represent the overall resistance between the wall and the bulk flow at the measuring positions shown in Figure 2. Eq. (11) is used to calculate the resistance due to the deposition of a scale layer on a surface. The heat flux used in Eq. (11) is calculated from numerical simulations reported in [19]. This is necessary in order to take into account the time-varying heat flux. While the power supplied by the heater was constant, the surface heat flux decreased as the scale layer increased due to increased heat leakages. The temperature values were read every minute, and values of \( q'' \) corresponding to those times were used in Eq. (11). The calculated values of \( R_f \) were then averaged after every 60 mins.

**Measurement Uncertainty**

Errors in temperature measurements were estimated to be \( \pm 0.5 \)°C for bulk temperatures and \( \pm 1.0 \)°C for wall temperatures. The uncertainty associated with voltage and current measurements was estimated to be equal to 5\% of the nominal reading. The deposit thickness was measured with a micrometer with an uncertainty of \( \pm 0.1 \) mm. Using the guidelines in [23], the uncertainty in the value of the fouling resistance was calculated to be 10\%.

**EXPERIMENTAL RESULTS AND DISCUSSIONS**

The scaling experiments were performed at three different Reynolds numbers: 11,000, 23,000, and 34,000. Using the geometry of the test section, the applicable dimensionless numbers were calculated and are given in Table 1. The data shown in the table correspond to an initial 40\% degree of supersaturation and bulk temperature \( 40 \)°C.

**Temperatures**

During the duration of the experiment, the bulk temperature was maintained constant at an average of \( 40 \)°C. The wall temperature, on the other hand, varied with position and in time. The wall temperature distribution at the start of the experiment is shown in Figure 4. The initial surface temperature, \( T_{w,init} \), varies from \( 65 \)°C at position 1 to \( 82 \)°C at position 5. The relatively low temperature at position 1 is due to a combination of hydrodynamic entrance effects and the no-heat zone. The presence of a no-heat zone is also responsible for the temperature at position 5 being lower than that at position 4 (Figure 5). In the entrance region, the heat transfer coefficient is very high, leading to more heat being taken away from the plate. It is shown later that the final thickness of the scale layer reproduces this initial wall temperature profile.

The wall temperature increases with time during the experiment, as shown in Figure 5. The changes observed occur because the formation of deposits on the heat transfer surfaces reduces the amount of heat that is taken away by the flowing fluid. The temperature at point 1 remains constant for a long time because few or no crystals form at that position. It is interesting to note how the temperatures change for positions 2–5 below 1500 mins. These changes are due to the formation of nucleates in the vicinity of positions 2–5.

**Solution Conductivity**

Electrical conductivity was used as a measure of the changes in the solution concentration. The conductivity was continuously measured, and the results are shown in Figure 6. In this

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Mass transfer coefficients and associated dimensionless numbers for different Reynolds numbers at position 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>Sc</td>
</tr>
<tr>
<td>11,000</td>
<td>586</td>
</tr>
<tr>
<td>23,000</td>
<td>586</td>
</tr>
<tr>
<td>34,000</td>
<td>586</td>
</tr>
</tbody>
</table>

Figure 4 Initial plate temperatures at different positions for different Reynolds numbers, with initial bulk concentration \( C_{b,init} = 3.0 \times 10^{-5} \) kg/m\(^3\) and bulk temperature \( T_b = 40 \)°C.
Wall temperatures as a function of time at different axial positions, with $Re = 23,000$ and initial bulk concentration $C_{b, init} = 3.0 \text{ kg/m}^3$. As can be seen in the figure, temperature changes have a huge influence on the values of the conductivity. Temperature corrections were made, and the corrected conductivity is plotted along side the measured values. It is clear from Figure 5 that temperature correction removes the variations. Overall, the results show that conductivity decreases with time. The decrease is due to the reduction in the amount of total ions, resulting from the $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ ions. These ions leave the solution to form solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Deposit Analysis

Deposit formation on the plate was monitored by taking pictures at different time instants. Initially, the layer is very porous and appears on the surface of the plate in a non-uniform manner, as shown in Figure 7. Figure 7 shows pictures of the surface of the plate at two different time instants during an experiment. The picture on the left shows the plate in the initial stage of scaling (well past the nucleation phase). Only some portions of the plate are covered with scale (lighter spots). In the picture on the right, the entire surface is seen to be covered with a scale layer. Close examination of the pictures shows the scale to appear as an agglomerate of needle-like structures. It is also observed that there is no preferred growth direction for the crystals. This is different from the observations reported in [9], where the gypsum crystals were observed to grow along the heat transfer surface oriented at a small angle from it. This observation may be due to the differences in the flow conditions between the two investigations. In the present work, flow was turbulent, while in [9], the flow was laminar. The presence of a diffusion boundary layer in laminar flow favors the directional growth of crystals, while the absence of a boundary layer in turbulent flow leads to crystals oriented in a random way.

Samples from scale deposits that formed on the plate were collected and analyzed using microscopic techniques. The morphology of the scale was studied using SEM. A typical picture from SEM analysis is given in Figure 8. The figure shows a view of the scale at the liquid-solid interface at the end of an experiment performed with $Re = 23,000$ and an initial bulk concentration, $C_{b, init} = 3.0 \text{ kg/m}^3$. The picture shows the scale to be porous and composed of crystals of various sizes. It is also observed from Figure 8 that some crystals, mostly of smaller size, appear to be loosely attached to the scale structure. These probably are crystals formed elsewhere in the system that then get transported to the top of the scale layer. The source of these crystals may be either bulk crystallization or tiny crystals breaking from the main scale due to fluid shear forces.

On average, however, the scale is dominated by prismatic habits, which are characteristic of calcium sulfate dihydrate (gypsum). That the composition of the scale was gypsum was confirmed using XRD measurements. A sample from the scale was analyzed and the resulting spectrum compared with a spectrum obtained from a standard sample of calcium sulfate dihydrate. The peaks in the two spectrums gave very good agreement.
The structure of the scale deposit as observed in Figure 8 was used to estimate the porosity, density, and thermal conductivity of the sample. The porosity was estimated using area measurements of SEM pictures. The picture is divided into small squares. The porosity is taken as a ratio of squares covering voids to the total number of squares. From this method, porosity is estimated to be equal to 0.4. The density and the thermal conductivity were estimated based on the equations presented in [24]. The scale can be viewed as being made up of pillars of solid CaSO₄·2H₂O interspaced with the CaSO₄ solution. Consequently the resistance calculated from the measured temperatures is a combination of series and parallel resistances due to the solid CaSO₄·2H₂O and CaSO₄ solution. This idealization of the scale layer by pillars is used to estimate the density and thermal conductivity of the scale layer. The density of the scale is given by:

\[ \rho_f = \rho_s (1 - \varepsilon) + \rho_l \varepsilon \]  

(12)

where \( \rho_s \) is the density of solid CaSO₄·2H₂O, \( \rho_l \) is the density of CaSO₄ solution, and \( \varepsilon \) is the porosity. With \( \rho_s = 2030 \) kg/m³, \( \rho_l = 991 \) kg/m³, and \( \varepsilon = 0.4 \), the density of the scale layer is estimated to be \( \rho_f = 1614 \) kg/m³.

The thermal conductivity is estimated by assuming that the solid CaSO₄·2H₂O and liquid CaSO₄ form a parallel arrangement. With such an arrangement, the thermal conductivity can be expressed as:

\[ \lambda_f = \lambda_s (1 - \varepsilon) + \lambda_l \varepsilon \]  

(13)

where \( \lambda_s \) is the thermal conductivity of solid CaSO₄·2H₂O and \( \lambda_l \) is the thermal conductivity of the CaSO₄ solution. Substituting \( \lambda_s = 2.13 \) W/m K and \( \lambda_l = 0.614 \) W/m K in Eq. (13) gives \( \lambda_f = 1.5 \) W/m K.

\[ \begin{align*} &\text{Initial Stage of Scale Deposition} \\ &\text{In the initial stages of scaling, a nucleation front is observed to move from the downstream side to the upstream side. Figure 9 gives a plot of the position of the front at a given time instant for experiments performed at Re = 23,000 and initial bulk concentration } C_{b,init} = 3.0 \text{ kg/m}^3. \text{ Experiment 1 on the right side was performed on a virgin surface. Despite the experiments being performed at similar conditions (velocity, temperature, bulk concentration), the results in Figure 9 indicate significant differences in the induction times. The highest induction times are observed for experiment 1, performed on a virgin surface. The difference observed can be attributed to changes in the surface heat transfer engineering} \\ &\text{vol. 27 no. 3 2006}\end{align*} \]
roughness arising from cleaning. Increased surface roughness may hinder the effectiveness of cleaning, increasing the possibility of tiny crystals remaining on the plate. Such crystals will act as initiation points during the next experiment, thereby reducing the induction time. This result is important to the practicing engineer as it underlines the importance of thoroughly cleaning fouled surfaces. The figure is generated by noting the time when the fouling resistance at a point becomes positive and remains so for the rest of the experiment. The scaling front exists because crystals forming on a heated plate start in regions where the temperature is highest. In those regions, the degree of supersaturation is high and, in accordance with Eq. (1), the nucleation rate will be high. With time, the accumulation of crystals then spreads to regions not yet covered by the deposit. This is observed in the fouling curves presented.

**Growth of Scale**

The rate of growth of calcium sulfate follows Eq. (3). The value of \( n \) has been reported to be between 2 and 4, depending on experimental conditions [9]. For the experiments reported here, the value of \( n \) is determined from concentration measurements. In terms of concentration, Eq. (3) can be expressed as:

\[
\frac{dC_b}{dt} = k_t A (C_b - C_s)^n
\] (14)

Figure 10 shows a plot of \(-\log\left(\frac{dC_b}{dt}\right)\) against \(-\log(C_b - C_s)\). The value of the slope of the line that best fits the data points is 2.2. This shows that under the conditions prevailing in the present study, \( n \) can be taken as equal to 2.

Figure 11 shows the set of graphs obtained for the calculated resistances at the five measuring points. The experiment was performed with \( \text{Re} = 23,000 \), \( C_{b,\text{init}} = 3.0 \) kg/m\(^3\), and \( T_b = 40^\circ\text{C} \). Scrutiny of the curves reveals three distinct regions, indicated in Figure 11 for measuring position 5 as A, B, and C. The three regions represent the stages associated with the scaling process. Region A represents the nucleation period, region B the growth phase, and region C the asymptotic phase.

The first period starts when there is no scale on the plate and ends when the plate contains enough nucleates to form a growing deposit. During this period, the conditions favorable for scale formation are being established. This period depends mainly on the surface condition of the plate, the degree of supersaturation, and the surface temperature. The last two conditions can easily be reproduced. Despite efforts to keep the plate surface condition constant, it was determined that maintaining the same surface quality for different experiments is extremely difficult. This partly explains why it is difficult to reproduce results for the nucleation phase. On the fouling time curve, the nucleation phase is represented by two time periods. The first one is a time period where fouling resistance is zero, which applies when the heat transfer surface is clean. In the second region, the fouling resistance is negative, which happens when nucleates forming on the surface make the surface rough. As a result, the rate of heat transfer is enhanced, and the wall temperatures decrease. Under the stated conditions, the nucleation time is estimated to be equal to between 3,000 to 4,000 mins (depending on position), being the time the fouling curves start rising.

The region covered by B shows that the fouling resistance increases with time. During this period, the thickness of the deposit layer increases as crystals continue forming on the plate. The rate of growth is represented by the gradient of the curves. The gradient is highest at points 3 and 4 and lowest at point 1. At positions 3 and 4, both the rate constant, \( k_t \), and the driving force, \( (C_b - C_s) \), are higher. This is mainly due to the temperature distribution of the liquid-solid interface. The rate constant, \( k_t \), increases with temperature, while the saturation concentration, \( C_s \), decreases with temperature, thereby increasing the driving force.

Finally, there is a region in which the fouling resistance remains reasonably constant. The decay in growth rate is for a small part caused by the decrease of the bulk concentration, \( C_b \). Another possible reason could be the reduction of the interface temperature arising from a decrease in the surface heat flux. The surface heat flux may be reduced due to increased heat losses to the surroundings as scales build up.
Included in Figure 11 is a plot of the solution concentration as a function of time. The concentration curve changes little during the induction period. The small drop noted is probably due to the \( \text{Ca}^{2+} \) and \( \text{SO}_4^{2-} \) ions leaving the solution as a result of nucleates forming on the plate. During the growth period, a distinctive decrease in concentration is noted. This occurs as the process of crystallization reduces the \( \text{Ca}^{2+} \) and \( \text{SO}_4^{2-} \) ions in the solution bulk.

**Rate Constant**

The rate constant is estimated by using the initial slopes of the fouling curves shown in Figure 11. The slope is calculated starting at the time instant when the fouling curve departs from the time axis (when time is approximately 4000 mins). Neglecting removal effects, the rate constant can be obtained from Eq. (3) when expressed as:

\[
k_r = \frac{\rho_f \lambda_f \frac{dR_f}{dt}}{(C_b - C_f)^2}
\]  

where \( \frac{dR_f}{dt} \) is the slope of the fouling curve. Equation (15) holds when in Eq. (3), \( C_f = C_b \) and \( \rho_f \) and \( \lambda_f \) are assumed to be constant. The condition \( C_f = C_b \) is valid when the rate of mass transfer is very high.

The calculated values of \( k_r \) are tabulated in Table 2. Using the information in the table, \( k_r \) is plotted against \( 1/T \), as shown in Figure 12. The value of \( T \) is taken to be equal to the wall temperature \( T_w \). This is justified because at the time instant of interest \( R_f = 0 \) and in view of the high thermal conductivity of copper, the interface temperature is approximately equal to the measured wall temperature. Following Eq. (4), the plotted rate constant values results in the expression:

\[
k_r = 93900 \exp \left(-\frac{7820}{T_i}\right)
\]

Also plotted in the figure are values from experiments of Bohnet [8] and Krause [17] for constant heat flux. On average, the value of the rate constant \( k_r \) obtained from the present experiments is about 20% higher than that reported in [8] and [17]. The energy of activation is about 65 kJ/mol. This value agrees very well with values reported in literature [9, 12].

It should be noted from Tables 1 and 2 that at \( \text{Re} = 23,000 \), values of \( k_r (C_b - C_f) \) are lower than the values of \( \beta \). This means that scaling in this case is mainly controlled by surface reaction effects.

**Final Deposit Thickness**

For the case shown in Figure 11, deposit samples were removed from the plate, and their thicknesses measured at different points with a micrometer. The results are shown in the first row of Table 3. The second and third rows of this table contains the values of fouling resistances from Figure 11 and those calculated using Eq. (7). It can be seen that the values from Figure 11 are higher than those calculated using Eq. (7). The differences may be attributed to the uncertainties in the measured thicknesses and in the estimated thermal conductivity value.

In Figure 13 the final thickness of the scale layer is plotted, together with the initial plate temperature, as a function of axial distance. The estimated uncertainties associated with the thickness and temperature are shown in form of error bars. It can be seen that the thickness profile closely resembles the initial wall temperature. This comes about because of the strong dependence of the growth rate on the reaction rate \( k_r \), which in turn is dependent on temperature (see Eq. (4)).

**Dependency on Velocity**

The influence of flow rate on scaling has been investigated with experiments performed at different velocities: 0.3 m/s, 0.6 m/s, and 1.0 m/s, corresponding to Reynolds numbers of

<table>
<thead>
<tr>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
</tr>
</tbody>
</table>

\[
\begin{array}{cccc}
\text{Measured thickness} & \pm 0.1 \text{ [mm]} & 0.9 & 1.1 & 1.4 & 1.5 \\
\text{Measured fouling resistance} & \times 10^{-4} \text{ m}^2 \text{ K}/\text{W} & 9.6 & 12.9 & 14.8 & 17.0 \\
\text{from Figure 12} & & & & & \\
\text{Calculated fouling resistance} & \times 10^{-4} \text{ m}^2 \text{ K}/\text{W} & 5.5 & 6.1 & 6.3 & 5.8 \\
\text{from Eq. (7)} & & & & & \\
\end{array}
\]

---

Table 2: Slopes and rate constants calculated from fouling curves presented in Figure 11

<table>
<thead>
<tr>
<th>Position</th>
<th>( T_w ) [^{\circ}C]</th>
<th>( C_i ) [kg/m^3]</th>
<th>( \frac{dR_f}{dt} ) [m^2 K/(W s)]</th>
<th>( k_r ) [m^3/(kg s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>80.0</td>
<td>1.93</td>
<td>( 8.1 \times 10^{-9} )</td>
<td>( 2.2 \times 10^{-5} )</td>
</tr>
<tr>
<td>3</td>
<td>83.2</td>
<td>1.92</td>
<td>( 1.12 \times 10^{-8} )</td>
<td>( 2.9 \times 10^{-5} )</td>
</tr>
<tr>
<td>4</td>
<td>84.1</td>
<td>1.92</td>
<td>( 1.15 \times 10^{-8} )</td>
<td>( 2.7 \times 10^{-5} )</td>
</tr>
<tr>
<td>5</td>
<td>82.4</td>
<td>1.92</td>
<td>( 1.10 \times 10^{-8} )</td>
<td>( 2.6 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Figure 12: Rate constant against \( 1/T \) for experiments, with \( \text{Re} = 23,000 \), \( C_{b, ini} = 3.0 \text{ kg/m}^3 \), and \( T_b = 40^\circ C \), compared to [8] and [17].
11,000, 23,000, and 34,000. To ensure that only differences in velocities were studied, the initial wall temperature at each point was maintained constant for each of the experiments. By maintaining the initial temperature distribution at a constant level, the rate constant, $k_r$, and the saturation concentration, $C_s$, were kept constant for the different experiments. To achieve this, the heat input was adjusted so that the initial wall temperature was equal to the temperatures shown in Figure 4. The fouling curves obtained at point 4 for this set of experiments are shown in Figure 14. From this figure, the induction period is observed to be directly proportional to the Reynolds numbers. At low Reynolds numbers, the boundary layer is large while fluid shear is low. The large boundary layer provides a large source of ions, thereby increasing the chances of embryo formation. The low fluid shear implies that the minute particles that manage to form on the plate have a higher chance of remaining there. That would lead to a reduction in the induction period.

It is further observed from Figure 14 that the rates of growth are independent of Re at 11,000 and 23,000. This is to be expected because the growth of calcium sulfate is controlled by a surface reaction mechanism, as already pointed out here and by Ritter [25]. At Re = 34,000, however, the rate of growth decreases by about 20%. Because the interface temperature is the same as in the experiments at low Reynolds numbers, the rate constant does not change. Therefore, the observed drop cannot be attributed to changes in the rate at which crystals are formed. A possible explanation for the drop in the rate of deposit growth could be removal. The high shear stress at high Reynolds numbers most likely makes removal of crystals from the scale layer significant.

**Dependency on Supersaturation**

Experiments were carried out to study the influence of supersaturation on the scaling process. While maintaining the other parameters constant, the bulk concentration was varied. Figure 15 shows fouling curves for various initial supersaturation levels ($S = 1.4, 1.6$, and $1.7$). The estimated uncertainty in the fouling resistance is included in the form of error bars. The graphs show that there is a strong dependence between the induction period and the degree of supersaturation. At $C_{b,\text{init}} = 1.4C_s$, a rather long induction period of up to 4,000 mins is observed. On the other hand, at $C_{b,\text{init}} = 1.7C_s$, the induction period is almost non-existent. The reduction of the induction period at a higher supersaturation is mainly due to the increase in the rate of nucleation at high supersaturation values as predicted by Eq. (1). Another reason may be the high probability of bulk crystallization, both at the solution preparation stage and during startup. With bulk crystallization taking place, particulate fouling also takes place. Particulate fouling has no induction period and might be the dominant mechanism during the initial stage of the experiment with 70% supersaturation. Figure 15 clearly shows that the slope of the fouling resistance curve increases with increasing supersaturation. Again, this is to be expected, because the rate of crystal growth is proportional to the square...
Can be concluded that scaling due to CaSO₄ results in a non-saturation. Studying the deposits formed revealed that the scale shown that the rate of scaling increased with increasing super-saturation. On the other hand, results have period is reduced by lowering the fluid velocity and increasing the deposit thickness. The results have shown that the induction profile of the surface temperature determines the final profile of the degree of supersaturation. It is also seen that the initial will act as initiation points. The rate of crystal growth increases areas where the temperature is high are favorable places for nucleate formation and hence results presented, it is deduced that areas where the temperature of deposit formation, nucleation, and crystal growth. From the parameters are examined regarding their influence on the stages crystallization during the runs.

**CONCLUDING REMARKS**

In this paper, an experimental investigation of scaling on a heat transfer surface has been described. The main parameters that affect scaling are surface temperature, flow velocity, and degree of supersaturation. The crystallization of calcium sulfate dihydrate on a flat plate has been studied, focusing on how the main parameters influence the overall process of scaling. These parameters are examined regarding their influence on the stages of deposit formation, nucleation, and crystal growth. From the results presented, it is deduced that areas where the temperature is high are favorable places for nucleate formation and hence will act as initiation points. The rate of crystal growth increases with increasing surface temperature. It is also seen that the initial profile of the surface temperature determines the final profile of the deposit thickness. The results have shown that the induction period is reduced by lowering the fluid velocity and increasing the degree of supersaturation. On the other hand, results have shown that the rate of scaling increased with increasing supersaturation. Studying the deposits formed revealed that the scale was made up of an assemblage of crystals of different sizes. It can be concluded that scaling due to CaSO₄ results in a non-uniform porous scale with a profile that reproduces the initial surface temperature distribution.

**NOMENCLATURE**

- \( A \) surface area, m²
- \( A' \) pre-exponential factor, 1/m³ s
- \( C_b \) bulk concentration, kg/m³
- \( C_{b,init} \) initial bulk concentration, kg/m³
- \( C_i \) concentration at solid-liquid interface, kg/m³
- \( C_s \) saturation concentration, kg/m³
- \( d_b \) hydraulic diameter, m
- \( D_l \) solution diffusion coefficient, m²/s
- \( \Delta E \) activation energy, J/mol
- \( J \) rate of nucleation, 1/m³ s
- \( k_r \) rate constant, m³/kg s
- \( k_{ro} \) pre-exponential factor, m³/kg s
- \( m' \) mass deposited per unit area, kg/m²
- \( n \) growth rate order index
- \( N \) Avogadro's number, molecules/mol
- \( q'' \) heat flux, W/m²
- \( R_f \) fouling resistance, m²K/W
- \( R_g \) gas constant, J/mol K
- \( \text{Re} \) Reynolds number
- \( S \) degree of supersaturation
- \( S_c \) Schmidt number
- \( S_h \) Sherwood number
- \( t \) time, s
- \( T \) temperature, K
- \( T_b \) bulk temperature, K
- \( T_i \) solid-liquid interface temperature, K
- \( T_w \) wall temperature, K
- \( V_m \) molar volume, m³/mol
- \( x \) axial distance, m
- \( x_{front} \) position of scale front, m

**Greek Symbols**

- \( \beta \) mass transfer coefficient, m/s
- \( \delta_f \) fouling thickness, m
- \( \epsilon \) porosity
- \( \kappa \) solution conductivity, mS/m
- \( \kappa_{corr} \) temperature-corrected solution conductivity, mS/m
- \( \kappa_{meas} \) measured solution conductivity, mS/m
- \( \lambda_f \) thermal conductivity of fouling, W/m K
- \( \lambda_l \) thermal conductivity of liquid, W/m K
- \( \lambda_s \) thermal conductivity of solid, W/m K
- \( \mu_f \) fluid viscosity, Pa s
- \( \rho_f \) density of fouling, kg/m³
- \( \rho_l \) density of liquid, kg/m³
- \( \rho_s \) density of solid, kg/m³
- \( \sigma \) interfacial tension, N/m

**REFERENCES**


Misheck Mwaba obtained his Ph.D. in 2003 from Eindhoven University of Technology, the Netherlands. He obtained his B.Eng. degree in 1989 from the University of Zambia and his M.Sc. degree in 1992 from UMIST, Manchester, UK. His MSc. degree thesis was on the prediction of stresses in a solidifying melt. For his Ph.D., he worked on the problem of fouling in industrial heat exchangers, focusing on the problem of scaling in cane sugar factories. He is currently working as a Postdoc at Carleton University, Ottawa, Canada. His main research interests are in fouling mitigation and in transport phenomena in Heat Pipes and Fuel Cells. He is a member of the American Society of Mechanical Engineers (ASME) and the Canadian Society for Mechanical Engineering (CSME).

Camilo Rindt received his M.Sc. and Ph.D. degrees from Eindhoven University of Technology, the Netherlands. Until the end of 1990, he worked in the field of biomechanics. Since 1991, he has been a lecturer on thermal transport phenomena in the field of energy technology. His main research interests are in the fields of conjugate heat transfer, radiation modeling, and fouling of heat exchangers. Regarding the latter topic, he is focusing on the fouling problems in waste incinerators and sugar plants.

Anton van Steenhoven is a professor of Energy Technology at the Department of Mechanical Engineering at the Eindhoven University of Technology, the Netherlands. He gained his Ph.D. in 1979 with a thesis about fluid mechanics of heart valves. His current research interests are the numerical and experimental analysis of fluid flow and heat transfer and its application to the design of energy equipment.

Marius Vorstman is an assistant professor in the Process Development Group of the Department of Chemical Engineering at the Eindhoven University of Technology, the Netherlands. He graduated from the same university in 1965. His research interests are in crystallization and separation technology.