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CRYSTALLISATION FOULING OF MIXED SALTS DURING CONVECTIVE HEAT TRANSFER AND SUB-COOLED FLOW BOILING CONDITIONS

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ABSTRACT

The mechanisms of mixed salt crystallisation fouling on heat transfer surfaces have been investigated for convective and sub-cooled flow boiling heat transfer. Effects of various operating parameters such as solution composition and hydrodynamics of the system, on crystallisation fouling of mixtures of calcium sulphate and calcium carbonate have been studied experimentally. The results of the experiments were used to develop a mechanistic model for prediction of fouling resistances. Model predictions were compared with the measured experimental data when calcium sulphate and calcium carbonate form and deposit on the heat transfer surface, simultaneously. Deviations ranging from 6% to 25% were observed which confirm the suitability of the model. Finally, the crystalline samples were analysed using Scanning Electron Microscopy, X-Ray Diffraction and Ion Chromatography techniques. Fractal analysis performed on Scanning Electron Microscopy photographs of the deposits was used to quantify deposit characteristics by introducing the fractal dimension as a new characteristic quantity.

INTRODUCTION

Scale deposition is one of the most important and serious problems faced by heat transfer equipment during operation. This phenomenon is known as a major engineering problem in process industries, since deposits on heat transfer surfaces create a barrier to the transmission of heat, increase pressure drop and promote corrosion of tube material. Scales sometimes limit or block pumps, tubing, casing, flow lines, heaters, tanks and other heat transfer or production equipment and facilities.

While fouling has already been recognized as one of the major unsolved problems in forced convective heat transfer, it is even more severe for boiling heat transfer. When the fluid is boiling on a surface, the fouling resistance may be many times greater than it would have been if boiling had been suppressed. Due to the mechanism of micro-layer evaporation, the local concentration at the heat transfer surface can be considerably increased, causing the acceleration of scale deposition.

Scale deposits are classified according to the physical and chemical processes that occur. Fouling occurring on the heat transfer surfaces of boilers and evaporators is usually a crystalline deposition caused by precipitation from solution of mineral salts which have inverse solubility curves. Since the thermal conductivity of these crystalline deposits is very low,

deposits of these salts will reduce the overall heat transfer coefficient significantly.

Mixed salt crystallisation fouling on heat transfer surfaces during convective heat transfer and sub-cooled flow boiling is a very complicated process. Its mechanism relates to many subjects such as momentum, heat and mass transfer, chemical kinetics, material science, etc which makes it difficult to express in mathematical terms. Hence, theoretical analysis alone can not provide a general equation for predicting fouling rates. It is, therefore, essential to understand the fundamental processes and parameters that affect the rate of fouling on heat transfer surfaces experimentally, before developing a semi-empirical model.

No information is available in the literature about crystallisation fouling of mixed salts and about the effect of operating parameters on this phenomenon, during sub-cooled flow boiling conditions. Furthermore, only a few experimental and theoretical investigations on crystallisation fouling of calcium sulphate or calcium carbonate under sub-cooled flow boiling conditions can be found in the literature. Hence there is a lack of experimental evidence and physical understanding with respect to this subject.

The objective of this study was to investigate crystallisation fouling phenomena for salt mixtures under convective heat transfer and sub-cooled flow boiling conditions and to suggest a mathematical model for prediction of this phenomenon. In the present investigation, the effects of various operating parameters such as solution composition and hydrodynamics of the system on crystallisation fouling of mixtures of calcium sulphate and calcium carbonate have been studied experimentally. The results of the experiments were used to develop a mechanistic model for prediction of fouling resistances, caused by crystallisation of mixed salts, under convective heat transfer and sub-cooled flow boiling conditions.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The measurements were performed in a flow circuit which included two parallel annular test heaters as shown schematically in Fig. 1. Each test section consisted of a 400 mm long cylindrical stainless steel rod with a 99.1 mm electrically heated section located 216 mm from the flow entrance. This test heater was manufactured by Ashland

Chemicals according to specifications by Heat Transfer Research Incorporated (HTRI). It was located concentrically within a surrounding vertical pipe and the test liquid was flowing through the annulus in upward direction.

Four stainless steel sheathed thermocouples were located closely below the surface of the heater rod. Three of these thermocouples were used to obtain information about the surface temperature. The remaining thermocouple was connected directly to a temperature controller. The test heater was connected to an adjustable power supply permitting variation of the heat flux between 0 and 450 kW/m². All experiments were conducted in constant heat flux mode.

The fluid was pumped from a temperature-controlled supply tank through the annular test sections. The flow rates were controlled by two automatic control valves behind the test section, and with the bypass line. The supply tank was maintained at a predetermined temperature with an internal cooling coil and three temperature-controlled band heaters on the external surface. The bulk temperature was measured with thermocouples located in mixing chambers before and after the test section.

corrosive nature of some of the electrolytes used in this investigation, all wetted parts were manufactured from stainless steel.

In this investigation, aqueous solutions of mixtures of calcium sulphate and calcium carbonate, the most common constituents of crystals formed on heat transfer surfaces, were used as test solutions. The range of the pH in the present investigation was between 6.5 and 7.5. Calcium nitrate and sodium carbonate were used to adjust the total alkalinity. The solubilities of the electrolytes in water were predicted using the SOLMINEQ88 software and the physical properties of the solutions were taken from the International Critical Tables (1926-1933). The criteria for selecting the salts were based on the solubility of the salts, the valence and size of the respective ions. The range of the experimental parameters in the present investigation is given in Table 1.

Table 1 Range of investigated operating parameters

v (m/s)	T_b (°C)	\dot{q} (kW/m ²)	[CaSO ₄] (g/l)	[T.A.] (g/l)	P (kPa)
0.5-2	50-90	100-450	1-2.5	0.0-0.3	105-150

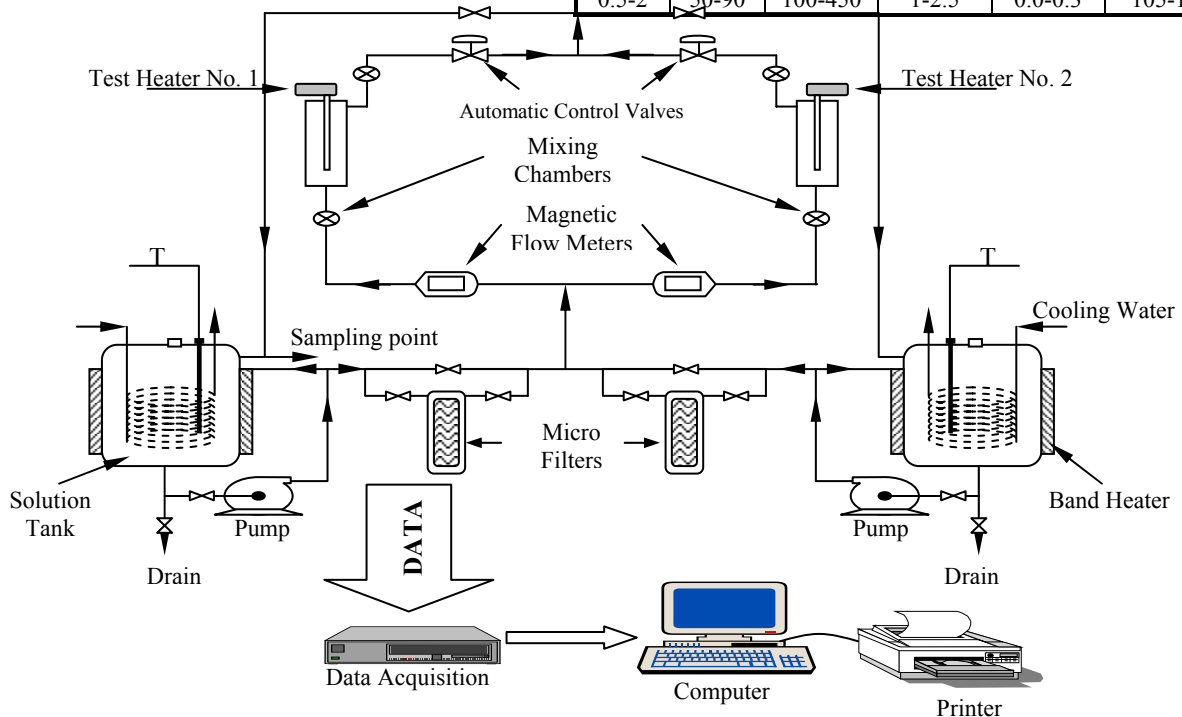


Fig. 1 Schematic diagram of test rig

A data acquisition system was used to measure temperatures, velocities and heat fluxes at pre-selected time intervals.

The solution was passed through a filter ("Betapure", Cuno Process Filtration Products Inc.) for removal of crystals and particulates in the solution before being fed to the test section. The presence of suspended material in the test solution can affect the dominant mechanism of fouling (Najibi et al., 1997). The filter had a rating of 2 μ m and was 0.5 m long. It was made of polypropylene and polyethylene. Due to the

EXPERIMENTAL RESULTS AND DISCUSSION

Operating conditions have a significant effect on the deposition of salts from solution by crystallisation on the heat transfer surface. Sometimes it is possible to reduce the fouling rate by controlling and adjusting the operational parameters. Hence a series of experiments was designed to investigate the effects of operating parameters such as fluid velocity, heat flux, surface and bulk temperature, and bulk

concentration on the fouling rate during convective heat transfer and during sub-cooled flow boiling. The effect of operating conditions on the rate of fouling must be determined by isolating one parameter at a time. Therefore, it was necessary to conduct experiments under controlled conditions, where certain parameters can either be constant or where the effects of these parameters are minimised.

During sub-cooled flow boiling of aqueous solutions, heat transfer occurs by convective and nucleate boiling simultaneously. The total heat transfer surface can be divided into two parts (Chen, 1966): the area with active bubble nucleation sites and the remaining area where forced convection predominates. As a result, scale formation on the heat transfer surface during sub-cooled flow boiling is a combination of the following two mechanisms:

1. In the area that is affected by the vapour bubbles, fouling occurs mainly due to the mechanism of bubble formation and micro-layer evaporation.

2. In the remaining area, fouling takes place by forced convection.

The nucleate boiling fraction, NBF, may be interpreted as a measure of the fraction of the heat transfer area affected by bubble growth mechanisms. It can be defined as (Najibi et al., 1997):

$$NBF = \frac{\alpha_{nb} S}{\alpha_{fb}} \quad (1)$$

For prediction of the flow boiling heat transfer coefficient, a modified version of the Chen model, which has been accepted as one of the best available correlations for pure fluids and mixtures (Najibi, et al., 1997) can be used, i.e.:

$$\alpha_{fb} = \alpha_c F + \alpha_{nb} S \quad (2)$$

For calculation of NBF, the predicted clean heat transfer coefficients at the beginning of each run can be used. Calculated values of NBF for the present experimental conditions at 80 °C are given in Table 2.

Table 2 NBF for the present experimental conditions

\dot{q} (kW/m ²) \ V(cm/s)	100	200	300	400
40	0.0007	0.270	0.460	0.570
60	0.0	0.090	0.301	0.436
80	0.0	0.011	0.166	0.313
100	0.0	0.0002	0.071	0.209

Table 2 shows that for the lowest heat flux and for the highest flow velocities, heat transfer occurs almost exclusively by forced convection. For all other velocities and heat fluxes, most of the heat transfer still occurs by forced convection. Therefore, it is expected that the forced convection mechanism significantly contributes to the total deposition rate.

The effects of operating variables on the rate of crystallisation fouling of mixed salts are discussed detail by Helalizadeh (2002).

DEVELOPMENT OF THE DEPOSITION MODEL

The deposition process on heat transfer surfaces where heating, cooling or evaporation of aqueous solutions containing various amounts of dissolved salts are involved, is a frequent engineering problem. It is hence necessary to analyse the possibility and severity of scale deposition before heating or cooling of process fluids or starting any water injection project in an oil reservoir. A reliable scale prediction model would be very useful for this important task. It could also be an effective tool to make decisions about the types of water treatment which may be applied to prevent scaling problems, i.e to determine the kinds and amounts of scale inhibitors that must be used in order to prevent or at least reduce the rate of scale deposition.

Several investigators have studied scale formation mechanisms in an effort to develop predictive models to be used for preventive treatments. Most of these studies have been devoted to fouling of single salts during forced convective heat transfer and little information is available on fouling during sub-cooled flow boiling. Najibi et al. (1997) investigated fouling during sub-cooled flow boiling of pure calcium sulphate and calcium carbonate. Their results however, can not be applied for scale formation of salt mixtures from aqueous solutions.

One area lacking detailed information is the mathematical description of mixed salt crystallisation fouling taking place on heat transfer surfaces. In this section, the formulation of a basic model for prediction of the deposition process, which can be used to identify the rate-controlling step, will be described. Such a mathematical model should include fluid dynamics, heat transfer, mass transfer and chemical reaction processes that give rise to the presence of fouling precursors and the subsequent events to form insoluble deposits.

To model the formation of deposits and to describe the effect of process parameters on this phenomenon, a volume element of fluid is considered as shown in Fig. 2. The model calculations include the appropriate conservation equations for the key species, which result in a series of mathematical equations that must be solved co-currently. Since the primary interest of this work is for flow in an annulus, the continuity equation applicable for a radial system is derived.

Applying a material balance for the reacting materials over the considered differential element, and assuming no mass is generated or lost, the amount of net mass change in the element during a time increment dt can be expressed as:

$$\dot{m}_{in} - \dot{m}_{out} = \frac{dm_d}{dt} \quad (3)$$

where

$$\dot{m}_{in} = \dot{V} C \quad (4)$$

$$\dot{m}_{out} = \dot{V} (C - dC) \quad (5)$$

and

$$\begin{aligned} \frac{dm_d}{dt} &= \frac{d(\rho_d V_d)}{dt} = \rho_d \frac{dV_d}{dt} = \rho_d \frac{\pi[(r+dr)^2 - r^2] dx}{dt} \\ &= \rho_d \frac{\pi[r^2 + (dr)^2 + 2rdr - r^2] dx}{dt} \end{aligned} \quad (6)$$

Since $(dr)^2 \ll 2rdr$,

$$\frac{dm_d}{dt} = \rho_d \frac{2\pi r dr dx}{dt} \quad (7)$$

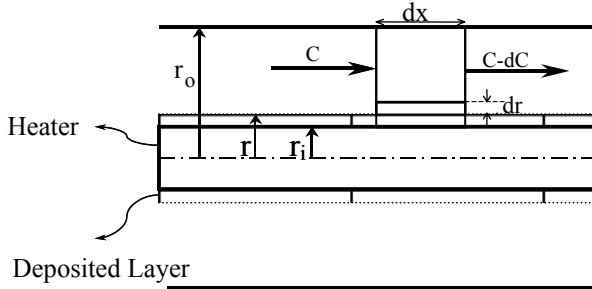


Fig. 2 Elemental volume of fluid flow in an annulus

Substitution in Eq. (3),

$$\dot{V} C - \dot{V} C + \dot{V} dC = \rho_d \frac{2\pi r dr dx}{dt} \quad (8)$$

Assuming that $dx/dt=v$ and after some mathematical manipulations, the continuity equation for the considered system results in,

$$\frac{dC}{dr} = \frac{2\rho_d r}{r_0^2 - r^2} \quad (9)$$

It is obvious that the radius of the deposited layer on the heat transfer surface, r , is a function of time, and increases as fouling proceeds. Therefore it is necessary to calculate this variation, according to the chain rule;

$$\frac{dr}{dt} = \frac{dr}{dC} \cdot \frac{dC}{dt} \quad (10)$$

The rate of change of concentration is generally determined on the basis of a unit volume, but the deposition rate needs to be expressed in terms of unit wall surface. Hence, the rate of change of concentration can be related to the rate of deposition according to:

$$\dot{m}_d = \frac{dC}{dt} \times \frac{\text{element volume}}{\text{element surface area}} = \frac{dC}{dt} \cdot \frac{V_e}{A_e} \quad (11)$$

Therefore,

$$\frac{dC}{dt} = \dot{m}_d \frac{A_e}{V_e} = \dot{m}_d \frac{2\pi r dx}{\pi(r_0^2 - r^2) dx} = \dot{m}_d \frac{2r}{r_0^2 - r^2} \quad (12)$$

By substitution of Eqs. (9) and (12) in Eq. (10),

$$\frac{dr}{dt} = \frac{r_0^2 - r^2}{2\rho_d r} \dot{m}_d \frac{2r}{r_0^2 - r^2} = \frac{\dot{m}_d}{\rho_d} \quad (13)$$

For a small time step, the deposition rate can be assumed constant. Hence by integration, the fouling radius is related to the deposition rate per unit heat transfer area by:

$$r_{d,n} = r_{d,n-1} + \frac{\dot{m}_{d,n-1}}{\rho_d} (t_n - t_{n-1}) \quad (14)$$

where n is the number of time steps.

The equation formulated in this section should be incorporated into the heat balance equation to calculate the fouling resistance. Fourier's law is a well-known equation for calculation of heat transfer by conduction. For heat conduction through the deposited layer, it can be written as:

$$\dot{Q} = -\lambda_d A \frac{dT}{dr} \quad (15)$$

or

$$\frac{\dot{Q} dr}{2\pi r L} = -\lambda_d dT \quad (16)$$

Assuming constant thermal conductivity of the deposit, the above first order ordinary differential equation can be solved with appropriate boundary conditions:

$$q_i = \frac{\dot{Q}}{2\pi r_i L} = \frac{\dot{Q}}{A_i} = \frac{\lambda_d (T_{s,n} - T_{d,n})}{r_i \ln \frac{r_{d,n}}{r_i}} \quad (17)$$

By comparing with Ohm's law in electrical engineering, the fouling resistance is related to the deposit radius through the following equation:

$$R_f = \frac{r_i \ln \frac{r_{d,n}}{r_i}}{\lambda_d} \quad (18)$$

Consequently, combining Eqs. (14) and (18) results in:

$$R_f = \frac{\left(r_i \ln \frac{r_{d,n-1} + \frac{\dot{m}_{d,n-1}}{\rho_d} (t_n - t_{n-1})}{r_i} \right)}{\lambda_d} \quad (19)$$

However, for evaluation of the fouling resistance, it is essential to calculate the deposition rate, \dot{m}_d , of sparingly soluble salts.

CALCULATION OF THE DEPOSITION RATE

For the calculation of the fouling resistance, it is essential to determine the net deposition rate of materials. It is generally believed that the net deposition rate is a combination of the opposing effects of deposition and removal rates:

$$\dot{m}_d|_{net} = \dot{m}_d - \dot{m}_r \quad (20)$$

For the development of the fouling model, it is essential to formulate a physical model for the possible steps taking

place in the overall fouling process, since the physical model and the mathematical analysis provide insights into the fouling mechanism. Fig. 3 represents a crystal of substance A which grows from a solution of A in solvent B . C_b is the concentration of A in the bulk of the solution and C^* is the saturation concentration of this substance. As the crystal surface is approached, the concentration will fall, and at the interface it will have a value of C_i , which is somewhere between C_b and C^* . $(C_b - C^*)$ is the overall supersaturation, while $(C_b - C_i)$ is the mass transfer concentration drop, which provides the driving force for mass transfer. $(C_i - C^*)$ is the true surface supersaturation, which provides the driving force for the surface-growth process.

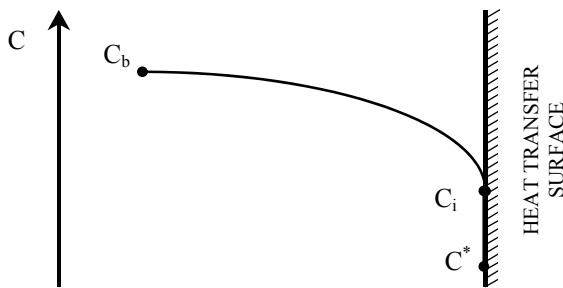


Fig. 3 Concentration of solution as a function of distance from crystal face

To form a deposit at the heat transfer surface, it is necessary that key components are transported from the fluid bulk to the heat transfer surface. In most cases, this occurs by diffusion. It is believed that the rate of mass deposition is equal to the mass flux of reactants carried to the reaction zone and can be expressed in terms of the mass transfer coefficient and the concentration driving force between the bulk of the fluid and the solid-fluid interface. Therefore,

$$\dot{m}_d = \beta(C_b - C_i) \quad (21)$$

where β is the mass transfer coefficient, which is a function of the degree of liquid phase turbulence. It can be calculated using a heat transfer correlation (e.g. Gnielinski, 1986) and the Colburn analogy (1933).

The second step in the formation of fouling deposits is the incorporation of key components into the crystal structure, i.e. the chemical reaction between the ions on the surface of the heat transfer equipment. However, it is evident that this incorporation is a very complicated process. It involves the physics of heterogeneous nucleation of crystals on the heat transfer surface, the chemistry of solid-liquid interfaces, the local chemical thermodynamics and the hydrodynamics of local flow. For this reason adequate mathematical modelling of this step, which completes the crystallisation fouling, is difficult. As suggested by Bott (1995), in order to avoid the problems of taking into account the details of the micro-phenomena by which new material may be incorporated into the crystal structure, it is possible to *lump* these effects together in terms of a *chemical reaction*. The rate of reaction under these circumstances will depend on the concentration

distribution of ions in the region of the interface between liquid and heat transfer surface.

However, the diffusion and reaction steps happen in series. Therefore, the mass flux of reactants to the reaction zone is balanced by the rate of chemical reaction. The rate of chemical reaction will be a function of the supersaturation at the surface, $(C_i - C^*)$, which must be equal to the rate of mass transfer. Assuming n_{th} order chemical reaction,

$$\dot{m}_d = k_r (C_i - C^*)^n \quad (22)$$

Equations (21) and (22) can be combined to eliminate the interface concentrations, i.e.

$$\left(\frac{\dot{m}_d}{k_r}\right)^{1/n} + \frac{\dot{m}_d}{\beta} - (C_b - C^*) = 0 \quad (23)$$

The reaction rate constant is generally a function of temperature. The temperature dependence of the reaction rate constant follows an Arrhenius type equation and can be calculated as follows:

$$k_r = k_o e^{-\frac{E}{RT}} \quad (24)$$

However, the deposition model contains several kinetic and physical parameters that must be determined experimentally. In the present investigation, frequency factors, activation energies, and order of reactions were obtained from batch reactor experiments and/or fouling experimental data. These kinetic constants can be found in Helalizadeh (2002). From the obtained results, it was concluded that the order of two for the proposed chemical reactions is satisfactory. These results also agree with those of previous investigations by Bohnet (1985) and Najibi et al. (1997).

After some mathematical manipulations and taking the negative root of the resulting quadratic equation, Eq. (23) can be expressed as:

$$\dot{m}_d = \left\{ \beta \left[\frac{1}{2} \left(\frac{\beta}{k_r} \right) + (C_b - C^*) - \sqrt{\frac{1}{4} \left(\frac{\beta}{k_r} \right)^2 + \frac{\beta}{k_r} (C_b - C^*)} \right] \right\} \quad (25)$$

Prediction of Deposition Rate of CaSO_4 and CaCO_3

In the previous section, it was assumed that the deposition process of any salt such as calcium sulphate and calcium carbonate takes place in two successive events. Firstly, calcium, bicarbonate and sulphate ions are transported from the bulk to the reaction zone by diffusion through the boundary layer. Then these ions react at the surface to form the crystalline solid phase products, which attach to the surface. These events are the combined effects related to various transport phenomena, chemical kinetics, solubility equilibria and fluid dynamics.

Calculations of the attraction forces in the lattice structure, shear force at the wall, lattice energy of crystalline deposits (i.e. calcium sulphate and calcium carbonate),

kinetic energy of the fluid, and a comparison between these forces confirms that removal can not take place due to the strong forces in the lattice structure. In other words, the removal rate can be neglected for crystallisation fouling (Helalizadeh, 2002).

In the proposed model, the path and sequence of precipitation is chosen based on the saturation index from the highest value of SI to the lowest one and on the basis of a limiting reactant concept. These concepts are compiled in a computer program, which has been written for the model calculations (Helalizadeh, 2002). In the development of simultaneous crystallisation fouling, two important concepts should be considered:

1. Scale components do not precipitate completely sequentially and independent of each other, but more or less co-precipitation takes place. Furthermore, there is a competition between ions for deposition, especially at higher degrees of supersaturation.

2. The more important shortcoming which is found in the literature is that the sequence of scale precipitation is determined based on solubility product values (Allen and Roberts, 1979). This can not be correct for general cases, because the concentration of those ions which form minerals with lower solubility product may be less than the required amount to precipitate, while concentrations of those ions which form minerals with higher solubility product may exceed the amount required to precipitate. In this case, it is obvious that minerals with higher solubility product will precipitate. Therefore, solubility product values can not be the determining factor for the precipitation sequence.

Effect of Boiling on Deposition Rate

The previous sections in this paper have largely focused on crystallisation fouling under convective heat transfer, but scale formation during boiling conditions occurs in equipments such as boilers and evaporators. This problem is more serious during nucleate boiling conditions because of the mechanisms of bubble formation, micro-layer evaporation and bubble detachment.

It is generally believed that when bubbles are formed on a heat transfer surface, the solution becomes supersaturated at the gas/liquid/solid interface. Micro-layer evaporation at the base of the bubbles causes the local supersaturation of salts such as calcium sulphate and calcium carbonate in the liquid beneath the bubbles to increase significantly, which results in the formation of deposits on the heat transfer surface (Najibi et al., 1997).

A bubble detaching from a nucleation site leaves behind a ring of deposit. If the foulant is highly soluble, it may re-dissolve as the bubble departs; if the foulant has a negative temperature coefficient of solubility, the deposit will stay on the heat transfer surface. This process is repeated over a period of time, and therefore, the deposit layer gradually builds up on the surface. The high heat transfer coefficients during boiling conditions are more affected by the formation of an additional heat transfer resistance due to the low thermal conductivity of deposit layers.

In this investigation, it was observed that the fouling characteristics of the sub-cooled flow boiling test fluid were significantly different from those occurring under single phase convective heat transfer conditions. The rate of deposition predicted by Eq. (25) was significantly less than the experimental data. In order to extend the analysis, it is essential to consider the effect of boiling since boiling enhances the fouling of heat transfer surfaces and also the mass transfer phenomenon. The effect of the extra deposition created on the heat transfer surface due to sub-cooled flow boiling is explicitly incorporated into Eq. (25) by including a factor, termed the *enhancement factor*, E . The inclusion of this enhancement factor results in modifying Eq. (25) to:

$$\dot{m}_d = E \left\{ \beta \left[\frac{1}{2} \left(\frac{\beta}{k_r} \right) + (C_b - C^*) - \sqrt{\frac{1}{4} \left(\frac{\beta}{k_r} \right)^2 + \frac{\beta}{k_r} (C_b - C^*)} \right] \right\} \quad (26)$$

E is a multiplier that accounts for the effect of bubble formation and micro-layer evaporation on fouling of heat transfer surfaces. It should be pointed out that bubble formation also disturbs the boundary layer, and therefore increases the mass transfer coefficient significantly.

The enhancement factor, E , was obtained by non-linear regression analysis of the experimental data in the sub-cooled flow boiling region:

$$E = 1 + 80 NBF \quad (27)$$

It can be observed that as the heat flux is increased, the number of active nucleation sites is increased. Consequently the enhancement factor is improved and Eq. (26) predicts that the deposition rate caused by the boiling mechanism is increased. Therefore the total fouling resistance during sub-cooled flow boiling conditions can then be calculated using Eqs. (19) and (26).

VALIDATION OF THE PROPOSED MODEL

In order to test the developed model, the fouling resistances predicted by the proposed model were compared with the experimental data during fouling runs of electrolyte solutions containing calcium, sulphate and bicarbonate ions (Helalizadeh, 2002). The fouling resistances were determined from Eqs. (19) and (26), by assuming the removal rate to be zero whereas the reaction rate constant, k_r , is expressed by Eq. (24) and the mass transfer coefficient of the reactant, β , is calculated using the analogy to a heat transfer correlation (e.g. Gnielinski, 1986).

Typical predictions of the proposed model are compared with the results of an experiment, when CaCO_3 and CaSO_4 form and deposit on the heat transfer surface simultaneously, in Fig. 4.

FRACTAL ANALYSIS

The term *fractal* has been introduced by Benoit Mandelbrot (1977) in 1975 to represent very irregular and

complicated shapes or phenomena having no characteristic length. Roughly speaking, a fractal set is a set that is more irregular than the sets considered in classical geometry. Mandelbrot argues that such geometric abstractions often fit the physical world better than regular arrangements or smooth curves and surfaces.

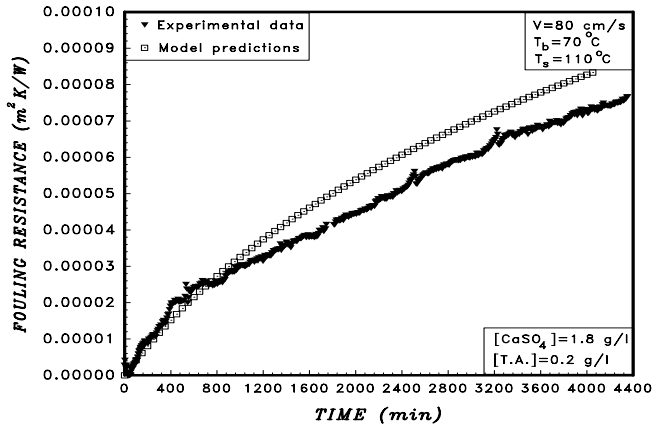


Fig. 4 Comparison of measured and predicted fouling resistances

Fractal theory is used to describe complicated and irregular shapes in nature by introducing a new quantity called the *fractal dimension* (Mandelbrot, 1977), which is a measure of the coarseness and irregularity of a structure. Hence, the fractal dimension may be regarded as an index of irregularity and complexity, that means a shape with a higher fractal dimension will be more complicated than another shape with a lower dimension.

To characterise the structures of aggregates such as crystal deposits, it is essential to measure the *fractal dimension* values. The fractal dimension of a crystal deposit is defined as a number, which quantitatively measures the roughness and irregularity aspect of the deposit. It defines the way in which the crystals occupy their space. Typical methods are Laser Light Scattering (LLS) or photographic methods which give values describing the crystal behaviour.

With respect to fouling investigations, the description of deposit roughness and complexity was of great interest. The concept of fractal theory has hence been used to characterise the surface texture of deposits. This study has been made easier with the advent of new instruments and software based on techniques utilising the availability of large capacity and high speed computers.

The fractal dimensions of the deposits may be a means to quantify the roughness, irregularity and strength of the deposits, i.e. their resistance against erosion by fluid shear forces. In the present investigation, fractal dimensions have been determined for deposits from about 30 experiments at different operating conditions with stainless steel and with modified heat transfer surfaces. Photographs of the deposits obtained by high resolution Scanning Electron Microscopy have been analysed with the OPTIMAS Image Analysis System by means of grey scale intensities of pixels, at the University of Surrey. From these data, fractal dimensions

have been computed using a modified box-counting method by the OPTIMAS software.

The results proved that crystallisation fouling on heat transfer surfaces exhibits fractal geometry. For the same operating conditions, the fractal dimensions for typical deposits of CaSO_4 , CaCO_3 and a $\text{CaSO}_4/\text{CaCO}_3$ mixture were 2.98, 2.56 and 2.85, respectively. The fouling rates for the three experiments were 4.13×10^{-5} , 6.229×10^{-5} and 15.83×10^{-5} ($\text{m}^2 \text{K})/(\text{kW min})$, and the perceived hardness of deposits increased from CaSO_4 via $\text{CaSO}_4/\text{CaCO}_3$ mixture to CaCO_3 . The latter observation agrees with the ranking according to fractal dimensions.

The results also show that the effect of operating conditions on the surface texture, i.e. fractal dimension, is strong. Typical variations of fractal dimension with operating conditions (i.e. heat flux) are given in Table 3. The deposit at the higher heat flux seems to be denser and more compact, hence the fractal dimension is lower for the higher heat flux. Furthermore, it was observed that with decreasing ionic strength, CaSO_4 - CaCO_3 ratio and increasing bulk temperature, the deposit becomes more compact and lower fractal dimensions were found. Experimental results show that deposits possessing lower fractal dimensions were more adherent. In these cases, it was more difficult to remove the deposit, and the fouling resistance during the test runs was higher than those with weaker deposits.

The measured fractal dimensions for modified (Bornhorst et al., 1999) and plain stainless steel surfaces show that this value is higher for treated surfaces than for untreated surfaces, for the same operating conditions. This agrees with previous observations that the deposits which were rarely found on the modified surfaces are more irregular and less compact (Bornhorst et al., 1999).

From the SEM analyses it is concluded that regular deposition, tightly packed and compact structures are formed at higher velocity, heat flux, bulk temperature and surface energy, while irregular, rough, weak and loose deposition is formed at higher ionic strengths and calcium sulphate concentration.

Table 3 Measured fractal dimensions at different heat fluxes

v (cm/s)	\dot{q} (kW/m^2)	T_b ($^\circ\text{C}$)	I (mol/l)	FD
80	200	80	0.088	2.72
80	250	80	0.088	2.68
80	300	80	0.088	2.55
80	350	80	0.088	2.44
80	400	80	0.088	2.41
80	450	80	0.088	2.36

CONCLUSIONS

This investigation was concerned with the mechanisms of mixed salt crystallisation fouling on heat transfer surfaces. The results of the measurements at different conditions were used to develop a mechanistic model for deposition from salt mixtures. The proposed model includes

transport and reaction processes and was developed based on forced convection data. The boiling effect was considered by inclusion of an enhancement factor, E . This model is able to predict all observed trends, i.e. the effect of variation in flow velocity, heat flux, bulk temperature, surface temperature, solution concentration, pressure and boiling phenomenon. The predicted fouling resistances were compared with the experimental data. Quantitative as well as qualitative agreement, i.e. trends, for measured and predicted fouling rates, are good. Considering the errors involved in the determination of physical properties and the approximate nature of the correlations, deviations ranging from 6% to 25% are a satisfactory indication that the proposed model can be recommended for the prediction of fouling resistances for mixed salt solutions.

The concept of fractal theory was used to characterise the structure of the deposits and it was found that the crystallisation fouling on heat transfer surfaces exhibits fractal geometry. Change in operating conditions and deposit composition alter the complexity and roughness of the deposited layer and consequently the fractal dimensions. Regular deposition, tightly packed and compact structures are formed at higher velocity, heat flux, bulk temperature and surface energy, while irregular, rough, weak and loose deposition is formed at higher ionic strengths and calcium sulphate concentration.

NOMENCLATURE

A	Area, m ²
C	Concentration of reacting material, kg/m ³
d	Diameter, m
E	Activation energy, J/mole
E	Enhancement factor, dimensionless
F	Enhancement factor, dimensionless
FD	Fractal dimension, dimensionless
I	Ionic strength, mol/l
k	Reaction rate constant, m ⁴ /kg s
L	Length, m
m	Mass, kg
\dot{m}	Rate of mass deposited, kg/m ² s
NBF	Nucleate boiling fraction, dimensionless
n	Order of reaction, dimensionless
\dot{Q}	Heat transfer rate, W
\dot{q}	Heat flux, W/m ²
R _f	Fouling resistance, m ² K/W
S	Suppression factor, dimensionless
T	Temperature, K
T.A.	Total alkalinity, g/l
t	Time, s
V	Volume, m ³
\dot{V}	Flow rate, m ³ /s
v	Fluid velocity, m/s
x	Thickness, m
Z	Valence of the ion, dimensionless
α	Heat transfer coefficient, W/m ² K
β	Mass transfer coefficient, m/s

λ	Thermal conductivity, W/m K
ρ	Density, kg/m ³

Subscript and Superscript

b	Bulk
c	Convective
d	Deposit
e	Element
fb	Flow boiling
h	Heat transfer
i	Inside
i	Interface
nb	Nucleate boiling
o	Outside
r	Removal
r	Reaction
*	Saturation

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