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MIXED SALT CRYSTALLISATION FOULING

BY

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ABSTRACT

The main purpose of this investigation was to study the mechanisms of mixed salt crystallisation fouling on heat transfer surfaces during convective heat transfer and sub-cooled flow boiling conditions.

To-date no investigations on the effects of operating parameters on the deposition of mixtures of calcium sulphate and calcium carbonate, which are the most common constituents of scales formed on heat transfer surfaces, have been reported. As part of this research project, a substantial number of experiments were performed to determine the mechanisms controlling deposition. Fluid velocity, heat flux, surface and bulk temperatures, concentration of the solution, ionic strength, pressure and heat transfer surface material were varied systematically. After clarification of the effect of these parameters on the deposition process, the results of these 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.

It was assumed that the deposition process of calcium sulphate and calcium carbonate takes place in two successive events. These events are the combined effects related to transport phenomena and chemical kinetics. The effect of the extra deposition created on the heat transfer surface due to sub-cooled flow boiling was considered by inclusion of an enhancement factor. The newly developed model takes into account the effects of all important parameters on scaling phenomena and also considers the simultaneous precipitation and competition of various minerals in the scale formation process. Model predictions were compared with the measured experimental data when calcium sulphate and calcium carbonate form and deposit on the heat transfer surface simultaneously. While deviations ranging from 6% to 25% between model predictions and measured experimental data can be considered good in the context of such a complex process, fouling morphology is clearly a factor to be considered in more detail. This is particularly problematic in the context of more complex fouling solutions encountered in industry.

Furthermore, 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 a new quantity called the fractal dimension.

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Chapter 1

INTRODUCTION

The process of heat transfer between two fluids that are at different temperatures occurs in many engineering applications. Heat exchangers, evaporators, boilers and condensers are devices to enhance or facilitate such a process. They are used in every aspect of industrial, commercial and domestic life concerned with heat transmission, and are often the major cost component of the total plant cost.

Although the process of heat transfer to liquid solutions is performed in industrial installations for different purposes, almost all of them encounter similar problems. After a period of operation, the heat transfer surface of heat transfer equipment may become coated with various deposits present in the flow system. Deposits include mineral salts precipitated from water, polymerisation of organic compounds, sedimentation from contaminated liquors and scale formed by corrosive action. These deposits are generally termed *fouling*. Hence, fouling or scale formation is a process in which undesirable materials, originally dissolved or suspended in process fluids, are deposited on heat transfer surfaces.

Scale deposition is one of the most important and serious problems which heat transfer equipments are generally engaged in. 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 the heat, increase pressure drop and promote corrosion of tube material. These effects reduce the heat transfer equipments performance significantly. Scales sometimes limit or block pumps, tubing, casing, flow lines, heaters, tanks and other heat transfer or production equipments and facilities. Fouling has hence for long been recognised as a serious constraint in the design and operation of heat transfer equipment.

While fouling has already been 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 in an equipment, 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 of solutes at the heat transfer surface can be considerably increased, causing the enhancement 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 a 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.

Crystallisation fouling is highly temperature-dependent and a degree of supersaturation is required before precipitation occurs. Its mechanism relates to many subjects such as momentum, heat and mass transfer, chemical kinetics, material science, etc which makes it difficult to explain 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.

Mixed salt crystallisation fouling on heat transfer surfaces during convective heat transfer and sub-cooled flow boiling is a very complicated process. 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. It is generally believed that the greatest understanding of fouling is obtained as a result of laboratory research on well-defined systems which are close to industrial practice.

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 effect of various operating parameters such as solution composition and hydrodynamics of the system for crystallisation fouling of mixtures of calcium sulphate and calcium carbonate, which are the most common constituents of scales formed on heat transfer surfaces, has been studied experimentally. The results have been used to determine the mechanisms which control deposition. The deposits have been analysed by Scanning Electron Microscopy and X-ray Diffraction, and characterised by their fractal dimensions. This study has provided a good insight into the mechanisms of the fouling phenomenon of mixed salts, and formed the basis for developing a mechanistic model for prediction of fouling resistances of salt mixtures.

In this thesis, a thorough literature review was primarily carried out to find the causes of scale deposition and the factors and parameters that affect scaling tendency in such operations. Chapter 2 provides some general aspects and fundamentals relevant to crystallisation fouling and reviews the most well known existing models on fouling phenomena during convective heat transfer and sub-cooled flow boiling. Fundamentals of solubility equilibria are discussed in Chapter 3, because the processes in the bulk of the fluid can strongly affect deposit formation on heat transfer surfaces. In this chapter, the most widely used calculation methods for predicting scaling tendency and quantifying scale precipitation of common deposits on heat transfer surfaces are addressed. Chapter 4 is concerned with details of experimental equipment and procedures used in this investigation.

Experimental results and factors influencing the fouling phenomenon are given and discussed in Chapter 5. In Chapter 6, a mathematical model is developed for prediction of fouling resistance. The development of the model is based on experimental data and empirical correlations that match our conditions. Furthermore the simultaneous deposition of scales and the competition of various ions to form scale, which are common phenomena, are reflected in the development of the model, allowing the effect of each material on the others to be taken into account. The new model has been applied to investigate the potential of scale precipitation on heat transfer surfaces, which is in good agreement with the experimental data. Chapter 7 contains a brief description of deposit characterisation using

Scanning Electron Microscopy, X-Ray Diffraction and fractal analysis. Finally the conclusions obtained in this study and recommendations for the future framework of the research programme are presented in Chapter 8.

Calibration techniques of magnetic flow meters and annular test heaters which were used in this work are explained in Appendices *A* and *B*. The figures of some fouling runs, which have not been shown in the main part of this report, are given in Appendix *C*. This report ends with the listing of computer programs, used in this investigation, in Appendix *D*.

Chapter 2

THEORY AND LITERATURE REVIEW

2.1 FOULING FUNDAMENTALS

One of the frequent problems facing the process industries today is the persistence of fouled heat transfer surfaces. Fouling causes an increase in the resistance to heat transmission and subsequent loss of thermal exchange capacity of the heat transfer equipment. The reduction in the performance of industrial heat transfer equipment due to the formation of fouling layers on heat transfer surfaces represents a significant process engineering problem as well as an economic problem for design and operation of these units. Hence, it is necessary to obtain more detailed information about this phenomenon.

2.1.1 Fouling Resistance

Fouling layers on heat transfer surfaces represent an additional resistance to the heat transmission and hence reduce the overall heat transfer coefficient and decrease the heat transfer equipment's performance. The overall effect is usually represented by a *fouling factor* or *fouling resistance*, R_f , which must be included along with the other thermal resistances making up the overall heat transfer coefficient.

For instance, Figure 2.1 shows a typical heat transfer surface with fouling layers on both sides of the plane wall, exposed to a hot fluid on one side and to a cooler fluid on the other side. The process of heat transfer from a hot fluid to a cold fluid involves various conduction and convection processes. Assuming the direction of heat flow to be one directional only, the total heat transfer rate is expressed by

$$\begin{aligned}\dot{Q} &= \alpha_i A (T_{bi} - T_{fi}) = \frac{\lambda_{fi}}{x_{fi}} A (T_{fi} - T_{si}) = \frac{\lambda_w}{x_w} A (T_{si} - T_{so}) \\ &= \frac{\lambda_{fo}}{x_{fo}} A (T_{so} - T_{fo}) = \alpha_o A (T_{fo} - T_{bo})\end{aligned}\tag{2.1}$$

where A is the total area for heat transmission, α is the convective heat transfer coefficient and λ is the thermal conductivity. The heat transfer process may also be represented in terms of thermal resistances corresponding to the well-known Ohm's law of electrical engineering. The overall heat transfer rate is calculated as the ratio of the overall temperature difference to the sum of the individual thermal resistances.

$$\dot{Q} = \frac{T_{bi} - T_{bo}}{\frac{1}{\alpha_i A} + \frac{x_{fi}}{\lambda_{fi} A} + \frac{x_w}{\lambda_w A} + \frac{x_{fo}}{\lambda_{fo} A} + \frac{1}{\alpha_o A}} = \frac{T_{bi} - T_{bo}}{\sum R} \quad (2.2)$$

Figure 2.1 Temperature distribution through a fouled heat exchanger wall

The overall heat transfer by combined conduction and convection is frequently expressed in terms of an overall heat transfer coefficient, U , defined by

$$\dot{Q} = U A \Delta T_m \quad (2.3)$$

In accordance with Equation (2.2), the overall heat transfer coefficient would be

$$U = \frac{1}{\frac{1}{\alpha_i} + \frac{x_f}{\lambda_f} + \frac{x_w}{\lambda_w} + \frac{x_{fo}}{\lambda_{fo}} + \frac{1}{\alpha_o}} \quad (2.4)$$

This is abbreviated to a simpler equation in which only one value of x_f/λ_f is included, if fouling is limited to one side.

In order to characterise the additional resistance to the heat flow due to the thermal resistance of the foulant layer, fouling resistances can be obtained by determining the values of U for both clean and dirty conditions in a heat exchanger. The fouling resistance is thus defined as

$$R_f = \frac{1}{U_f} - \frac{1}{U_c} = \frac{x_f}{\lambda_f} \quad (2.5)$$

Here U_f and U_c are the fouled and clean heat transfer coefficient respectively.

From the standpoint of heat exchanger design, another case for consideration would be that of a double pipe heat exchanger. In this application, one fluid flows in the inside of the smaller tube while the other fluid flows in the annular space between the two tubes. In this situation, different areas are involved in the calculations, i.e. in high pressure systems with thick tube walls there may be an appreciable difference in the internal and external surface areas of the tubes. When the area ratios, A_i/A_o are significantly less than unity, the overall heat transfer would be expressed by

$$\dot{Q} = \frac{T_{bi} - T_{bo}}{\frac{1}{\alpha_i A_i} + \frac{\ln r_i/r_f}{2\pi \lambda_f L} + \frac{\ln r_o/r_i}{2\pi \lambda_w L} + \frac{\ln r_{fo}/r_o}{2\pi \lambda_{fo} L} + \frac{1}{\alpha_o A_o}} = \frac{T_{bi} - T_{bo}}{\sum R} \quad (2.6)$$

where the subscripts i and o pertain to the inside and outside of the smaller inner tube.

2.1.2 Time Dependency of Fouling Phenomenon

It is clear from the above that the accuracy of the overall heat transfer coefficient or overall heat transfer resistance is limited by the reliability of the constituent parts. In design procedures, the heat transfer coefficients α_o and α_i are frequently well defined from correlations involving Nusselt, Prandtl, Reynolds and Grashof numbers. Similarly, the conduction thermal resistance is determined from calculations involving properties and dimensions of the material of the walls. Such detailed calculations are not available for determining the fouling resistances, R_{fi} and R_{fo} . There are various compilations of experience-based fouling resistances showing appropriate values for different metal-fluid combinations. The main compilation of R_f values is that of the Tubular Exchanger Manufacturers Association, TEMA, (1988).

Currently, most engineers use fixed values of fouling resistance such as those specified by TEMA. Little account is taken of the various factors that influence fouling and there is clearly a need for an alternative approach. Although the TEMA data are probably still the best option available, there are shortcomings of these standards. For example, fouling resistances are only available for a limited number of process streams with limited operating conditions. For crude oil fouling, not enough information is available on plate heat exchangers, compact heat exchangers or finned tubes (Hewitt and Müller-Steinhagen, 2000). There is no consideration of the influence of process parameters such as flow velocity, bulk and surface temperature on fouling even though these parameters are known to have a significant effect. Moreover, an analysis of the problems associated with the use of TEMA fouling resistances shows that the fouling factors are around 2.5 times of TEMA values, even at the beginning of the fouling period (Jones and Bott, 1998).

The selection of fouling resistance, R_f , determines the extra surface area that has to be added to a heat exchanger to maintain the required performance until the level of fouling represented by R_f is approached. The assumption of constant values for the internal and external fouling resistances suggests that, when put in service, the new heat exchanger instantaneously deteriorates to the fouled condition. Of course this does not occur, it deteriorates gradually instead. Fouling resistance is zero when the heat exchanger is first

put into service and it increases progressively to eventually become the dominant thermal resistance, depending on the fluids and service conditions.

There is hence a substantial time lapse before the heat exchanger fouling resistance approaches the design value selected from some experience-based source. When first put into service, the heat exchanger will operate without fouling resistance and, therefore, with an excess of heat transfer area. In many cases involving boiling, the fouling resistance is the main resistance. Thus when the heat exchanger is new, the available temperature difference may be so great as to carry the process into the film boiling region, with the possibility of enhanced surface corrosion and consequently accelerated development of fouling resistance. In other cases, a heat exchanger with zero fouling resistance may be so effective as to overcool the process stream. To compensate, the cooling fluid flow rate may be reduced. Therefore the fluid velocity is decreased and as a result its surface temperature is increased which enhances the fouling phenomenon.

Therefore, fouling is a time-dependent phenomenon. Nevertheless, the current method for designing industrial boilers and heat exchangers exposed to a fouling environment is to use constant fouling resistances taken from tables of doubtful accuracy or similar experience-based sources (Müller-Steinhagen, 1993). By using a constant value for the fouling resistance at the design stage, one can estimate what may happen to the equipment performance but not when it will happen. Thus, it is probable that the equipment will have to be taken out of service for cleaning at an inconvenient and economically undesirable time. In order to provide a satisfactory surface area for an acceptable period of operation, it is therefore necessary to be able to predict the dependence of fouling resistance on both time and operational parameters. The ability to conduct such modelling would also help to determine optimum cleaning cycles, the evaluation of anti-fouling treatments and the identification of process control strategies.

2.1.3 Fouling Resistance - Time Curves

The process of deposit formation can be divided into an initiation or nucleation step followed by mass transfer from the bulk of the fluid to the surface, and attachment of the

transported material to the surface. Some removal of material may take place at the same time, and the deposit may change its composition or form as a result of ageing processes. The mechanisms and rates of these processes are determined by a number of factors of which the fluid velocity, fluid composition and temperature are the most important. Usually, removal rates increase with increasing amounts of deposit whereas deposition rates are independent of the amount of deposit, but do depend on the changes caused by deposits such as increase in flow velocity and surface roughness.

In practice, the variation of fouling resistance with time follows one of four curves: a linear increase, a falling rate curve that does not reach an asymptote, a formation and breakdown of deposits (sawtooth) and an asymptotic form. Combination of the deposition and the removal terms associated with different fouling mechanisms can produce these curves.

These most common fouling curves obtained on heat transfer surfaces are shown in Figure 2.2. Curve *A* describes a process starting with clean surface having zero fouling resistance, which then develops at a constant rate with time. This form is generally characteristic of tough, hard, adherent deposits and indicates that the deposition rate is constant and there is no removal or that the difference between deposition rate and removal rate is constant. Curve *B* shows that the rate of solid deposition is slowing down with increasing thickness of the layer. This type of fouling curve may be obtained even though there is no removal, due to retardation mechanisms that increase as the deposit builds up.

Curve *C* describes a process where the fouling resistance develops at a progressively declining rate, asymptotic to an ultimate constant value. This type of fouling curves is generally characteristic of soft or weak deposits, which are removed easily due to the shearing force of the fluid flowing past them. This behaviour can be obtained if the deposition rate is constant and the removal rate is proportional to the thickness of the deposit. Curve *D* is observed when a build up of deposit is suddenly removed due to thermal stress between heat transfer surface and deposits or periodic changes of conditions occur e.g. commercial cooling tower water (Bansal and Müller-Steinhagen, 1993).

The family of curves *E*, *F*, *G* and *H* all share an *induction period* in which there is little or no build-up of fouling resistance, followed by a period of increasing build-up. Induction period is frequently observed with new or clean surfaces. The induction period or delay time, t_D , is frequent but not consistent and not generally a reproducible characteristic of any fouling curves. The delay time in scaling is associated with the initial nucleation process, which must occur before crystal growth can begin. This nucleation time normally decreases as the degree of supersaturation increases (Banchero et al., 1960).

Sometimes the fouling curve shows negative values of the fouling resistances. This is believed to be due to the changing flow characteristic near the wall, i.e. increase in surface roughness or number of active bubble nucleation sites, as a result of deposit formation at early stages. This process continues until the additional heat transfer resistance overcomes the advantage of increased turbulence.

Figure 2.2 Typical fouling resistance-time curves

Fouling curves of more complex shapes can sometimes be broken down into one or more of the above simpler modes. For example, the sawtooth-shaped curves can be broken into a collection of linear rising curves, with the drops between them denoting periodic sloughing-off deposit into the flowing stream.

In crystallisation fouling, it is generally believed that crystals are strongly attached to the heat transfer surface. Linear fouling curves have been reported by many authors for crystallisation fouling (Reitzer, 1964, Hosson, 1968, Ritter, 1983 and Najibi et al., 1997) whereas other authors (Watkinson and Martinez, 1975 and Bohnet, 1987) have claimed asymptotic behaviour for crystallisation fouling.

2.1.4 Influence of Fouling on Pressure Drop

The formation of deposits on heat transfer surfaces causes an increase in frictional pressure drop due to increased surface roughness and restricted cross-sectional flow area. According to Chenoweth (1987), more heat exchangers are taken out of service because of excessive pressure drop than because of reduced heat transfer. A rough estimate of the pressure drop inside a fouled tube can be made if it is assumed that the deposit is distributed uniformly over the tube wall. The frictional pressure drop in clean cylindrical tubes is calculated from Equation (2.7)

$$\Delta p = f \frac{\rho L v^2}{2d} \quad (2.7)$$

where the friction factor for smooth tubes is

$$f = 0.00056 + 0.5 \text{ Re}^{-0.32} \quad (2.8)$$

and for rough tubes is

$$f = 0.014 + 1.056 \text{ Re}^{-0.42} \quad (2.9)$$

If the fouling resistance, R_f , and the thermal conductivity, λ_f , of a layer of foulant deposit are known or can be estimated, the inside diameter of the flow area of a fouled tube, d_f , can be determined by Equations (2.10) and (2.11):

$$R_f = \frac{d \ln(d / d_f)}{2 \lambda_f} \quad (2.10)$$

$$d_f = d e^{-2 \lambda_f R_f / d} \quad (2.11)$$

The pressure drop for the fouled tube is obtained by using Equation (2.7) in conjunction with Equations (2.9) and (2.11) as

$$\Delta p = \frac{(0.014 + 1.056 \text{ Re}^{-0.42}) \rho L v^2}{2 d e^{(-2 \lambda_f R_f / d)}} \quad (2.12)$$

where L is the total length of the tube, v is the fluid velocity and ρ is the fluid density (Chenoweth, J. M., 1987).

2.1.5 Types of Fouling

Fouling is classified into five main categories with five sequential events for each category, based on the mechanism of fouling, and the physical and chemical processes that occur (Epstein, 1983). The five categories are:

1. Crystallisation Fouling: Crystallisation fouling is the precipitation of a dissolved substance from the solution onto the heat transfer surface. It will occur when and wherever a fluid becomes supersaturated with respect to dissolved inorganic salts. Every salt has a solubility limit at a given temperature. If this limit is exceeded, precipitation will occur. This may be the result of cooling, heating, evaporation, change in chemical composition or mixing. Normal solubility salts e.g. NaCl, CaCl₂ etc. precipitate on cold surfaces whereas inverse solubility salts e.g. CaSO₄, CaCO₃, Li₂SO₄ etc. precipitate on hot surfaces. Usually inverse solubility salts are the ones which cause more problems.

Crystallisation fouling is usually considered to be the mechanism responsible for fouling of sparingly soluble salts. In this type of fouling, the crystals may nucleate in the bulk fluid, but more frequently form on solid surfaces. Once deposit nuclei have been formed, only a very small supersaturation is required for growth to occur on them. The fundamental driving force for deposition is the difference between the chemical potential of the substance in the solution and at the surface of the deposit. For a fluid of a given composition, crystallisation fouling is usually determined mainly by velocity and temperature, particularly surface temperature.

2. Particulate Fouling: Particulate fouling is the accumulation of particles suspended in the process fluid on the heat transfer surface. In some cases, the deposition occurs due to gravity, in which case it is referred to as sedimentation fouling. The suspended particles may be pollutants, upstream corrosion products, or products from chemical reactions occurring in the bulk of the fluid. This type of fouling is more likely to deposit in low flow regions and stagnant areas. The mechanical resistance to break off a purely particulate deposit is lower than for an adherent crystalline one, and it can be successfully removed by mechanical techniques such as brushes.

3. Chemical Reaction Fouling: This is caused by deposit formation on the heat transfer surface by a chemical reaction in which the surface material itself is not a reactant but may act as a catalyst. This type of fouling depends upon the chemical composition of the stream and the temperature. Chemical reaction occurs on the heat transfer surface and the solid product remains on the surface. In common with other chemical reaction, a characteristic of chemical reaction fouling is that the rate of reaction increases exponentially with temperature. Since the reaction rate constant varies exponentially with temperature (Arrhenius equation), higher temperatures promote chemical reaction fouling. Coke formation, cracking and polymerisation of hydrocarbons are examples for this type of fouling.

4. Corrosion Fouling: Corrosion fouling is the accumulation of corrosion products on the heat transfer surface. Here the heat transfer surface itself reacts to produce adherent

corrosion products. Surface corrosion contributes to fouling in different ways. On one hand, corrosion products form a layer of heat-resisting deposit and act as a catalyst, hence stimulating other fouling processes. On the other hand, as a result of corrosion, the surface will be roughened. This increases the number of nucleation sites and consequently promotes crystallisation fouling. In seawater applications corrosion of the heat transfer surfaces is a major problem.

5. Biological Fouling: Biological fouling is the growth and deposition of organic films consisting of organisms and their products. Development of living organisms on heat transfer surfaces is the basis of this type of fouling. Biological fouling requires water, a source of organisms, and nutrient for them to support themselves and populate. These organisms may be divided into micro-organisms, such as bacteria and macro-organisms, such as seaweed. Biofouling differs in a number of ways from other categories of fouling. It is normally limited to temperatures between 0 °C to 60 °C, and the rate of growth depends upon the temperature, organisms concerned and the nutrients available. They can cause corrosion problems with a variety of materials, including stainless steel.

Some industrial process streams are complex and more than one category of fouling occurs at the same time which complicates the problem.

The above fouling mechanisms generally occur in five consecutive steps: initiation period or delay period, mass transport, formation of deposit, removal or auto-retardation and ageing.

Initiation Period: When a cleaned heat exchanger has been put into operation, initially heat transfer coefficients may remain unchanged for a period of time. During this time, nuclei for crystallisation are formed or nutrients for biological growth are deposited. This is called initiation period or delay period and may be any time from few seconds to several days. For crystallisation fouling and for chemical reaction fouling, the initiation period decreases with increasing surface temperature and degree of supersaturation (Bansal, 1993).

Mass Transport: To form a deposit at the heat transfer surface, it is necessary that at least one key component is transported from the fluid bulk to the heat transfer surface. In most cases, this occurs by diffusion. Concentration difference, temperature difference or some other parameters can control mass transfer of a reactant.

Formation of Deposit: This step involves the attachment of the foulant to the heat transfer surface. After the foulants have been transported to the heat transfer surface, they should stick to the surface. Some of the important factors that contribute to deposit adhesion are; Van der Waals forces, electrostatic forces and surface tension forces. If the total matter available for deposition sticks to the heat transfer surface, the concentration at the wall, C_w , becomes zero. The deposition is then controlled by the diffusion to the heat transfer surface. If C_w is only slightly less than C_b , fouling is reaction or sticking controlled.

Removal or Auto-retardation: Depending on the strength of the deposit, removal forces may start immediately after the first deposit has been laid down. The net deposition is, therefore, the result of the deposition rate and the removal rate acting simultaneously. Removal may occur as a result of the shear stress exerted by the fluid, turbulent bursts, dissolution and thermal shock where large temperature gradients are available. The removal rate is influenced by deposit strength, but no values for deposit strength are available in the open literature. It is reasonable to expect that this would depend upon deposit composition and porosity, another quantity for which few data are available. Therefore, the removal process is not nearly as well understood as the formation process.

Ageing: Every deposit is subjected to ageing. Physical and chemical changes may start to occur as soon as the foulant is deposited. Deposits may react with the heat transfer surface or with the fluid constituents. Their physical structure may also change due to operating conditions. Ageing may increase the strength of the deposit by polymerisation, re-crystallisation, de-hydration (e.g. transformation of gypsum to calcium sulphate anhydride increases the deposit strength significantly) or weaken the structure of the deposit by stresses which induce a removal mechanism. Ageing is the least investigated and understood step and is usually ignored in modelling attempts.

2.1.6 Fouling During Boiling Conditions

When a liquid being heated is below its boiling temperature and the heat transfer surface is below the temperature at which bubbles form, the transfer of heat is by single phase forced

convection. When the temperature of the heat transfer surface is higher than the saturation temperature, bubbles may form at the heated surface. This phenomenon is referred to as *boiling*. Therefore, boiling is a process in which a liquid undergoes a change of phase at specific nucleation sites on a hot surface. By this mode of heat transfer, a large amount of heat can be removed with a relatively low thermal driving force. If the temperature of the heated wall is gradually increased above the saturation temperature of the liquid passing over it, nucleate boiling starts first at the larger nucleation sites and gradually extends to the smaller sites as the amount of superheat of the surface is increased.

Boiling can be divided into pool boiling and flow boiling, depending on the bulk motion of the fluid. When the heated surface, which has a temperature above the solution saturation temperature, is submerged in a liquid that is stationary in a vessel, this leads to the situation known as *pool boiling*. On the other hand, when the liquid is moving over the heated surface, then the condition is called *flow boiling*.

Flow boiling is subdivided into sub-cooled flow boiling and saturated flow boiling. Sub-cooled nucleate boiling occurs if the bulk of the liquid is still below saturation temperature, otherwise it is called saturation nucleate boiling or two phase convective boiling. Therefore, sub-cooled boiling occurs when the liquid enters the equipment at a temperature below its saturation temperature, while the heat transfer surface temperature is above the saturation temperature. Bubbles detaching from the heat transfer surface will then collapse and condense in the sub-cooled bulk liquid. Sub-cooled boiling can occur over a considerable length of heat transfer equipment and may represent up to 50% of the total heat duty.

It should be noted that bubbles do not form on a heated surface until the degree of superheat is sufficient for the pressure inside a nucleation site to overcome the force due to surface tension tending to prevent the growth of the bubble. As the amount of superheat is increased, the number of nucleation sites where bubbles grow increases, and consequently there is a rapid increase in the rate of heat transfer. A liquid may be superheated above its saturation temperature if no nuclei are present to initiate boiling. However, most industrial installations and process liquids contain surface inhomogeneities, cavities, sufficient

quantities of nuclei in the form of solid particles and dissolved gases for the amount of the superheat to be negligible. Sub-cooled nucleate boiling ends when the bulk of the liquid reaches its boiling temperature, and the bubbles begin to form a two-phase boiling mixture.

When a sub-cooled liquid flows past a heated solid surface, a rapid increase in the heat transfer rate at the solid surface is observed once boiling commences. Two major mechanisms have been discussed to describe this phenomenon. The first mechanism is based on the additional turbulent mixing, or micro-convection, which is achieved near the surface due to the growing and collapsing bubbles. The second mechanism focuses on latent heat transport through the bubble. When a vapour bubble grows on a solid surface, a thin liquid layer, called a microlayer, is formed beneath the bubble. The top of the bubble quickly grows beyond the thermal boundary layer into the cooler bulk liquid. Latent heat is transported through the bubble, with the microlayer evaporating while simultaneous condensation occurs at the colder bubble cap. (Najibi et al., 1997)

The two fundamental characteristics of flow boiling are:

- i- For heat fluxes below the onset of nucleate boiling, only the forced convective mechanism is present and the heat transfer coefficient is largely independent of heat flux over a wide range of flow velocity.
- ii- In fully developed nucleate boiling, the flow boiling heat transfer coefficient is substantially independent of flow velocity.

Butterworth and Shock (1982) recommended the correlation of Davis and Anderson (1966) for the determination of the temperature of the wall for the onset of nucleate boiling, T_{ONB} .

$$T_{ONB} = T_s + \left[\frac{8 \sigma \dot{q} T_s}{\lambda_l \Delta h_v \rho_g} \right]^{0.5} \quad (2.13)$$

A similar correlation with the addition of an empirical correction factor was put forward by Frost and Dzakowic (1967), who claimed to be able to cover a wider range of liquids. Their correlation is;

$$T_{ONB} = T_s + \left[\frac{8 \sigma \dot{q} T_s}{\lambda_l \Delta h_v \rho_g} \right]^{0.5} Pr_l \quad (2.14)$$

Where T_{ONB} is the temperature of the wall at the onset of nucleate boiling, T_s is the saturation temperature of the liquid in K, $\dot{q}$ is the heat flux in W/m^2 , Pr_l is the Prandtl number of the liquid, Δh_v is the latent heat of vaporisation in J/kg , λ_l is the thermal conductivity of the liquid in W/mK , ρ_g is the vapour density in kg/m^3 and σ is the surface tension of the liquid in N/m .

The appearance of nucleate boiling increases the formation of deposits on heat transfer surfaces (Jamialahmadi et al., 1989), because of the higher surface temperature, increasing number of active nucleation sites and local supersaturation due to evaporation. The major contribution to deposition is due to the evaporation at the base of growing bubbles. In evaporators, fouling is usually more severe in the sub-cooled boiling entrance region, due to the low flow velocity and turbulence level.

For modelling of the fouling phenomenon during convective heat transfer and sub-cooled flow boiling, an accurate prediction of heat transfer coefficients is essential. On the other hand, for estimating the heat transfer coefficient in flow boiling conditions, it is first necessary to estimate the single-phase convective heat transfer and nucleate boiling heat transfer coefficients.

There are numerous investigations on the prediction of heat transfer coefficients during forced convective and boiling conditions. Steiner and Taborek (1992) used an asymptotic additional model for prediction of flow boiling heat transfer coefficients. Their main reason for developing their model was placed on a sound mechanistic model, which would respect all the established principles of pool and convective boiling. Clearly predictable behaviour and correctly converging to the extreme values of all parameters was the other objective. If the heat flux is below a certain value q_{ib} , the term for nucleate boiling α_b is not included. The suggested correlation includes many constants which have been curve-fitted to the

13,000 data points for vertical flow boiling available in a data bank of Karlsruhe University. The proposed basic equation for the local flow-boiling coefficient is written as:

$$\alpha_{fb} = \left[(\alpha_{nbf})^n + (\alpha_{cb})^n \right]^{\frac{1}{n}} = \left[(\alpha_{nb,o} F_{nbf})^n + (\alpha_{Lo} F_{lp})^n \right]^{\frac{1}{n}} \quad (2.15)$$

$\alpha_{nb,o}$ is the local nucleate pool boiling heat transfer coefficient based on standardised conditions of heat flux and reduced pressure. Any predictive method may be used to estimate the pool boiling heat transfer coefficient itself, but the procedure developed by Gorenflo (1988, 2001) has been recommended for the prediction of this part of the heat transfer coefficient. F_{nbf} is a correction factor to $\alpha_{nb,o}$ which compensates for differences between pool boiling and flow boiling conditions. This parameter includes pressure, heat flux, surface roughness and a correction factor for the microstructure of the heating surface, respectively. In the final form, it is written as:

$$F_{nbf} = F_p \left[\frac{\dot{q}}{\dot{q}_o} \right]^n \left[\frac{R_a}{R_{a,o}} \right]^{0.133} F_{wm} \quad (2.16)$$

where

$$F_p = 1.2 p_r^{0.27} + 2.5 p_r + \frac{p_r}{1 - p_r} \quad (2.17)$$

and for all fluids except cryogenics, the expression for n is:

$$n = n(p_r) = 0.9 - 0.3 p_r^{0.3} \quad (2.18)$$

F_{wm} is a correction factor for the microstructure of the surface material and is given by (Gorenflo, 2001),

$$F_{wm} = \left(\frac{\lambda \rho c}{\lambda_o \rho_o c_o} \right)^{0.25} \quad (2.19)$$

The effect of surface roughness on the heat transfer coefficient is small and was neglected for the present investigation.

α_{Lo} is the local convective heat transfer coefficient, based on the total (liquid plus vapour) mass velocity assumed as liquid. The Gnielinski (1986) correlation has been used to predict α_{Lo} in this model. This correlation deals with single phase heating of the liquid, i.e. where boiling has been suppressed by the pressure being greater than the saturation pressure and the temperature at the heat transfer surface is below that required to initiate nucleate boiling. F_{fp} is the two-phase flow multiplier to the convective α_{Lo} value, accounting for enhancement of the coefficient in the liquid-vapour mixture.

For many industrial applications, where x is limited by the critical x which occurs at dryout point, the following correlation for F_{fp} is given:

$$F_{fp} = \left[(1 - x)^{1.5} + 1.9 (x)^{0.6} \left(\frac{\rho_L}{\rho_G} \right)^{0.35} \right]^{1.1} \quad x \leq 0.6 \quad (2.20)$$

The reference heat flux in this model varies for different groups of substances and for inorganic fluids including water is $20,000 \text{ W/m}^2$. For distilled water, the reference heat transfer coefficient, $\alpha_{nb,o}$, for a reference heat flux of $\dot{q}_o = 20,000 \text{ W/m}^2$ and a reduced pressure of $p_{ro} = 0.1$ is $6000 \text{ W/m}^2\text{K}$. n is an exponent that indicates the range of transition between the nucleate boiling and convective components. By evaluating the Karlsruhe data bank by regression analysis n is obtained to be 3.0 (Steiner and Taborek, 1992).

Some other investigators divide the total heat transfer surface into two parts: the area affected by active nucleation sites and the remaining heat transfer area which is controlled by the forced convective mechanism. Chen (1966) studied the flow of boiling saturated water and organic fluids in vertical channels with both flow boiling and nucleate boiling contributions to heat transfer. The Chen model is an additive method, combining the convective and nucleate boiling contributions to flow boiling heat transfer, i.e.:

$$\alpha_{fb} = \alpha_c F + \alpha_{pb} S \quad (2.21)$$

where α_c is the convective heat transfer coefficient that would be found for the liquid phase flowing alone and in this model was calculated by using the Dittus-Boelter correlation. Chen used the analysis of Forster and Zuber (1954) to calculate α_{pb} , which is the nucleate boiling contribution. Chen used experimental data from different sources obtained with water or one of several organic fluids to determine experimental value of F , the convective boiling enhancement factor compared with the heat transfer coefficient for the liquid flowing alone. In other words, F is a multiplier that accounts for the apparent increase in velocity due to the presence of the vapour and is a function of the Martinelli (1948) parameter X_{tt} .

$$X_{tt} = \sqrt{\frac{(dp/dz)_l}{(dp/dz)_g}} \quad (2.22)$$

where dp/dz is the single phase pressure gradient due to friction. Subscript l denotes the value when liquid is flowing alone and subscript g is the value when the vapour is flowing alone. This parameter can be calculated from;

$$X_{tt} = \left(\frac{1-x}{x}\right)^{0.9} \cdot \left(\frac{\rho_v}{\rho_l}\right)^{0.5} \cdot \left(\frac{\mu_l}{\mu_v}\right)^{0.1} \quad (2.23)$$

F is used to modify the Reynolds number in existing forced convection heat transfer correlations.

$$Re_{tp} = Re \cdot (1-x) \cdot F^{1.25} \quad (2.24)$$

The suppression factor S accounts for the fact that α_{pb} is found from pool boiling correlations which are claimed to over-predict nucleate flow boiling due to the thinner boundary layer and the lower effective superheat in the surrounding of the bubble. S is defined as the ratio of the mean superheat around the growing bubble to the wall superheat and is found to be a function of the two phase Reynolds number, Re_{tp} . Collier (1967) has shown the following equations to fit the curve proposed by Chen:

$$F = 1 \quad \text{for} \quad \frac{I}{X_u} \leq 0.1 \quad (2.25)$$

$$F = 2.35 \cdot \left[\frac{I}{X_u} + 0.213 \right]^{0.736} \quad \text{for} \quad \frac{I}{X_u} > 0.1 \quad (2.26)$$

$$S = \frac{1}{1 + 2.53 \times 10^{-6} \times Re_p^{1.17}} \quad (2.27)$$

All of the discussed models require the local vapour mass quality x , defined as:

$$x = \frac{\dot{m}_{vap}}{\dot{m}_{vap} + \dot{m}_{liq}} \quad (2.28)$$

For sub-cooled flow boiling, x can be estimated from the empirical equations suggested by Schröder (1988) as follows:

The actual vapour quality is related to the phase change number by:

$$x = Ph - Ph_n \cdot \exp\left(\frac{Ph}{Ph_n} - 1\right) \quad (2.29)$$

For positive values the phase change number gives the thermodynamic vapour quality.

$$Ph = \frac{h - h_{sat}}{\Delta h_v} \quad (2.30)$$

Ph_n is the phase change number which is a function of the boiling number, Bo , and the Peclet number, Pe .

$$Ph_n = \frac{-Bo}{\sqrt{\left(\frac{455}{Pe}\right)^2 + 0.0065^2}} \quad (2.31)$$

The phase change number can also be related to the boiling number and a characteristic length that gives the distance from $Ph = 0.0$ to any position of interest.

$$Ph = -4 \cdot Bo \cdot \frac{\Delta L}{d_h} \quad (2.32)$$

From Equation (2.30) the phase change number at the beginning of the heated section can be calculated which gives the characteristic length, ΔL , from Equation (2.32). From ΔL the length coordinate for the thermocouple position can be calculated.

$$\Delta L_t = \Delta L - X_t \quad (2.33)$$

Substituting ΔL_t into Equation (2.32) gives the phase change number at the thermocouple location, which with Equation (2.29) gives the local vapour quality.

Equation (2.21) implicitly suggests the following relationship between the contributions of single phase forced convective heat transfer and boiling heat transfer.

$$\dot{q} = \dot{q}_{fc} + \dot{q}_b \quad (2.34)$$

For Equation (2.34) to be valid for sub-cooled flow boiling the nucleate boiling heat transfer coefficient must be redefined. The nucleate boiling heat transfer coefficient is defined for the case where the liquid bulk is at saturation temperature:

$$\alpha_{nb} = \frac{\dot{q}_b}{T_s - T_{sat}} \quad (2.35)$$

When the fluid is sub-cooled Equation (2.35) should be modified such that Equation (2.34) holds. Hence the sub-cooled boiling heat transfer coefficient is defined as:

$$\alpha_{sb} = \alpha_{nb} \frac{(T_s - T_{sat})}{(T_s - T_b)} \quad (2.36)$$

Najibi et al. (1997) measured heat transfer coefficients of electrolyte solutions for a wide range of concentrations, flow velocities, bulk temperatures and heat fluxes during sub-cooled flow boiling. By comparing the measured heat transfer coefficients and flow boiling models predictions, Najibi et al. concluded that the Chen model and associated correlations

are suitable for prediction of sub-cooled flow boiling heat transfer coefficients of electrolyte solutions. Therefore in the present study, for prediction of heat transfer coefficients during sub-cooled flow boiling, a modified version of the Chen model has been used. The modification replaces old heat transfer correlations with updated alternatives.

In the present investigation, for prediction of convective and nucleate boiling heat transfer coefficients, the Gnielinski (1986) and Gorenflo (1988, 2001) equations have been used, respectively, because of their better prediction and agreement with our experimental conditions. To predict local heat transfer coefficient during turbulent flow in annuli, the Gnielinski equation is in the form of;

$$Nu = \frac{\frac{f}{8} (Re - 1000) Pr}{1 + 12.7 \sqrt{\frac{f}{8} (Pr^{2/3} - 1)}} \left(1 + \frac{1}{3} \left(\frac{D}{x} \right)^{2/3} \right) \left(\frac{Pr}{Pr_w} \right)^{0.11} \left(0.86 \left(\frac{d_i}{d_o} \right)^{-0.016} \right) \quad (2.37)$$

The friction factor for turbulent flow in technically smooth pipes is to be calculated according to:

$$f = (1.82 \log_{10} Re - 1.64)^{-2} \quad (2.38)$$

For prediction of nucleate boiling heat transfer coefficients the Gorenflo (1988, 2001) equation has been used. The Gorenflo correlation is in the form of;

$$\alpha_{nb} = \alpha_o F_p \left(\frac{\dot{q}}{\dot{q}_o} \right)^n \left(\frac{Ra}{Ra_o} \right)^{0.133} \left(\frac{\lambda \rho c}{\lambda_o \rho_o c_o} \right)^{0.25} \quad (2.39)$$

where

$$F_p = 1.2 p_r^{0.27} + 2.5 p_r + \frac{p_r}{1 - p_r} \quad (2.40)$$

and

$$n = n(p_r) = 0.9 - 0.3 p_r^{0.3} \quad (2.41)$$

The heat transfer correlation is a function of heat flux, reduced pressure and pipe roughness. A heat transfer coefficient at reference pressure and reference heat flux is also introduced which is calculated using the Stephan and Preußer method or determined experimentally. (Steiner and Taborek, 1992). Cooper (1984) in his work states that roughness has greater effects at lower p_r , which implies that the effect of roughness cannot be represented by a multiplier applied to the correlation. However, in the Gorenflo correlation the effect of roughness is applied as a multiplier to the main correlation. Nevertheless there is a view that roughness has little effect, provided it exceeds a certain value.

Gorenflo suggests that the reference heat transfer coefficient α_o is calculated for a reference heat flux $\dot{q}=20,000 \text{ W/m}^2$ and a reduced pressure of $p_{ro}=0.1$ using the correlation suggested by Stephan and Preußer (1979) or to be measured. Since the reference roughness in the Gorenflo correlation is $1 \mu\text{m}$, and the surface roughness of the heater used in this study was measured to be $1.02 \mu\text{m}$, the effect of roughness is eliminated.

As it will be discussed in Chapter 6, for modelling of crystallisation fouling during convective heat transfer and sub-cooled flow boiling conditions, an accurate prediction of heat transfer coefficients is essential. For this reason, the above correlations were compiled in the constructed computer program for predicting convective heat transfer coefficient, nucleate boiling heat transfer coefficient and sub-cooled flow boiling heat transfer coefficient, for various electrolyte solutions at different conditions. The physical properties of the electrolyte solutions were also compiled in the computer program. The listing of this computer program is given in Appendix D.

2.1.7 Fouling Costs

The costs of fouling to industry are difficult to assess accurately, but may be roughly divided into four components; energy losses due to decreased thermal efficiencies and increased pressure drop, higher capital cost for oversized plants, maintenance costs including cleaning of heat exchangers and use of antifoulants, and production losses due to plant shutdown time for cleaning or due to reduced overall plant efficiency (Müller-Steinhagen, 1993 and Bott, 1995). For example, when a fouling layer is formed on a heat

transfer surface, it will act as an additional layer of insulation. In order to achieve a required heat transfer rate with a fouled heat exchanger, the heat transfer area must be over-designed which increases the manufacturing costs. Those larger and heavier heat exchangers consequently lead to higher installation and running costs. In addition, mitigation techniques may require changes in the plant layout and regular maintenance, which increase the running costs.

Heat exchanger fouling is a major economic problem. The overall annual fouling cost of heat exchanger surfaces in the highly industrial countries was estimated to about 0.25% of the Gross National Product (GNP) in 1984 (Müller-Steinhagen, 1993). Müller-Steinhagen has summarised the total fouling costs for some countries based on 1984 economic data. These values are shown in Table 2.1.

Table 2.1 Total fouling costs for some countries

Country	Fouling Cost (million \$US)
UK (1978)	700-930
West Germany	1533
USA (1982)	8000-10000
Japan	3062
Australia	260
New Zealand	35

2.1.8 Fouling Mitigation and Control

The objectives of fouling control are *preventing solids from forming, preventing solids from adhering to themselves and to the heat transfer surfaces and removing solids from the surfaces*. Therefore, for prevention purposes, nucleation should be avoided either by adjusting operating conditions such as temperature, or by pre-treatment of fluids to remove fouling precursors. Failing this, conditions need to be chosen that maximise the removal process.

Generally, scale formation can be controlled by one or more of the following methods:

1. *Physical removal of impurities that contribute to the scaling potential (external treatment).*

Conditioning the incoming process fluid by external pre-treatment is a method of reducing or minimising the deposit-forming potential in large systems. Of all the pre-treatment methods, lime/soda softening and sodium zeolite softening are the most frequently used. These systems are designed primarily to reduce the concentration of the dissolved calcium ions.

2. *pH control.* The second approach taken to minimise scaling is pH depression. Traditionally, when the problem is calcium carbonate deposition, the pH of the feed is depressed with the addition of sulphuric acid, sulphamic acid ($\text{NH}_2\text{SO}_3\text{H}$) or hydrochloric acid. This procedure reduces the calcium carbonate saturation index to a more negative value (This concept will be discussed in Chapter 3).

3. *Use of chemical treatment.* Anti-foulants can often be used with a minimum of capital investment for solving operational problems caused by fouling. Information is needed on the most effective anti-foulant for a particular fouling problem and the optimum injection rate of the anti-foulant. A laboratory fouling test method, which provides this information, is described by Haluska and Show (1975).

Additive performance can be affected by several factors. These include average molecular weight, system pH and system temperature. No universal inhibitor exists for all kinds of scale. Different inhibitors have different degrees of effectiveness even for various hydration forms of the same scale. It is accepted that crystal modifiers improve the cleanliness of heat transfer surfaces for the following reasons:

- a) When crystal distortion occurs, irregular-shaped crystals can not pack tightly together.
- b) Because of the resulting surface defects, the formed crystals are smaller in size and usually less adherent to metal surfaces.

However, the success of any anti-foulant program depends on the following parameters:

- i) Understanding of the fouling mechanism.
- ii) Developing the correct treatment regulations for the problem.
- iii) Understanding the economic trade off between the cost of the program and the benefits (Hewitt and Müller-Steinhagen, 2000)

4. Mechanical fouling mitigation. A well-established method of reducing fouling is to increase the wall shear stress by raising the flow velocity or by increasing the turbulence level. It is often suggested that the threshold conditions of fouling and also fouling rates are related to the shear stress at the surface. Inside a tube, the shear stress, τ_w (N/m²), is related to the friction factor f and the pressure gradient (Pa/m) by the relationship:

$$\tau_w = \frac{f \rho v^2}{2} = \frac{d}{4} \frac{dp}{dz} \quad (2.42)$$

where ρ is the fluid density and v is the fluid velocity. It has been suggested that, above a certain shear stress, fouling does not occur. Therefore, the simplest approach to achieve fouling mitigation by improved heat exchanger design is to try to have shear stresses which are above their threshold values. This can sometimes be achieved by increasing fluid velocity. For example, when the fouling liquid is flowing through the tubes, an increase in the number of tube side passes will increase the tube velocity and produce shear stresses which are above the threshold values, thus preventing fouling. Of course, it is sometimes impossible to achieve this velocity within the other system constraints such as pressure drop and number of tube passes.

5. Low surface temperature. The rise in fouling resistance as the heat transfer surface temperature goes up is caused by increased supersaturation, reaction rate, stickability or biological growth. Reducing the surface temperature usually leads to lower heat fluxes and, therefore, larger heat exchangers. Raising flow velocity not only leads to high wall shear stress, but also leads to high film coefficients and hence, to the desired lower surface temperature.

6. Surface Coatings and Treatments. The relationship between surface energy and foulant adhesion has been intensively studied. It has been shown that the poorest foulant adhesion occurs on materials that have low surface energies. Up to now, several low-energy coatings, for examples, fluoropolymers and silicone polymers, have been developed. Although these surfaces do accumulate fouling, the attachment is more loosely adhered and quite easily detached. However, as the coatings themselves provide a significant additional resistance to heat transfer due to their low thermal conductivity, their use in heat exchangers is limited.

A novel solution to this problem has recently been suggested by Ion Beam Implanting or Unbalanced Magnetron Sputtering foreign ions into the metal surface (Müller-Steinhagen and Zhao, 1997, 1999). They found that ion implantation and unbalanced magnetron sputtering have the greatest potential for preparing low fouling surfaces. Unlike commonly used coatings, any additional heat transfer resistance of alloy layers is negligible, because the thickness of the alloy layer is only about 1-3 μm . The coating also meets wear resistance and welding requirements. By implanting or sputtering foreign ions onto the metal surface, Müller-Steinhagen and Zhao (1997, 1999) achieved a substantial reduction in CaSO_4 scale formation during pool boiling.

Rough surfaces provide ideal nucleation sites for the growth of all types of deposits and therefore promote fouling. The use of electro-polished stainless steel evaporator tubes in pulp and paper, chemical and food processing industries has allowed longer operation periods between cleaning. If the heat transfer resistance of the tube material is not a major problem, polytetrafluoroethylene, polypropylene tubing or glass-lined tubing can be used. The beneficial aspect of smooth heat transfer surfaces is lost once the original surface is covered with a continuous dirt coating.

It should be mentioned that mechanical and chemical cleaning are commonly used methods to remove deposits from the shell side of heat exchanger tube bundles. In general, the bundles are first pulled out, and then immersed in various liquids to loosen or soften deposits. They are then subjected to a combination of high-pressure hydroblasting, rodding, sawing, scrapping, scratching, and in some cases an occasional light

sandblasting. Chemical cleaning is often more effective than mechanical cleaning. In some cases, it can be done while the equipment is still in service. But the main disadvantage of chemical cleaning is the inability of the chemical solution to penetrate plugged tubes.

2.2 PREVIOUS INVESTIGATIONS

Several investigators have studied the mechanisms of crystallisation fouling in an effort to understand and develop predictive models. Most of these studies have been applied to fouling during forced convective heat transfer. Pool boiling and sub-cooled flow boiling are important heat transfer mode from an industrial point of view, but little information is available on fouling of salts during sub-cooled flow boiling. In what follows, only crystallisation fouling of calcium sulphate and calcium carbonate is reviewed:

Numerous papers and patents have been published in the field of scale formation on heat exchanger surfaces under forced convective heat transfer. Detailed information can be found in the review books of Garrett-Price et al. (1985), Melo et al. (1987), and Bott (1995), and the review papers of Hasson (1979), Epstein (1987), Somerscales (1988) and Müller-Steinhagen (1989). Contrariwise, a review of the existing literature on boiler fouling reveals that data in this field are limited and that there have not been any attempts to summarise the published results (Jamialahmadi and Müller-Steinhagen, 1993).

The first reference in the literature on boiler fouling seems to be due to Leidenfrost (1756), who reported that always after the complete evaporation of a drop of water, a thin layer of deposit was left on the heated surface. The earliest direct reference to fouling may be due to Davy (1850), who reported on the deposits formed in the boilers of steamships. From 1802 to about 1860 these boilers were fed from the water in which the vessel was floating. If this was fresh water, fouling was apparently non-existent, but the salt water drawn from the ocean caused fouling. This could be advantageous because it protected the boiler from corrosion, but on a long journey the effects on the steam-raising capacity of the boiler could result in a gradual decrease in the speed of the ship as the journey progressed.

Before the work of Partridge and White (1929), it was believed that the deposit was formed by the impingement on the heating surface of solid material suspended in the solution. Based on his experimental observations, Partridge proposed the following mechanism to explain the origin of rings occurring on the boiling heat transfer surface: Due to the local increase in heat transfer surface temperature under the bubble and due to fast evaporation at the triple interface, steam and water would throw down a deposit. This deposit would tend to remain at the boiling heat transfer surface if the salt has negative solubility in water and it would tend to be redissolved, if the deposit salt has positive solubility.

The first systematic investigation of the effects of fouling on boiling heat transfer has probably been reported by Palen and Westwater (1966). Saturated aqueous solutions of calcium sulphate were boiled on electrically heated test strips of oxidised aluminium for up to 12 hours. The heat flux was varied between 40000 W/m^2 and 400000 W/m^2 . The amount of scale deposited was weighed and was found to be linear with time and proportional to the square of the heat flux.

Nancollas et al. (1978) studied growth and phase transformation of calcium sulphate dihydrate and hemihydrate crystals from 70 to 130°C . They concluded that the growth rate of calcium sulphate dihydrate seed crystals is independent of the fluid dynamics of the system, suggesting that the rate is not diffusion controlled but depends on the surface reaction.

Gill and Nancollas (1980) studied the kinetics of growth of calcium sulphate crystals on heated metal surfaces during forced convective heat transfer. They developed a kinetic model for calcium sulphate crystal growth and concluded that the rate constant is independent of surface area.

Sheikholeslami and Watkinson (1986) studied the scaling of calcium carbonate on the surface of copper and mild steel plain heat exchanger tubes and on an externally finned mild steel tube during forced convective heat transfer. In most of their experiments they observed a linear increase in fouling resistance values with time under constant heat flux.

They found that the rate is clearly higher in the plain tube at equal velocity and for both steel tubes, the rate generally decreases with increasing velocity for fluid velocity greater than 0.3 m/s. They also mentioned that falling scaling rates with increasing velocity are commonly found where particulate fouling dominates or where deposits are fragile.

Jamialahmadi and Müller-Steinhagen (1989-1993) studied the effects of fouling on nucleate pool boiling heat transfer systematically over a wide range of heat fluxes for various foulant concentrations. It was shown that the clean heat transfer coefficient at the beginning of each experiment increases with increasing heat flux. The general shape of the heat transfer coefficient versus time curves is remarkably concordant. It is characterised by a sharp decrease to a minimum, followed by an increase to a maximum and a subsequent gradual decrease towards an asymptotic value. However, the extent of the variations in heat transfer coefficient with time is strongly affected by the adjusted process conditions.

A recent comprehensive literature review by Jamialahmadi and Müller-Steinhagen (1993) on the mechanisms of boiler fouling reveals that experimental fouling data under boiling conditions in general and under sub-cooled flow boiling in particular are scarce and incomplete. They have suggested that the scale deposition has a significant effect on the boiling phenomena by changing the characteristics of the heat transfer surface. The deposit provides favourable bubble nucleation conditions and reduces the wall superheat required for bubble formation. Deposits also change the interfacial tension between the growing bubbles and the heated surface. Initial crystal formation on the surface provides sites for rapid crystal growth. Cavities and impurities on the surface have similar effects.

Sheikholeslami (2000) has studied the co-precipitation characteristics of calcium sulphate and calcium carbonate in a temperature-controlled batch reactor under various operating conditions. Co-precipitation results have been compared with crystallisation results of single salts. Sheikholeslami has pointed out that induction period and kinetics of co-precipitation of these two salts follow that of pure calcium carbonate. Calcium sulphate was precipitated in form of Gypsum and had a needle shape structure, while calcium carbonate had a spiral growth and was precipitated in form of Calcite. Sheikholeslami has

concluded that the relationship between the thermodynamic concentrations of Ca^{2+} for pure calcium sulphate and calcium carbonate solutions depended on the pH of the solution. The precipitate structure was affected by co-existence of salts; the co-precipitation resulted in calcium carbonate crystals interwoven by calcium sulphate crystals.

2.2.1 Fouling Models

The physical phenomena underlying heterogeneous crystallisation are many and complex and extend into many disciplines. They involve the physics of heterogeneous nucleation of crystals on the heat transfer surface, the chemistry of the two/phase solid-liquid interface, the local chemical thermodynamics and the hydrodynamics of local flow. For this reason adequate mathematical models for describing crystallisation fouling are difficult to formulate. As pointed out 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 lattice, it is possible to “lump” these effects together in terms of a chemical reaction. The rate of reaction under these circumstances will depend upon the concentration distribution of ions in the region of the interface between liquid and heat transfer surface.

So far a number of models have been proposed for different types of fouling. Because of the difficulty involved in reproducible measurements of the fouling resistances and the complex nature of the deposit formation, mathematical modelling is very difficult. Most of the models that have been proposed are highly simplified because they are based on assumptions such as (Bansal, 1993);

1. Only one type of fouling is usually considered
2. The fouling layer is assumed to be homogeneous
3. The deposit surface roughness is neglected
4. Changes in physical properties of the streams are omitted
5. The initial condition of the surface is not considered

Furthermore, models only consider some of the variables such as, velocity, time, concentration, and temperature whereas other parameters which are more difficult to evaluate are neglected, e.g. effect of simultaneous action of different fouling mechanisms, nature and condition of surface, properties of foulant stream, design of the equipment, fluctuations in operation and ageing. In this section some of the important fouling models are briefly discussed.

Almost all of the available models have been developed based on the general material balance equation:

$$\begin{array}{lcl} \text{Net rate} & = & \text{Rate of formation} - \text{rate of removal} \\ \text{of fouling} & & \text{of deposit} \quad \text{of deposit} \end{array} \quad (2.43)$$

or

$$\frac{dR_f}{dt} (\rho_f \lambda_f) = \dot{m}_d - \dot{m}_r \quad (2.44)$$

Where:

dR_f/dt = net rate of fouling accumulation

$\dot{m}_d$ = deposition rate

$\dot{m}_r$ = removal rate

Deposition rate depends on the type and mechanism of fouling while removal rate depends on both the hardness and adhesive force of the deposition and the shear stress which is a result of the flow velocity. The wide range of possible combinations results in the great variety of possible final formulations.

McCabe and Robinson Model (1924)

The earliest mathematical model for crystallisation fouling of evaporators was published by McCabe and Robinson in 1924. The basis for this model is the simple assumption that the quantity of scale deposited in an evaporator at any time is proportional to the quantity of liquid which has been evaporated and therefore to the heat which has been transferred

to that time. Hence, in their model, the solid mass deposited per unit surface area was correlated as:

$$\dot{m}_d = a \dot{q} \quad (2.45)$$

No information of the physical meaning of a is given and a removal mechanism function is also not considered. It is also not clear how the physical properties of the process fluid were taken into account.

Kern and Seaton Model (1958)

The second model which appeared in the literature was suggested by Kern and Seaton in 1958, more than a quarter of a century later. They observed that fouling curves often followed a pattern in which after an initial period of fast fouling build-up, the fouling resistance tended to remain nearly constant. This behaviour could be described by the following equation:

$$R_f = R_f^* (1 - e^{-\theta t}) \quad (2.46)$$

where R_f^* is the asymptotic fouling resistance for $t=\infty$, and θ is a coefficient representing the inverse of a relaxation time, i.e. a *time constant*. The persistent observation by Kern and Seaton, that industrial heat exchangers often fouled asymptotically, led them to introduce the idea that net measured fouling was the difference between two simultaneous processes, a deposition process and a removal process. Hence,

$$\frac{dR_f}{dt} = \phi_d - \phi_r \quad (2.47)$$

In this model, ϕ_d remains constant and is independent of time whereas ϕ_r depends directly on the actual value of R_f . Both are defined as:

$$\phi_d = \left(\frac{dR_f}{dt} \right)_{t=0} = a_3 C v \quad (2.48)$$

$$\phi_r = \theta R_f = a_4 \tau_s x_f \quad (2.49)$$

where a_3 and a_4 are constants of proportionality, C is the foulant concentration, v is the flow velocity, τ_s is the shear stress at the fluid-deposit interface, and x_f is the thickness of the deposit layer. The integration of Equation (2.47) in conjunction with Equations (2.48) and (2.49) yields:

$$R_f = \frac{\phi_d}{\theta} (1 - e^{-\theta t}) = \frac{a_3 C v}{a_4 \lambda_f \tau_s} (1 - e^{-\theta t}) \quad (2.50)$$

This is similar to Equation (2.46) with $R_f^* = \frac{\phi_d}{\theta} = \frac{a_3 C v}{a_4 \lambda_f \tau_s}$. This model predicts asymptotic fouling behaviour with R_f^* being the fouling resistance after an infinite time of operation.

Before solving this model, one needs to find an expression for R_f^* and θ as a function of operating variables.

The above model forms the fundamentals behind most models that have later appeared in the literature and which differ essentially by the functional dependence of ϕ_d and ϕ_r . According to this model, an asymptotic fouling value will be obtained when the removal rate becomes equal to the deposition rate.

Reitzer Model (1964)

Reitzer proposed a model for crystallisation of salt solutions in which the deposition rate is calculated with the aid of a combined diffusion-reaction coefficient K and the concentration difference between the bulk liquid concentration, C_b and saturation concentration, C^* as follows:

$$\dot{m}_d = K (C_b - C^*)^n = a_1 U_f^n \quad \Delta T = \text{const.} \quad (2.51)$$

$$\dot{m}_d = K (C_b - C^*)^n = a_2 \quad \dot{q} = \text{const.} \quad (2.52)$$

The combined diffusion-reaction coefficient reflects both the mass transfer by diffusion and the reaction. The exponent n represents the order of reaction and U_f denotes the overall heat transfer coefficient for the fouled heat transfer surface.

Reitzer assumed that for highly agitated systems with slow crystalline growth, n would be equal to the order of the reaction, i.e. to the number of ions taking part in the formation of each molecule of solid. For mass transfer controlled systems, n is equal to 1.

In this model, the change of fouling thickness is related to the mass build-up of scale as follows:

$$\dot{m}_d = A \rho_f \left(\frac{dx_f}{dt} \right) \quad (2.53)$$

where A is a constant. Assuming a linear temperature-solubility relation and n^{th} order chemical reaction for crystal growth, his analysis resulted in the following two expressions for constant ΔT and constant heat flux, respectively:

$$\frac{1}{\alpha^{n+1}} = \frac{1}{\alpha_0^{n+1}} + a_1 \left(\frac{k_r}{\rho_f \lambda_f} \right) \left(\frac{\Delta T}{\alpha_i} \right) t \quad (2.54)$$

$$\frac{1}{\alpha} = \frac{1}{\alpha_0} + a_2 \left(\frac{k_r}{\rho_f \lambda_f} \right) \left(\frac{\dot{q}}{\alpha_i} \right)^n t \quad (2.55)$$

where a_1 and a_2 are constants and k_r is a combined diffusion-reaction mass transfer coefficient. Since the fouling resistance, R_f , is defined as;

$$R_f = \frac{1}{\alpha} - \frac{1}{\alpha_0} \quad (2.56)$$

the Reitzer model for fouling resistance under constant heat flux operation is linearly dependent on time and suggests no asymptotic fouling resistance.

Watkinson and Epstein Model (1969)

Watkinson and Epstein (1969) proposed a transfer-adhesion-release model to explain their experimental results with both gas oils and sand-water slurries. They assumed that deposition was caused by mass transfer of suspended particles to the wall followed by adhesion of some particles on the wall, and that removal is a first order function of deposit thickness, as proposed by Kern and Seaton (1959). The net rate of fouling was given by:

$$\frac{dR_f}{dt} = \frac{a_1(C_b - C_w) \exp(-E_{act}/RT)}{U_f} - a_2 v^2 f x_f \quad (2.57)$$

where C_b and C_w represent the particulate concentrations in the bulk and at the wall respectively, v represents the bulk linear velocity, f represents the friction factor and a_1 and a_2 represent coefficients in the equation. Watkinson and Epstein showed that Equation (2.57) correctly predicted the dependency of initial fouling rate on temperature, T , and mass flux as found in experiments. However, the model does not predict the correct dependency of asymptotic fouling resistance on flow rate (Crittenden et al. 1987).

Taborek et al. Model (1972)

About thirty years ago, Taborek et al. described fouling as the major unsolved problem in heat transfer. Taborek et al. used the Kern and Seaton (1958) model in its basic form and developed correlations for deposition and removal terms. They introduced into the deposition term the probability of adhesion of the deposit to the solid wall, and defined the water quality $\mathcal{Q}$, which is assumed to be a function of saturation index, and the activation energy E , which is combined with the gas constant R and the surface temperature T_s , according to an Arrhenius relationship. They also assumed that the shear

stress τ_s on the surface of the fouling layer is responsible for the removal of solids, and attempted to describe the strength of the fouling layer by an empirical structure parameter Ψ . The deposition and removal terms are defined as follows;

$$\dot{m}_d = a_5 P \Omega^n \exp\left(-\frac{E}{RT_s}\right) \quad (2.58)$$

$$\dot{m}_r = \frac{a_6 \tau_s \dot{m}_d^P}{\Psi} \quad (2.59)$$

Here, P is the sticking (adhesion) probability, which in most cases is assumed to be equal to one.

Watkinson and Martinez Model (1975)

Watkinson and Martinez studied the effects of tube side velocity and bulk temperature on calcium carbonate scale formation on copper heat exchanger tubes under constant wall temperature conditions. They found that the fouling resistance for each tube at first increases with velocity, passes through a maximum and then decreases. They also found that at constant inlet temperature, the tube diameter has a weak effect on fouling resistance. A mathematical model based on the Reitzer (1964) and Kern and Seaton (1958) models including the removal term was used to predict their results.

This model in its basic form is given as:

$$R_f = R_f^* (1 - e^{-Bt}) \quad (2.60)$$

where, the parameter B is unknown and should be obtained from experimental data. R_f^* is the asymptotic value of the fouling resistance and for second order crystallisation fouling reactions is defined by the following equation:

$$(R_f^*)^3 + \frac{2}{\alpha_i} (R_f^*)^2 + \frac{R_f^*}{\alpha_i^2} - \frac{0.0002751T - 0.08489}{(\alpha_i v)^2} = 0 \quad (2.61)$$

α_i is the inside heat transfer coefficient and v is the flow velocity. Equation (2.61) can be solved by analytical or numerical techniques.

Even though CaCO_3 deposits are much stronger than the particulate deposits considered by Kern and Seaton (1958), the removal rate was assumed to be directly proportional to the deposit thickness in this model.

Hasson et al. Model (1968-1981)

Hasson et al. developed a model based on measurements of calcium carbonate scale deposition on the surface of a tubular constant heat flux heat exchanger. This is one of the few models that takes into account water chemistry. They examined the effect of parameters such as flow velocity, scale surface temperature and water composition on scale growth by measuring the scale deposition rates. It was found that within the range of investigated surface temperatures (67 to 85 °C) and Reynolds numbers (13000 to 42000), calcium carbonate deposition is mainly controlled by the diffusion rate of Ca^{2+} and HCO_3^- ions.

Hasson et al. also developed an ionic diffusion model to predict fouling rates of CaCO_3 in cooling water. The model was based on the radial diffusion of Ca^{2+} and CO_3^{2-} ions from the bulk of the fluid followed by crystallisation of CaCO_3 on the wall and did not take into account the removal term because of the adherent nature of CaCO_3 scale.

The rate of crystallisation fouling of CaCO_3 per unit interfacial area was expressed based on the reaction-controlled mechanism:

$$\dot{m}_d = k_r ([\text{Ca}^{2+}]_i [\text{CO}_3^{2-}]_i - K_{sp}) \quad (2.62)$$

The bracketed parameters are the interfacial concentrations and K_{sp} is the solubility product of CaCO_3 at the deposit-water interface. Since the diffusion process depends on

the concentration of all the diffusing species present in the water, it should first be determined which of the present species is predominant. At low pH values, most of the carbonate is in the form of HCO_3^- ions, and the tendency towards formation of CO_3^{2-} ions increases with increasing pH. In the case of low pH values, either CO_2 or HCO_3^- ions will control the rate of diffusion as follows:

$$\dot{m}_d = \beta([Ca^{2+}] - [Ca^{2+}]_i) = \beta([CO_2] - [CO_2]_i) = \frac{\beta}{2}([HCO_3^-] - [HCO_3^-]_i) \quad (2.63)$$

β represents the convective mass transfer coefficient which can be considered to be identical for all carbonate species due to their similar diffusivity values. After eliminating the interface concentrations and some mathematical manipulations, the fouling rate is found by the solution of the following equation:

$$K_1 \left(\frac{\dot{m}_d}{k_r} + K_{sp} \right) \left(\frac{\dot{m}_d}{\beta} + [CO_2] \right) = 4K_2 [Ca^{2+}]^2 \left(1 - \frac{\dot{m}_d}{\beta[Ca^{2+}]} \right) \left(\frac{[HCO_3^-]}{2} - \frac{\dot{m}_d}{\beta} \right)^2 \quad (2.64)$$

where K_1 and K_2 are the first and second dissociation constants, K_{sp} is the molar solubility product and k_r is the reaction rate constant. In Hasson's work, these constants are given as:

$$\log K_1 = \frac{-17052}{T} - 215.21 \log T + 0.12675T + 545.56 \quad (2.65)$$

$$\log K_2 = \frac{-2902.39}{T} - 0.023791T + 6.498 \quad (2.66)$$

$$\log K_{sp} = -0.01183(T - 273.2) - 8.03 \quad (2.67)$$

$$k_r = \exp \left(41.04 - \frac{10417.7}{T} \right) \quad (2.68)$$

After some simplifications, Equation (2.64) reduces to:

$$\dot{m}_d = \frac{0.5\beta b[Ca^{2+}]\left[\left(1 + \frac{4ac}{b^2}\right)^{0.5} - 1\right]}{a} \quad (2.69)$$

where

$$a = 1 - \frac{4K_2k_r[Ca^{2+}]}{K_1\beta} \quad (2.70)$$

$$b = \frac{[CO_2]}{[Ca^{2+}]} + \frac{4K_2k_r[HCO_3^-]}{K_1\beta} + \frac{K_{sp}k_r[CO_2]}{\beta[Ca^{2+}]} \quad (2.71)$$

and

$$c = \frac{K_2k_r[HCO_3^-]^2}{K_1\beta[Ca^{2+}]} - \frac{K_{sp}k_r[CO_2]}{\beta[Ca^{2+}]^2} \quad (2.72)$$

The mass transfer coefficient β is calculated using a Dittus-Boelter type equation (Hasson et al., 1968):

$$\beta = 0.023 Re^{0.85} Sc^{0.33} \frac{D}{d_{eq}} \quad (2.73)$$

Ritter Model (1983)

Ritter studied fouling of calcium sulphate and lithium sulphate on the surface of electrically heated tubes during forced convective heat transfer under constant heat flux conditions. Based on his experimental results he concluded that, unlike cooling tower water fouling with its typical asymptotic curves, pure crystallisation fouling is characterised by an induction period without fouling, followed by fouling at a constant rate. The induction period and the fouling rate of both salts were found to be a function of the supersaturation of the solution and of the mass transfer coefficient. Calcium sulphate fouling was found to be mass-transfer controlled, while lithium sulphate fouling was reaction-rate controlled.

Ritter considered all possible parameters in correlating both the induction period and the fouling rate of calcium sulphate. The correlating equations for calcium sulphate are given as follows:

For the induction period:

$$\theta = \frac{2.1 \times 10^{-4} \rho}{\beta \left(\frac{C_b - C^*}{C^*} \right)^2} \quad (2.74)$$

and for the fouling rate:

$$\frac{dR_f}{dt} = \frac{1.9 \times 10^{-9} \beta}{\rho} \left(\frac{C_b - C^*}{C^*} \right)^2 \quad (2.75)$$

In this model the induction period, θ , is in hours and the fouling rate is in $m^2 K/W.s$. Ritter has not described the type of solution and also the operating conditions under which these results were obtained.

Nancollas Model (1983)

Nancollas studied fouling of sparingly soluble salts such as calcium sulphate and calcium carbonate and suggested that the rate of crystallisation is controlled by the reaction kinetics, rather than the diffusion process. In his model, activation energies for crystal growth are considerably higher than those to be expected for simple bulk diffusion. Nancollas also pointed out that fluid velocity has little effect on the crystallisation rate at the crystal surface, which suggests that diffusion is not the controlling mechanism. Therefore, for a reaction-controlled system, Nancollas stated that the rate of crystallisation of a salt with the generalised formula $M_a X_b$ is given by the following equation:

$$\text{Rate} = \frac{d(M_a X_b)}{dt} = -k_r S K_{sp}^{n/v} \sigma^n \quad (2.76)$$

where

K_{SP} = solubility product

n = order of reaction

$\nu = a + b$

S = some function of the surface area

$$\sigma = \left[(M^{m+})^a (X^{x-})^b \right]^{1/\nu} - K_{SP}^{1/\nu}$$

In above equation, concentrations or activities of the lattice ions may be used. In this model, the rate of crystallisation of common scales such as calcium sulphate and calcium carbonate, follows a parabolic relationship with supersaturation, assuming second order reactions. Nancollas concluded that the rate of crystal growth is dependent on the degree of supersaturation, ratio of solid to solution, dynamics of stirring (agitation) and the temperature parameters. Finally, it was stated that for a surface controlled process, the activation energy would be of the order of 40 J/mol as compared to 12 J/mol for a process controlled by diffusion (Bott, 1995).

Bohnet Model (1987)

Bohnet and co-workers investigated scaling of aqueous calcium sulphate solutions under forced convective conditions, using a test rig with an annular test section. Contrary to many investigators, asymptotic fouling resistance versus time curves were found, probably due to the presence of suspended particles in the test solution. The presence of suspended solids in the test solution may have caused the dominant deposition mechanism to be a combination of crystallisation and particulate fouling. The presence of particulate fouling lowers the strength of the deposit and increases the removal rate, and consequently causes the fouling resistance curves to show asymptotic behaviour.

This model is one of the most detailed models available in the literature on crystallisation fouling. A two-step approach consisting of mass transport and crystallisation reaction has been combined with an expression for deposit removal, to model the fouling rates. During crystallisation fouling the deposition rate can be diffusion controlled, reaction controlled

or a combination of both. Bohnet et al. proposed different rates based on the controlling mechanism as follow:

1. For diffusion controlled deposition:

$$\dot{m}_d = \beta(C_b - C_i) \quad (2.77)$$

2. For reaction controlled deposition:

$$\dot{m}_d = k_r(C_i - C^*)^n \quad (2.78)$$

where C_b , C_i and C^* are bulk, interface and saturation concentration, respectively, and n is the order of reaction. Eliminating the interfacial concentration, C_i , in Equations (2.77) and (2.78) and considering crystallisation fouling of calcium sulphate as a second order reaction, the deposition rate becomes:

$$\dot{m}_d = \beta \left[\frac{1}{2} \left(\frac{\beta}{k_r} \right) + (C_b - C^*) - \sqrt{\frac{1}{4} \left(\frac{\beta}{k_r} \right)^2 + \left(\frac{\beta}{k_r} \right) (C_b - C^*)} \right] \quad (2.79)$$

In this model, the nature of the deposit has been incorporated into the removal rate equation. Bohnet suggested that the removal rate is directly proportional to the fluid shear stress and inversely proportional to the deposit shear strength. The shear strength of the deposit layer depends on layer thickness x_f , inter-crystalline adhesion force P , linear expansion coefficient of deposit δ , number of fault points in the layer, N_f , temperature drop in the fouling layer ΔT , and equivalent crystal diameter d_p .

$$\sigma_f = a_6 \frac{P}{N_f x_f (1 + \delta \Delta T) d_p} \quad (2.80)$$

The removal rate was assumed as:

$$\dot{m}_r = a_6 \frac{\tau_f}{\sigma_f} \rho_f \left(\frac{\mu g}{\rho} \right)^{\frac{1}{3}} \quad (2.81)$$

Replacing the shear stress in Equation (2.81) by ρv^2 , and introducing Equation (2.80) leads to:

$$\dot{m}_r = \frac{a_7}{P} \rho_f (1 + \delta \Delta T) d_p (\rho^2 \mu g)^{\frac{1}{3}} x_f v^2 \quad (2.82)$$

The number of fault points, N_f , in the fouling layer has been incorporated into the parameter a_7 , and the parameter a_7/P is given by:

$$\frac{a_7}{P} = 52.5 v^{0.82} \quad (2.83)$$

Combining deposition and removal rates, the fouling resistance can be expressed as a function of the asymptotic fouling resistance and a time constant:

$$R_f = R_f^* (1 - e^{-\theta}) \quad (2.84)$$

The asymptotic fouling resistance, R_f^* and the time constant θ are given by:

$$R_f^* = \frac{\beta P}{\rho_f \lambda_f a_7 (1 + \delta \Delta T) d_p (\rho^2 \mu g)^{\frac{1}{3}} v^2} \times \left[\frac{\beta}{2k_r} + (C_b - C^*) - \sqrt{\frac{1}{4} \left(\frac{\beta}{k_r} \right)^2 + \frac{\beta}{k_r} (C_b - C^*)} \right] \quad (2.85)$$

$$\theta = \frac{a_7}{P} (1 + \delta \Delta T) d_p (\rho^2 \mu g)^{\frac{1}{3}} v^2 \quad (2.86)$$

Some recommended values of a_7 , P , δ and N_f can be found in (Bohnet, 1987).

Although this model is very advanced in terms of considering the properties of deposits, it is very difficult to measure most of the variables such as P , δ and N_f . There is also no

information about the wide variation in the size of the crystals, which changes continuously.

Müller-Steinhagen and Branch Model (1988, 1991)

Müller-Steinhagen and Branch used Hasson's ionic diffusion model (1968-1981) to determine calcium carbonate scaling rates in double pipe heat exchangers. In their model, the fouling rate can be calculated from the deposition flux:

$$\frac{dR_f}{dt} = \frac{dm}{dt} \cdot \frac{1}{(\rho\lambda)_f} \quad (2.87)$$

An average value of 5000 kgW/m^4 can be used for $(\rho\lambda)_f$ following suggestions by Sheikholeslami and Watkinson (1986). For fouling rates below $10^{-6} \text{ m}^2\text{K/kJ}$ and fluid velocities below 0.8 m/s , the rate of crystallisation fouling can be estimated from Equation (2.69). Above this velocity, the equation should be modified to include a removal rate term.

Branch and Müller-Steinhagen (1991) also modelled CaCO_3 fouling in shell and tube heat exchangers by combining Hasson's scale formation model (1968-1981) with the Schlünder-Gaddis model (1979) for the prediction of the temperature distribution. The computed results allow assessment of clean heat exchanger design rules and of the effects of fouling on the efficiency of heat exchanger configurations. For the calculations described below it was assumed that a tube-side cooling water flow is heated by a non-fouling fluid on the shell-side. The solutions given in Table 2.2 were considered for the investigation:

Table 2.2 CaCO_3 solutions used for shell and tube heat exchanger modelling

SOLUTION				
	1	2	3	4
$[\text{Ca}^{2+}]$, mol/lit	0.004	0.006	0.008	0.01
[T.A.], mol/lit	0.004	0.004	0.004	0.004

From the above four solutions, (1) was sub-saturated, (2) was just saturated and (3) and (4) were super-saturated. Increasing the degree of supersaturation, in this case increasing $[Ca^{2+}]$, increases the extent of fouling. The supersaturation can be altered in a number of ways. A common fouling mitigation procedure is to reduce the degree of supersaturation by decreasing the pH of the solution.

It was shown that a small amount of deposition might be advantageous for the overall performance of the heat exchanger. Therefore, the best result was obtained for $pH = 6.5$. The thin $CaCO_3$ deposit produced for this pH furthermore acts as a protection against corrosion. Reducing the pH below a value of 6.3 does not cause any reduction of fouling. Heat exchanger configurations that do not show a maximum in their effectiveness curve also have an optimum pH. The optimum pH can be found by variation of the water treatment program or, less expensive, by computer modelling.

Branch and Müller-Steinhagen have concluded that since there are numerous combinations of fouling solution, fouling mechanism and heat exchanger configuration, selection of optimum exchangers will be specific to the problem at hand. However, the above results do not only apply qualitatively to $CaCO_3$ scaling, but to any fouling where deposition increases with wall superheat.

Chan and Ghassemi Model (1991)

Chan and Ghassemi used conservation equations and surface reaction kinetics to model scaling of heat transfer surfaces by calcium carbonate. Multi-species reaction rates were used in their model to predict the calcium carbonate fouling rates during forced convective heat transfer. In this model, the deposition is assumed to occur by the two processes of mass transport to and crystallisation reaction on the heat transfer surface. This model was then used to predict $CaCO_3$ scaling in a laminar falling film and in a turbulent annular flow system.

Chan and Ghassemi (1991) have shown that under steady state condition and when there is no reaction in the bulk of the solution, the continuity equation for cylindrical coordinate is reduced to:

$$v_z(r) \frac{\partial C_i}{\partial z} = D_{i,eff} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i}{\partial r} \right) \right] \quad (2.88)$$

Here, z and r are z -axis and r -axis in cylindrical coordinates. Equation (2.88) should be solved numerically with the following boundary conditions:

$$\text{at } r = kR: D_i \frac{\partial C_i}{\partial r} = k_r \left([Ca^{2+}] - [Ca^{2+}]^* \right)^2 \quad (2.89)$$

$$\text{at } r = R: \frac{\partial C_i}{\partial r} = 0 \quad (2.90)$$

$$\text{at } z = 0: C_i = C_i^0 \quad (2.91)$$

where kR is the location of liquid/solid interface in r direction. The fouling rate is then calculated from the numerical solution of Equation (2.88) in conjunction with the following equation:

$$\dot{m}_d = D_{i,eff} \left(\frac{\partial C_i}{\partial r} \right) \quad (2.92)$$

Najibi et al. Model (1997)

The previously discussed models have largely focused on crystallisation fouling under forced convective heat transfer, but heat transfer under boiling conditions occurs in equipment such as steam boilers, evaporators for the concentration of solutions prior to crystallisation or for the desalination of sea water. While fouling is already a substantial problem in forced convective heat transfer, it is more severe during boiling heat transfer for the following reasons:

- Due to the mechanism of bubble formation, the local concentration of foulants near the heat transfer surface may increase by several orders of magnitude.

- Heat transfer coefficients for boiling are considerably higher than forced convection values and are, therefore, more affected by the formation of an additional heat transfer resistance.

From the industrial point of view, pool boiling and sub-cooled flow boiling are important heat transfer modes, but hardly any research work on fouling during these mechanisms can be found in the literature. Najibi performed many experiments on calcium sulphate and on calcium carbonate scale deposition during sub-cooled flow boiling in a vertical annulus. For the investigated range of flow velocity, an almost linear increase in fouling resistance with time has been observed, except during the initial period of the experiments. The deposition rate was found to be controlled by different mechanisms, depending on flow velocity and surface temperature. Different trends were observed for conditions where convective heat transfer or nucleate boiling dominate.

Based on experimental results, Najibi et al. (1997) developed a mechanistic model for prediction of crystallisation fouling rates of calcium sulphate and calcium carbonate during sub-cooled flow boiling. This model is developed based on the initial deposition rate and the removal rate is ignored. In this model, the heat transfer surface is divided in two parts, namely the area affected by vapour bubbles and the remaining area where forced convective heat transfer occurs. Therefore, the overall fouling rate can be presented by the following equation:

$$\frac{dR_f}{dt}(\rho_f \lambda_f) = NBF \cdot \dot{m}_{nb} + (1 - NBF) \cdot \dot{m}_{fc} \quad (2.93)$$

where NBF is the Nucleate Boiling Fraction, i.e. the fraction of the total heat transfer affected by bubble formation and detachment. As the heat flux increases, the number of active nucleation sites increases and Equation (2.93) shows that the fouling caused by the boiling mechanism will increase. The Chen (1966) model is used to calculate the fraction of heat transferred by nucleate boiling, NBF :

$$NBF = \frac{\alpha_{nb} S}{\alpha_{fb}} \quad (2.94)$$

Because of the high level of turbulence created by the departure of the vapour bubbles from the nucleation sites, it is assumed that crystallisation fouling in the boiling zones is reaction rate controlled and second order, and given by:

$$\dot{m}_{nb} = K_{1,0} \exp\left(\frac{-E}{RT_s}\right) (\gamma C_b - C_s^*)^2 \quad (2.95)$$

where γ is the concentration effect in the microlayer beneath the vapour bubble. A value of 1.5 was obtained for this parameter.

For the crystallisation fouling rate in the area affected by forced convection, it is assumed that deposition takes place in two steps. In the first step, the ions are transported to the surface by molecular diffusion through the boundary layer formed between the crystals and the solution and in the second step, the ions will react at the surface to form the solid phase of calcium sulphate or calcium carbonate. According to this model, the fouling rate during forced convective heat transfer is a second order reaction which can be represented by the following equation:

$$\dot{m}_{fc} = \beta \left[\frac{1}{2} \left(\frac{\beta}{K_2} \right) + (C_b - C_s^*) - \sqrt{\frac{1}{4} \left(\frac{\beta}{K_2} \right)^2 + \left(\frac{\beta}{K_2} \right) (C_b - C_b^*)} \right] \quad (2.96)$$

where

$$K_2 = K_{2,0} \exp\left(\frac{-E}{RT_s}\right) \quad (2.97)$$

The parameters and physical properties of calcium sulphate and calcium carbonate, which are used in this model, are given in Table 2.3.

This model predicts a linear relationship between fouling rate and time, rather than decreasing or asymptotic fouling. For the investigated range of parameters, this agrees with the measured trends. However, experimental results of this study have shown that for very high heat fluxes ($> 400,000 \text{ W/m}^2$) bubble growth and departure generates forces which may cause parts of the scale to detach from the heat transfer surface. This removal mechanism is not included in the Najibi et al. model and is probably the reason why this model somewhat overpredicts the fouling rate during sub-cooled flow boiling, while the predicted fouling rates for forced convective heat transfer are more accurate.

Table 2.3 Parameters and physical properties used in the Najibi et al. (1997) model

Parameters Salts	$K_{1,0}$ ($\text{m}^4/\text{kg.s}$)	$K_{2,0}$ ($\text{m}^4/\text{kg.s}$)	E (kJ/kmol)	ρ_d (kg/m^3)	λ_d (W/m.K)
Calcium sulphate	2.9×10^{10}	5.7×10^{11}	112517	2165	2.23
Calcium carbonate	9.8×10^{11}	9.8×10^{11}	122150	2705	1.942

Chapter 3

SOLUBILITY EQUILIBRIA

Water is the basis of aqueous solutions and an excellent solvent for many compounds. Some dissolve in it as molecules while others, called electrolytes, dissociate and dissolve not as neutral molecules but as charged species called ions. Compounds which exist as solid ionic crystals dissolve in water as ions and most of them are highly soluble in water. Highly soluble is a somewhat vague description, but generally means soluble to at least the extent of forming 0.1 to 1.0 molar aqueous solutions. Salts which are less soluble in water than this, are called slightly soluble salts or sparingly soluble salts. Certain combinations of these ions are compounds which have very little solubility in water.

The problem of solubility equilibria falls within the field of water chemistry. Solubility equilibria are present whenever a solid substance is in contact with a solution, and as with all equilibrium constants they reflect the actual concentrations in solution. Thus if these concentrations are altered, by addition of reagents, removal of material, addition of water, or by other chemical reactions or equilibria, solid material may come out of solution or precipitate from solution, or on the other hand solid material may dissolve or go into solution. The following section briefly reviews the fundamental principles related to this topic and the scale formation in the associated processes.

3.1 GENERAL SOLUBILITY CONSIDERATIONS

Solubility is defined as the limiting amount of a solute which can be dissolved in a solvent under a given set of physical conditions. Therefore this term refers to the concentration of a solute when the solution is in equilibrium with the pure solute. Under these conditions the solution is called saturated. A solution which contains less than this maximum concentration is called an unsaturated solution. It is sometimes possible to prepare solutions which are more concentrated than a saturated solution, although these solutions are unstable and the excess solute will sooner or later separate from the solution. Such

solutions are called supersaturated solutions. A supersaturated solution will often lose the excess solute immediately if a suitable site such as a crystal of solute is introduced into the solution.

Variations of temperature, pressure, pH and the relative concentrations of other substances in solution control the solubility of a given salt in a solvent. Therefore, the solubility of a given substance will vary for different solvents and is defined at a certain temperature since the solubility often changes with temperature. It is often expressed in units of mol/l which is called molar solubility.

Solubility calculation may be used to predict the formation of certain types of scales. The values obtained from these calculation procedures should be taken as guidelines. They indicate the degree of scaling tendency, or the likelihood of scale formation. It should be emphasised that if scale formation is indicated by calculation, it should serve as a warning. If it has been planned to use a possible water source, those which show scaling tendencies should be avoided or provision made for treatment. Similarly, one should avoid mixing waters which would result in a composite analysis which indicates scaling tendency under the system conditions. A calculated scaling tendency in an existing system should focus attention on the fact that scale formation is likely and one should begin to monitor the system for signs of scale formation immediately.

It is extremely critical that the values of the various parameters used in solubility calculations be measured on the water sample immediately after it is taken in the field. Valid solubility calculations can not be made from laboratory water analysis, because of the time lapse between sampling and analysis. This is true because some of the critical parameters change very quickly after sampling. Ideally, the water analysis would be conducted at system temperature and pressure. Sometimes this is not possible, but it should be analysed as quickly as possible. Some of the parameters that begin to change immediately after sampling are:

i) Temperature

This is a critical parameter in the formation of all scales.

ii) pH

When the pressure is reduced, any dissolved acid gases such as H_2S and CO_2 will begin to escape from the solution and the pH will begin to rise. An accurate pH value is essential for predicting the solubility of several scales.

iii) Bicarbonate and Carbonate Ions

The loss of dissolved CO_2 will have a direct effect on the bicarbonate and carbonate concentrations. Therefore, the concentrations of these ions must be determined immediately.

3.1.1 Solubility Product Principle

When a sparingly soluble salt such as CaSO_4 is added to water, Ca^{2+} and SO_4^{2-} ions from the crystal lattice of the solid pass into solution until the solution becomes saturated. In the saturated solution, an equilibrium exists between the ions in solution and ions present in the solid crystal lattice:

At a given temperature and pressure the amount of CaSO_4 dissolved is constant. Furthermore, the product of the concentrations of the ions in the saturated solution is also constant. This constant is called the solubility product constant.

$$K_{SP} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \quad (\text{at saturation}) \quad (3.2)$$

where K_{SP} is the solubility product constant and $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ are the calcium and sulphate ion concentrations, respectively. Based on this principle, it is possible to evaluate a solution with respect to the possibility of precipitation of the dissolved salt in terms of the solubility product constant and the actual concentrations of the ions in the solution.

If there is a solution which contains a given amount of dissolved CaSO_4 and the concentrations of Ca^{2+} and SO_4^{2-} are $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ respectively, the possibilities are as follows:

i) $[\text{Ca}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}$	the solution is saturated with CaSO_4 .
ii) $[\text{Ca}^{2+}][\text{SO}_4^{2-}] < K_{\text{sp}}$	the solution is subsaturated with CaSO_4 , precipitation can not occur.
iii) $[\text{Ca}^{2+}][\text{SO}_4^{2-}] > K_{\text{sp}}$	the solution is supersaturated with, precipitation can occur.

Thus, precipitation can occur only in the last case. However, it may not occur in practice due to the fact that solutions often remain supersaturated until sufficient energy is available to initiate nucleation of the crystalline solid from solution.

3.1.2 Supersaturation Ratio

Continuing with the example of CaSO_4 dissolved in water, the *supersaturation ratio* is defined as the ratio of the ionic product to the solubility product constant:

$$\text{IP} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \quad (3.3)$$

$$\text{SR} = \frac{\text{IP}}{K_{\text{sp}}} = \frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{K_{\text{sp}}} \quad (3.4)$$

where IP is the ionic product and SR is the supersaturation ratio. Thus, it is also possible to express the conditions necessary for precipitation in terms of the supersaturation ratio:

i)	$\text{SR} = 1$,	the solution is saturated with CaSO_4 .
ii)	$\text{SR} < 1$,	the solution is subsaturated with CaSO_4 and precipitation can not occur.
iii)	$\text{SR} > 1$,	the solution is supersaturated with CaSO_4 and precipitation can occur.

3.2 DISSOLUTION AND PRECIPITATION

The process of dissolution occurs when a solute is placed in contact with a solvent and dissolves to form a solution. If the solvent is removed from a solution, by a process such

as evaporation, eventually the solute will be found to separate from the remaining solution. This separation is called the precipitation of a solid. Once the solubility of dissolved material is exceeded, some of the dissolved salts may precipitate out to form deposits.

Therefore, the processes of dissolution and precipitation are the reverses of each other. Taken together, they form a dynamic equilibrium. Whenever a supersaturated solution forms, the equilibrium state will sooner or later be achieved by precipitation of a solid salt. Whenever an unsaturated solution is present in contact with a solid salt, the equilibrium state will sooner or later be achieved by dissolution of all or part of the solid salt.

Dissolution of a solid salt does not take place uniformly from the surface of salt crystals. Sections of the solid salt having a greater surface-to-volume ratio, such as small crystals or projections from the surface, tend to dissolve more rapidly than the bulk of the crystals. Likewise, precipitation does not occur uniformly throughout a solution. Precipitation proceeds through two stages called nucleation and crystal growth. Nucleation is the process of formation of tiny crystalline nuclei in the solution, while crystal growth is the ordered growth of these nuclei into larger well-formed crystals. Crystal growth can occur only after nuclei are formed.

As it was stated before, water has a limited capacity for maintaining compounds in solution, and once this capacity or solubility is exceeded, the compounds precipitate from solution as solids. Therefore, precipitation of solid materials which may form scale will occur if:

- a) the water contains ions which are capable of forming compounds of limited solubility and
- b) there is a change in physical conditions or water composition which lowers the solubility below the present concentrations.

The factors affecting scale precipitation, deposition and crystal growth can be summarised as follows:

- i) Supersaturation
- ii) Mixing of two unlike waters having incompatible compounds in solution
- iii) Change of temperature
- iv) Change of pressure on solution
- v) Evaporation
- vi) Agitation
- vii) Contact time and
- viii) pH

The major limiting economic factor in evaporation processes is the degree to which seawater or industrial fluids can be concentrated before scale formation occurs. For example, seawater becomes saturated with respect to calcium sulphate anhydrite when it is evaporated at 100°C to two-thirds of its original volume (Langelier et al., 1957). However, solid precipitates may either stay in suspension in the water, or may form a coherent scale on a surface such as a heat transfer surface or a pipe wall. As an illustration, when water is injected in oil reservoirs to enhance oil recovery, formation plugging may occur by filtration of suspended particles from the water or, a solid scale may form on the formation face. Either is undesirable. The difficulty of removal may vary with the type of plugging that has occurred. On the other hand, scale formation on pipe walls frequently restricts flow through injection and production flowlines and tubing strings.

In processes such as evaporation and crystallisation, various salts will precipitate in a certain order, depending on operating temperature, pressure, pH, ionic strength of solution, etc. The solubility of most salts increases with increasing temperature and, as a rule, these salts do not crystallise on heated surfaces unless the concentrations are very high. Scale deposits are formed from those salts whose solubilities are generally limited and, in most instances, decrease with increasing temperature.

Some interesting situations occur when the formed crystal is a hydrate. As the temperature increases, a point may be reached where the hydrate becomes unstable and begins to lose water. The new form will have a different solubility curve with temperature. For example, the solubility of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ increases rapidly with

increasing temperature from 0° to 32.4° C. Above 32.4° C, the stable form is Na_2SO_4 . The solubility of the anhydrous form decreases as the temperature increases.

3.3 COMMON ION EFFECT

The concentration of ions in solution is affected by all equilibria and all species present in the solution. The simplest and most significant effect is called the common ion effect. The common ion effect is observed whenever an ion in solution is common to two different salts which serve as its sources. Addition of the second salt adds the common ion, which is a product of the dissolution of the first. The effect of adding the product ion will be to decrease the solubility of the first salt. The data required to calculate the magnitude of this effect in aqueous solutions are the molar solubility constants.

The common ion effect is an application of LeChatelier's Principle. If a soluble salt containing a common ion is mixed to a slightly soluble salt equilibria, it will affect the position of the equilibrium of the slightly soluble salt system. Adding the common ion to the salt solution, by mixing the soluble salt, will increase the concentration of the common ion. According to LeChatelier's Principle that will place a stress upon the slightly soluble salt equilibria. The equilibrium will respond so as to undo the stress of added common ion. This means that the equilibria will shift so that the common ion will be reduced which means a shift to the direction that reduces the solubility of the slightly soluble salt in the system.

3.4 COMMON SCALES

Of the many possible water formed scales, only a few are commonly found on heat transfer surfaces and in oilfield waters. These scales are listed in Table 3.1 along with the primary variables which affect their solubility.

The most common scale deposits are calcium carbonate, calcium sulphate, barium sulphate and to a lesser extent strontium sulphate. However, the principal constituents

that cause fouling problems in seawater and in most other industrial installations are calcium sulphates (Gypsum, Hemi-hydrate and Anhydrite) and calcium carbonate (Aragonite, Calcite and Vaterite). The deposition of calcium carbonate can theoretically be controlled by maintaining a slightly acidic pH. Calcium sulphate, however, is not significantly affected by pH and tends to precipitate in various forms once the solution becomes supersaturated. Investigating the effects on heat transfer, calcium carbonate crystals are better insulators than calcium sulphate. This insight is gained by reviewing the thermal conductivity data.

As it was stated previously, scale deposits usually form as a result of crystallisation and precipitation of minerals from solutions. The direct cause of scaling is frequently pressure drop, temperature change, mixing of two incompatible waters or exceeding the solubility product. For example, in the petroleum industry, water is injected in petroleum reservoirs to enhance oil recovery. During water injection processes, incompatibility between injected and formation waters is the main reason of scale deposition. Hardly any source of water is available in large enough quantities, which is fully compatible with all compounds in the formation into which the water is injected. Native formation water (connate water) is in chemical and thermodynamical equilibrium with its own environment (e.g. rock, hydrocarbons, dissolved gases, ions, etc.). In contrast, injection water is in equilibrium with its own environment that is generally quite different from that in the formation to be injected.

Therefore mixing of these waters can lead to chemical reactions between their species, and each type of mineral of which supersaturation is reached will precipitate out of solution. Even returning produced brine to its parent formation may lead to scaling problems. This is because, when water is co-produced with other reservoir fluids, dissolved reactive gases such as CO_2 and H_2S evolve from the water resulting in rapid change of pH and composition of the water. Therefore, produced brine has not exactly the same properties of the water that exist in the formation and incompatibility between these waters may be probable.

Table 3.1 Most common scales

Name	Chemical Formula	Primary Variable
Calcium Carbonate Aragonite Calcite Vaterite	CaCO_3 CaCO_3 CaCO_3	Partial Pressure of CO_2 , Temperature, TDS
Calcium Sulphate Gypsum Hemi-Hydrate Anhydride	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ CaSO_4	Temperature, Pressure, TDS
Barium Sulphate	BaSO_4	Temperature, Pressure, TDS
Strontium Sulphate	SrSO_4	Temperature, Pressure, TDS
Iron Compounds Ferrous Carbonate Ferrous Sulphide Ferrous Hydroxide Ferric Hydroxide Ferric Oxide	FeCO_3 FeS $\text{Fe}(\text{OH})_2$ $\text{Fe}(\text{OH})_3$ Fe_2O_3	Corrosion, pH, Dissolved Gas

Hence, the most important factor related to precipitation fouling is the supersaturation level of the deposit forming species. Almost all researchers expressed the rate of crystallisation of salts with respect to the degree of supersaturation driving force. Therefore, accurate understanding of saturation concentration of the salts and salt mixtures under various operating conditions is essential for the prediction of the deposition rate on heat transfer surfaces. This section of the thesis will focus on CaSO_4 and CaCO_3 because their presence causes many industrial problems.

3.4.1 Calcium Sulphate

Palache (1951) has reported that calcium sulphate is present in three distinct lattice structures. They are:

Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Dihydrate
Bassanite	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	Hemihydrate
	CaSO_4	Anhydrite

These crystals differ chemically by the amount of water contained in their structure. The anhydrite lattice has the closest packing, highest density and most stable arrangement of any calcium sulphates. This partly explains its reactivity at temperatures above 42 °C, whereas at the lower temperatures the dihydrate crystal (Gypsum) predominates (Wells, 1962). The phase transitions are shown in Figure 3.1.

Figure 3.1 Phase transitions in the calcium sulphate-water system

In the present investigation, bulk temperatures are 50-80 °C and surface temperatures are 98-120 °C. It may therefore be possible to observe hemihydrate and anhydrite scale next to the heat transfer surface, while dihydrate is the predominant form of calcium sulphate deposited next to the process fluid.

3.4.1.1 Saturation Concentration

The precipitation of calcium sulphate from water results from the reaction:

Most of the deposited calcium sulphate found in this investigation as well as in sea water desalination plants was in the form of hemi-hydrate whereas most calcium sulphate deposits found in oil fields are Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which is the stable form at temperature of 40°C or less. Above this temperature, anhydride (CaSO_4) may be found, although hemi-hydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$) may form under certain conditions. Generally Gypsum is the stable form at low temperature, whereas anhydride is formed at higher temperatures (Vetter, 1976).

a) Effect of Temperature

The solubility of calcium sulphate in water is shown in Figure 3.2 as a function of operating temperature (Landolt-Bornstein, 1985). At temperatures higher than 40°C, the solubility of calcium sulphate decreases with increasing temperature for ordinary solid phases. Gypsum solubility increases with temperature up to about 40°C, then decreases with temperature as shown in Figure 3.2. Under normal operating conditions, the hottest portion of the solution is the layer next to the heat transfer surface. Any precipitation is, therefore, expected to take place there.

This is quite different from the temperature-solubility behaviour of CaCO_3 , which will be discussed in the next sections. First of all, Gypsum is considerably more soluble than CaCO_3 in the normal temperature range of interest. Secondly, the maximum in the Gypsum curve shows that an increase in temperature could either increase or decrease the solubility of Gypsum depending on the temperature at the beginning. This is clearly different from CaCO_3 where an increase in temperature always decreases the solubility.

The temperature at which scale changes from Gypsum to anhydride or hemi-hydrate is a function of many factors, including pressure, dissolved solid concentration, flow

conditions and the rate at which different forms of calcium sulphate can precipitate out from solution. Predicting which form of calcium sulphate will precipitate under a given set of conditions is very difficult, although anhydrite precipitate would be expected above 40 °C in preference to Gypsum due to its lower solubility. In temperatures higher than 100 °C, anhydrite may precipitate out directly from the solution. Moreover, if calcium sulphate precipitates in the form of Gypsum on heat transfer surfaces, dehydration of the Gypsum crystals could be expected to occur, and depending on operating conditions, hemi-hydrate or anhydrite might be formed with passage of time.

Figure 3.2 Solubility of calcium sulphate in water as a function of temperature

In the petroleum industry, it has been reported that calcium sulphate initially precipitates in the form of Gypsum for temperature range of 40 to 100 °C (NIOC files). Since the temperature range which is encountered in oilfield production operations either in disposal water injection or seawater injection and also in surface production facilities is not more

than 100 °C, it is quite clear that calcium sulphate may precipitate in the form of Gypsum and then depending on temperature change to other morphologies of this scale. Therefore, it is reasonable to accept that Gypsum solubility is the limiting parameter in deposition of calcium sulphate in oilfields and thus the Gypsum solubility product must be used in scale related calculations.

b) Effect of Dissolved Salts

The solubility of calcium sulphate increases with increasing concentration of other ions present in the solution if they are not common ions, on account of the increase in ionic strength. For example, the solubility of calcium sulphate in seawater is higher than in distilled water, because of the presence of substantial amounts of other ions such as sodium and chlorine. These ions are mostly formed from the dissolution of sodium chloride.

Figure 3.3 Solubility of Gypsum in NaCl brines at 70 °C

The presence of NaCl or dissolved salts other than calcium or sulphate ions increases the solubility of Gypsum or anhydride just as it does for CaCO_3 , up to a salt concentration of about 150000 mg/l. Further increases in salt content decrease calcium sulphate solubility as shown in Figure 3.3 (Carlberg and Matches, 1973).

c) Effect of Pressure

The solubility of calcium sulphate, like all other scales in water, increases with increasing pressure. This increase in solubility is due to the fact that when the scale is dissolved in water, there is a decrease in the total volume of the system.

When this phenomenon occurs, pressure affects solubility in proportion to the change in volume. A simplified expression for the effect of pressure on the solubility of calcium sulphate in water can be derived from basic thermodynamic relationships and is given by Fulford (1967) as:

$$\ln \frac{[\text{CaSO}_4, 1 \text{ atm}]}{[\text{CaSO}_4, P \text{ atm}]} = \frac{(\Delta P) \cdot (\Delta V)}{2 R T} \quad (3.7)$$

where:

$[\text{CaSO}_4, 1 \text{ atm}]$ = Solubility of CaSO_4 at atmospheric pressure

$[\text{CaSO}_4, P \text{ atm}]$ = Solubility of CaSO_4 at P atmosphere

ΔP = (P-1) atmospheres

ΔV = Volume decrease (ml/mol) when CaSO_4 is dissolved in a given volume of water

R = Gas constant = 82.05 ml.atm/mol.K

T = Absolute temperature, K

Although this expression can be used to approximate the effect of pressure on the solubility of calcium sulphate as well as of other scales, it should be noted that the values

of ΔV are a function of salinity, pressure, and temperature as well as of the specific compound involved. In the case of calcium sulphate, the effects of temperature and pressure on ΔV values are small and can be neglected. However, ΔV values decrease significantly as the total dissolved solids (TDS) content of the water increases. Therefore, pressure has less effect on high TDS waters than on fresh waters (Vetter and Philips, 1970).

The effect of pressure and temperature on anhydrite solubility is shown in Figure 3.4 (Dickson et al., 1963). It should be noted that the pressure effect decreases as temperature increases. For example, pressure drop can be a major cause of CaSO_4 scale formation in producing wells in oilfields.

Figure 3.4 Effect of pressure and temperature on CaSO_4 (anhydrite) solubility

For the purpose of calculation of sulphate scales solubility at elevated pressure, Equation (3.7) could be used. Use of this equation needs the knowledge of the value of ΔV , volume

change resulting from solution of sulphate salts in water. ΔV values must be measured in the laboratory. Because of the lack of complete data for ΔV values in the range of interest, this method was not chosen for calculation of solubility product at elevated pressure. In the following paragraphs, new empirical equations will be introduced which predict the effect of pressure and water salt content on the solubility of calcium sulphate (Gypsum and anhydride) with better precision.

Empirical equations were developed from the correlation of solubility with pressure. The proposed pressure equations are able to predict the solubility change caused by increase in pressure up to 5×10^4 kPa. Table 3.2 displays the equations and the values of the pressure parameters (Yuan and Todd, 1990). In these equations, K_{sp} and $K_{sp,r}$ are the stoichiometric solubility products at pressure P and at reference pressure P_r , respectively. Pressure is expressed in bar, temperature is in Kelvin and J is on molal basis. Maximum pressures and solution ionic strengths within which the pressure equations are valid, and pressure equation coefficients are given in this table. It must be noted that ionic strength in these equations has been expressed in molal unit which is not exactly equal to molar ionic strength. Therefore, for using these equations, all of the concentrations must be converted to molal. This can be done by using the following equation:

$$J = \frac{meq / l}{Z \left(1000 SG - \frac{TDS}{1000} \right)} \quad (3.8)$$

where J = Concentration of the ion, molal

meq/l = Concentration of the ion in milli-equivalents per litre

Z = Valence of the ion

SG = Specific gravity of the brine

TDS = Total dissolved solids, mg/l

The following correlation was developed for the prediction of density of the brine when the total dissolved solid concentration is known, by regression analysis of SOLMINEQ88 output data (Helalizadeh et al., 1999). The specific gravity of the brine is obtained by dividing the density of the brine by the density of pure water.

$$\rho_w = 62.45 + 0.458TDS + 1.589 \times 10^{-3} \times TDS^2 \quad (3.9)$$

ρ_w is in lb/ft³ and TDS is the percentage of total dissolved solids. When the pressure and/or temperature are higher than standard conditions, the density is determined by dividing the density at standard conditions by the formation volume factor of the water at actual conditions (Craft et al., 1991).

Table 3.2 Effect of pressure on sulphate scales solubility products

$K_{sp} = R^2 K_{sp,r} \quad (3.10)$						
$R_{Anhydride} = \text{Exp} \left\{ \left[A(P - P_r) + B(P^2 - P_r^2) \right] \text{Exp}(C_j^{0.5} + D_j) \right\} \quad (3.11)$						
$R_{BaSO_4} = \text{Exp} \left\{ \left[A(P - P_r) + B(P^2 - P_r^2) \right] \text{Exp}(C_j^{0.5} + D_j) \right\} \quad (3.12)$						
$R_{SrSO_4} = \text{Exp} \left\{ \left[A(2 - T/298)(P - P_r) + B(P^2 - P_r^2) \right] \text{Exp}(C_j^{0.5} + D_j) \right\} \quad (3.13)$						
$R_{Gypsum} = 1 + 0.69(R_{Anhydride} - 1) \quad (3.14)$						
SULPHATE	P _{max}	J _{max}	A	B	C	D
BaSO ₄	500	6.0	0.82×10 ⁻³	0.27×10 ⁻⁶	0.5468	0.1022
SrSO ₄	414	2.0	0.18×10 ⁻²	-0.17×10 ⁻⁵	0.1	-0.4
CaSO ₄	500	6.0	0.5×10 ⁻³	0.12×10 ⁻⁵	-0.988	0.229

Barium sulphate and calcium sulphate solubility products at elevated pressure are calculated by these equations. For calcium carbonate, previously mentioned equations for calculation of solubility product and saturation index already include the effect of pressure.

d) Effect of pH

pH has little or no effect on the solubility of calcium sulphate (It has a small effect at pH<3).

3.4.1.2 Solubility Calculations

Solubility values for salts such as CaSO_4 , BaSO_4 , and SrSO_4 can be calculated using the following equation, provided that values of K_{sp} are known for each compound:

$$\text{Solubility (meq/l)} = S = 1000 [X^2 + 4 K_{sp}]^{1/2} - X \quad (3.15)$$

Where X is the excess common ion concentration. The derivation of this equation follows.

a) The Common Ion Effect

The maximum solubility of a slightly soluble salt is obtained when the concentrations of the cation and anion are equal. For example for a saturated solution of CaSO_4 in water, where the Ca^{2+} and SO_4^{2-} concentrations, are equal to S mol/l:

$$K_{sp} = (S)(S) = S^2 \quad (3.16)$$

$$S = (K_{sp})^{1/2} \quad (3.17)$$

The solubility of calcium sulphate is equal to S mol/l that is simply the square root of the molar solubility product constant.

However, in most natural water, the cation and anion concentrations are not equal. In this case, the difference between the two concentrations is called the excess common ion concentration. The presence of excess common ions reduces the solubility of the salt unless a complex ion or ion pair, such as neutral magnesium sulphate, forms and offsets the effect.

For example, a saturated solution of CaSO_4 in water, where the Ca^{2+} and SO_4^{2-} concentrations are unequal is considered.

Ca^{2+} concentration = S , mol/l

CO_4^{2-} concentration = $S + X$, mol/l

In this case, the sulphate ion concentration has arbitrarily been selected as the larger of the two. The amount by which the sulphate ion concentration exceeds the calcium concentration, X , is the excess common ion concentration.

$$K_{sp} = (S) (S + X) = S^2 + SX \quad (3.18)$$

The calcium sulphate solubility is equal to S mol/l since that is the maximum amount of calcium sulphate which can be formed by combining S moles of Ca^{2+} with $(S+X)$ moles of SO_4^{2-} . By rearranging:

$$S^2 + SX - K_{sp} = 0 \quad (3.19)$$

Taking the positive root of the quadratic equation:

$$S = \frac{-X + (X^2 + 4K_{sp})^{1/2}}{2} \quad (3.20)$$

For a divalent ion:

$$S \text{ (eq/l)} = (X^2 + 4K_{sp})^{1/2} - X \quad (3.21)$$

or:

$$S \text{ (meq/l)} = 1000 [(X^2 + 4K_{sp})^{1/2} - X] \quad (3.22)$$

The actual concentration of $CaSO_4$ in the solution of interest is equal to the smaller value of the Ca^{2+} and SO_4^{2-} concentrations (expressed in meq/l), since the smaller concentration limits the amount of calcium sulphate which can be formed.

The calculated calcium sulphate solubility, S (meq/l), is compared with the actual concentration to determine if scale formation is likely.

- i) If $S =$ Actual concentration, then the water is saturated.
- ii) If $S >$ Actual concentration, then the water is subsaturated and scaling is unlikely.
- iii) If $S <$ Actual concentration, then the water is supersaturated and scaling is likely.

This formula can be used to calculate the solubility of any divalent salt such as $CaSO_4$, $BaSO_4$ or $SrSO_4$.

b) Calcium Sulphate (Gypsum) Solubility Calculation

The most commonly used method of predicting the solubility of Gypsum in solutions such as oilfield brines is that of Skillman, McDonald and Stiff (1969). They measured the solubility product constant in simulated oilfield brines.

The following procedure is recommended to assess the possibility of Gypsum precipitation from a given solution.

1. Calculation of molar ionic strength of the solution.
2. Obtaining the appropriate value of K_{sp} for the temperature of interest.
3. Determining the excess common ion concentration, X , in mol/l.
4. Calculation of the solubility of Gypsum in meq/l as discussed previously.
5. Calculation of actual concentration of Gypsum in water, which is equal to the smaller of the Ca^{2+} or SO_4^{2-} concentrations expressed in meq/l.
6. Comparing the calculated solubility with the actual concentration to determine if precipitation of Gypsum is likely.

Most of the deposited calcium sulphate found in this investigation, as well as in seawater desalination plants and other industries, was in the form of hemi-hydrate, the solubility of which has been studied in detail by Marshal and Slusher (1960). Najibi et al. (1997) developed the following correlation for the prediction of the saturation concentration of calcium sulphate hemi-hydrate as a function of ionic strength of the solution and surface temperature by non-linear regression analysis of their data.

$$C^* = 136 \left(10^{a+bz} \right) \quad (3.23)$$

where C^* is in kg/m^3 and parameters a , b and z are:

$$\begin{aligned} a &= 2.047 - 0.01136T \\ b &= -6.5832 + 0.0226T \end{aligned} \quad (3.24)$$

and

$$z = \frac{\sqrt{I}}{1 + 1.5\sqrt{I}} \quad (3.25)$$

T is the absolute temperature in K , and I is the ionic strength expressed in kmol/m^3 .

3.4.1.3 Saturation Index

For any salt precipitation, the supersaturation potential can be expressed in various ways. A widely used expression for characterising the supersaturation potential is the saturation index. The saturation index, SI , of a salt is defined as the logarithm of the ratio between the activity product of its ions and the solubility product at the appropriate temperature. Scaling indices use the chemistry of an aqueous solution to indicate whether the solution has the potential for scaling or corrosion. Determining whether deposition of a salt is thermodynamically possible (i.e. $SI > 0$), therefore, requires knowledge of the concentrations and activity coefficients of all the ions present in the solution.

Although the overall chemical composition of a solution may be known from analysis, the distribution of ions between different species such as H_2SO_4 , HSO_4^- , SO_4^{2-} requires the solution of a series of simultaneous equations corresponding to the chemical equilibria in solution, for which the equilibrium constants are known at the required temperature. Although complex functions and computer codes exist for calculating calcium sulphate solubilities as a function of temperature, pressure and ionic strength, a number of simplified saturation indices have been devised and are widely used.

Oddo and Tamson (1994) developed the following relatively simple functions for calculating the solubility of various calcium sulphate scales:

$$SI = \log \left\{ [\text{Ca}^{2+}] [\text{SO}_4^{2-}] \right\} + A + B T + C T^2 + D P + E I^{1/2} + F I + G I^{1/2} T \quad (3.26)$$

The coefficients for various calcium sulphate crystals are summarised in Table 3.3.

Table 3.3 Coefficients of Equation (3.26)

Coefficients CaSO₄	A	B	C	D	E	F	G
Gypsum	3.47	1.8×10^{-3}	2.5×10^{-6}	-5.9×10^{-5}	-1.13	0.37	-2×10^{-3}
Hemihydrate	4.04	-1.9×10^{-3}	11.9×10^{-6}	-6.9×10^{-5}	-1.66	0.49	-0.66×10^{-3}
Anhydrite	2.52	9.98×10^{-3}	-0.97×10^{-6}	-3.07×10^{-5}	-1.09	0.50	-3.3×10^{-3}

Free sulphate and calcium ion concentrations can be calculated from the following equations respectively:

$$[SO_4^{2-}] = \frac{-\left\{1 + K_s(\Sigma C_M - C_{SO_4})\right\} + \left\{\left(1 + K_s(\Sigma C_M - C_{SO_4})\right)^2 + 4K_s C_{SO_4}\right\}^{0.5}}{2K_s} \quad (3.27)$$

$$[Ca^{2+}] = \frac{C_{Ca}}{(1 + K_s [SO_4^{2-}])} \quad (3.28)$$

The parameter K_s in Equations (3.27) and (3.28) is given by:

$$\log K_s = 1.86 + 4.5 \times 10^{-3}T - 1.2 \times 10^{-6}T^2 + 10.7 \times 10^{-5}P - 2.38I^{0.5} + 0.58I - 1.3 \times 10^{-3}I^{1/3}T \quad (3.29)$$

where T = Temperature, °F

P = Total pressure, psia

I = Ionic strength, mol/l

C_{SO_4} = Total sulphate concentration, mol/l = (g SO_4^{2-} /l)/96

C_{Ca} = Total calcium concentration, mol/l = (g Ca^{2+} /l)/40

$\Sigma C_M = C_{Ca} + C_{Ba} + C_{Sr} + C_{Mg}$, mol/l

A negative saturation index indicates a non-scaling condition. A zero saturation index indicates an equilibrium condition, and a positive saturation index indicates that scale may form on the heat transfer surface.

3.4.2 Calcium Carbonate

Calcium carbonate is by far the most commonly encountered scale compound. According to Palache (1951), calcium carbonate can form Calcite, Aragonite and Vaterite lattice structures. However only Calcite and, to a lesser degree, Aragonite occur in nature. Calcite and Aragonite are the only forms of calcium carbonate thermodynamically stable at temperatures and pressures encountered by the water treatment industry. The Calcite structure is somewhat more dense (more closely packed) than that of Aragonite.

Calcite scale is the most common form of calcium carbonate which is encountered in oilfield production operations. Its crystals have the greatest stability in oil field circumstances. Calcium carbonate crystals are generally large, but when the scale is formed with impurities in the form of finely divided crystals, the scale appears uniform.

Deposition of CaCO_3 scale or sludge results from precipitation of calcium carbonate according to the following equation:

As it will be seen later, calcium carbonate scale can also be formed by combination of calcium and bicarbonate ions and this reaction is the major cause of calcium carbonate scale deposition on heat transfer surfaces and in oilfield operations. This is because only a small percentage of the bicarbonate ions dissociate at the pH values found in most process fluids of industrial installations and injection waters of oilfields to form H^+ and CO_3^{2-} , as shown in Figure 3.5 (Patton, 1986).

Calcium carbonate contains a basic anion, which influences the hydronium ion concentration of its aqueous solutions. Thus if no auxiliary reagent is employed to maintain a constant pH, the hydronium ion concentration becomes dependent upon the extent to which calcium carbonate dissolves. Hence the aqueous solution of saturated calcium carbonate becomes basic as a consequence of the following reactions, which take place in aqueous solutions and cause crystallisation of calcium carbonate:

The total carbon concentration is defined as:

$$C_T = [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] + [\text{CO}_3^{2-}] \quad (3.36)$$

Figure 3.5 Ionisation of carbonic acid at different pH values

To determine the carbonate solubility, the chemistry of carbonic acid solutions should first be understood. Dissociation of strong acids and bases in pure water is complete, hence the hydrolysis effect of water is negligible and the pH can be calculated using the

molar mass of the substance added. However, in the case of weak acids or bases, the dissociation is not complete and the pH can not be determined by the above method.

Calcium carbonate is the salt of a diprotic weak acid H_2CO_3 which has three different equivalence points with respect to H_2CO_3 , HCO_3^- and CO_3^{2-} . HCO_3^- and CO_3^{2-} are the conjugate base of a weak acid which increase the pH of the solution. On the other hand, total alkalinity is a term for expressing the solubility equilibria of such substances that cause the formation of ions reacting with strong acid, i.e. with H^+ ions. This parameter has a conceptual significance and is also a readily measurable quantity. Total alkalinity, equivalent/l, can be easily visualised, by considering that water containing a weak carbonic acid at total carbon species concentration, C_T , has reached its given pH through addition of a concentration $[\text{B}^+]$ of a strong base. Therefore, based on the electroneutrality condition through the proton balance equation,

$$[\text{H}^+] + [\text{B}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (3.37)$$

The equivalent strong base concentration defines the total alkalinity (T.A.):

$$[\text{T.A.}] = [\text{B}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (3.38)$$

3.4.2.1 Saturation Concentration

It was previously mentioned that calcium carbonate crystals exist in three forms, namely Aragonite, Calcite and Vaterite. Since all three forms of this salt have an inverse solubility, their solubilities in water will decrease as temperature increases. This trend is illustrated in Figure 3.6, where the solubilities of various calcium carbonates are plotted as a function of temperature (Plummer and Busenberg, 1982). Therefore, the saturation concentration will decrease near the heat transfer surface. If the concentration of the solution exceeds the saturation concentration, crystallisation fouling of calcium carbonate will occur. Scanning Electron Microscopy and X-Ray analysis of calcium carbonate deposits revealed that more than 98% of the deposited calcium carbonate found in this investigation was in the form of Aragonite, the solubility of which has been studied in detail by Plummer and Busenberg (1982).

Figure 3.6 Solubility of calcium carbonate in water as a function of temperature

The equilibrium constant for the dissociation of calcium carbonate is written as:

$$K = \frac{a(\text{Ca}^{2+}) \cdot a(\text{CO}_3^{2-})}{a(\text{CaCO}_3)} \quad (3.40)$$

where a is the activity of species. More commonly, the above equation is written in the form;

$$K \cdot a(\text{CaCO}_3) = a(\text{Ca}^{2+}) \cdot a(\text{CO}_3^{2-}) = K_{sp} \quad (3.41)$$

If the molar concentrations are taken as good approximations to the activities, which in dilute solutions they are, then the solubility product of calcium carbonate is defined as:

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \quad (3.42)$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the saturation concentration. Supersaturation occurs when the concentration of ions increases beyond the saturation concentration.

In water, in the absence of common ion effects, the solubility of calcium carbonate (Aragonite) becomes the square root of the solubility product, K_{sp} , which is given by the following equation (Plummer and Busenberg, 1982):

$$\log(K_{sp}) = -171.9773 - 0.077993T + \frac{2903.293}{T} + 71.595 \log(T) \quad (3.43)$$

Here, T is the absolute temperature in K , and K_{sp} is in molar units.

3.4.2.2 Effective Parameters

Solubility of calcium carbonate is greatly influenced by partial pressure of carbon dioxide, temperature and concentration of other salts in the solution. Effective parameters for calcium carbonate scaling tendency are discussed as follows:

a) Carbon Dioxide Partial Pressure

Calcium carbonate precipitation is usually caused by pressure drop releasing CO_2 from bicarbonate ions (HCO_3^-). The effect of partial pressure of CO_2 on the pH of water is shown in Figure 3.7 at three different operating temperatures (Cowan and Weintritt, 1976). When CO_2 is released from water, the pH increases, the solubility of dissolved carbonate decreases and consequently the more soluble bicarbonates are converted to less soluble carbonate.

It is obvious that $CaCO_3$ is soluble in acidic solutions but is insoluble in basic solutions. In a solution containing $CaCO_3$, the distribution of the carbon species is significantly affected by the pH. In order to take into account the effect of pH on the solubility of calcium carbonate the dissociation constants of carbonic acid should be taken into consideration.

When carbon dioxide comes in contact with water, it dissolves and forms carbonic acid according to Equation (3.44). The ionisation of carbonic acid is illustrated by the following equations:

Therefore;

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (3.47)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (3.48)$$

where K_1 and K_2 are the first and second molar dissociation constants of carbonic acid, which are functions of operating temperature and can be calculated from the following equations (Plummer and Busenberg, 1982):

$$\log(K_1) = -356.3094 - 0.06091964T + \frac{21834.37}{T} + 126.8339 \log T - \frac{1684915}{T^2} \quad (3.49)$$

$$\log(K_2) = -107.8871 - 0.03252849 T + \frac{5151.79}{T} + 38.92561 \log T - \frac{563713.9}{T^2} \quad (3.50)$$

As an illustration, the first ionisation constant, K_1 , for Equation (3.45) is 4.54×10^{-7} at 25°C, and the second ionisation constant, K_2 , for Equation (3.46) is 5.61×10^{-11} at 25°C. Simultaneous solution of Equations (3.38), (3.47) and (3.48) for the three different unknowns yields:

$$[\text{CO}_3^{2-}] = \frac{[T.A.] + [\text{H}^+] - [\text{OH}^-]}{2 \left(1 + \frac{[\text{H}^+]}{2K_2} \right)} \quad (3.51)$$

$$[HCO_3^-] = \frac{[T.A.] + [H^+] - [OH^-]}{\left(1 + \frac{2K_2}{[H^+]}\right)} \quad (3.52)$$

$$[CO_2] = \frac{[T.A.] + [H^+] - [OH^-]}{\frac{K_1}{[H^+]} \left(1 + \frac{2K_2}{[H^+]}\right)} \quad (3.53)$$

Thus, by knowing pH and $T.A.$ of the solution and the dissociation constants for carbonic acid, the concentrations of all species present in the solution can be calculated. Replacing the calculated concentrations and operating temperature in Equations (3.42) and (3.43), the tendency of the solution for crystallisation fouling of calcium carbonate can be determined.

From the above equations, it can be seen that carbon dioxide gas dissolves in water and forms carbonic acid. The carbonic acid ionises to form hydrogen ions and bicarbonate ions. Since the second ionisation constant of carbonic acid is much smaller than the first ionisation constant, bicarbonate ions vastly outnumber the number of carbonate ions present under normal circumstances. It is believed that dissolved calcium carbonate does not exist in solution as calcium ions and carbonate ions, but as calcium ions and bicarbonate ions. Thus, the precipitation of calcium carbonate can be expressed by the following equation:

From the principle of LeChatelier, it can be seen that by increasing the concentration of carbon dioxide, more calcium bicarbonate is formed. A decrease in carbon dioxide content in this system at equilibrium would result in the formation of calcium carbonate. Therefore, the solubility of calcium carbonate is greatly influenced by the carbon dioxide content of the water. The amount of CO_2 that will dissolve in water is proportional to the partial pressure of CO_2 in the gas over the water, which is the product of mole fraction of CO_2 in the gas phase and the total pressure of the system. Therefore, if either the system pressure or the percentage of CO_2 in the gas phase were increased, the amount of CO_2

dissolved in the water would also increase. Figure 3.7 illustrates the effect of CO_2 partial pressure on the pH of the water containing little or no dissolved minerals (Cowan and Weintritt, 1976). This data should not be applied to brine since the presence of dissolved minerals changes the relationship between pH and the amount of dissolved CO_2 .

Figure 3.7 Effect of CO_2 partial pressure on pH of water

The effect of CO_2 partial pressure on the solubility of CaCO_3 in pure water at 20 °C is shown in Figure 3.8 (Miller, 1952). This diagram illustrates that the CaCO_3 solubility increases with increasing CO_2 partial pressure. The effect becomes less pronounced as the temperature increases. The reverse is also true. It is one of the major causes of CaCO_3 scale deposition. At any point in the system where a pressure drop occurs, the partial pressure of CO_2 in the gas phase decreases, CO_2 comes out of solution and the pH of the water rises. This shifts Equation (3.54) to the right and may cause CaCO_3 precipitation.

Figure 3.8 Effect of CO₂ partial pressure on calcium carbonate solubility at 20 °C

b) Effect of pH

The amounts of CO₂ present in the water affect the pH of the water and the solubility of calcium carbonate. However, it really does not matter what causes the acidity or alkalinity of the water. The lower the pH, the less likely is CaCO₃ precipitation. Conversely, the higher the pH, the more likely it is that precipitation will occur. However, its value must be known with the best precision possible and for the real conditions.

c) Effect of Total Pressure

The solubility of calcium carbonate in a two-phase system increases with increased pressure for two reasons:

i) Increased pressure increases the partial pressure of CO_2 and increases the solubility of CaCO_3 in water as previously explained.

ii) Increased pressure also increases the solubility due to thermodynamic considerations, as it was discussed for the case of calcium sulphate.

In single-phase (water) systems, such as a water injection system, increased pressure increases the solubility of calcium carbonate solely due to thermodynamic considerations.

d) Effect of temperature

Contrary to the behaviour of most materials, calcium carbonate becomes less soluble as temperature increases. The hotter the water, the more likely CaCO_3 precipitation. Hence, a water which is non-scaling at bulk conditions may experience scale formation on heat transfer surfaces. The same phenomenon will occur in oilfields in the injection well if the downhole temperature is sufficiently high.

This is also the reason why CaCO_3 scale is often found in fired heaters of heating equipment. The general behaviour of CaCO_3 solubility as a function of temperature was shown in Figure 3.6.

e) Effect of Dissolved Salts

Calcium carbonate solubility increases as the dissolved salt content of the water increases. Actually, the higher the total dissolved solids content (not counting calcium, bicarbonate or carbonate ions), the greater the solubility of CaCO_3 in the water and the lower the scaling tendency.

In summary, the likelihood of calcium carbonate scales forming;

- i) Increases with increasing temperature
- ii) Increases as partial pressure of CO_2 decreases
- iii) Increases as the pH increases
- iv) Increases as total dissolved solid content decreases

3.4.2.3 Saturation Index

It was previously stated that it is common to express the degree of supersaturation and hence the possibility of precipitation of salts from solutions in term of saturation indices. The Saturation Index (SI) of a salt was defined as the logarithm of the ratio between the activity product of its ions and the solubility product at the appropriate temperature. For the case of CaCO_3 , this is given by;

$$SI = \log \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \quad (3.55)$$

The saturation index, which will be referred to SI, is a measure of the degree of supersaturation, and thus the driving force available to cause precipitation. The larger the value of SI, the greater the likelihood that scaling will occur. It does not predict the amount of scale which will precipitate. Determining whether deposition of a salt is thermodynamically possible (i.e. $SI > 0$), therefore, requires knowledge of the concentrations and activity coefficients of all the ions present in the solution.

The thermodynamic activities of the ions to be used in Equation (3.55) can be calculated from the chemical analysis of the water if the level of dissolved salts is not too high, using, for example, the expression of Davies (1981) for the activity coefficients γ_1 and γ_2 of mono and divalent ions for ionic strength up to 0.1:

$$\log_{10} \gamma_1 = -A \left[\frac{I^{0.5}}{1 + I^{0.5}} + 0.3I \right] \quad (3.56)$$

$$\gamma_2 = \gamma_1^4$$

where

$$A = \frac{1.8246 (10^6)}{[78.54T(1 - 0.004579(T - 25) + 1.19(10^{-5})(T - 25)^2)]^{3/2}} \quad (3.57)$$

with T in $^{\circ}\text{C}$. The ionic strength I is obtained by;

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (3.58)$$

where the summation is over all ions present and m_i and z_i are the molar concentrations and their charges, respectively. Approximately

$$I \approx 2.5 (10^{-5}) \text{TDS} \quad (3.59)$$

where TDS is the concentration of total dissolved solids in mg/l.

In practice, ionic concentrations are sometimes used in place of the thermodynamic activities to obtain an approximate value of SI. This approximation is valid in dilute solutions, but can lead to serious errors in more concentrated ones.

Another supersaturation potential parameter for CaCO_3 that has been proposed for pipe deposition studies is the Driving Force Index, DFI, defined by:

$$DFI = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \quad (3.60)$$

where K_{sp} is the solubility product. The significance of this equation has not been clarified in the literature, but it is obvious that precipitation occurs when the DFI is greater than one.

Although there is agreement with respect to the definition of the saturation index, different investigators have used different nomenclature to describe this term as shown in Table 3.4.

Table 3.4 Saturation indices for calcium carbonate

INVESTIGATOR	INDEX NAME	ABBREVIATION
Langelier	Langelier Saturation Index	LSI
Ryznar	Ryznar Stability Index	RSI
Stiff & Davis	Stability Index	SI
Oddo & Tomson	Saturation Index	I_s

Langelier Saturation Index (1939)

If calcium carbonate fouling is the primary concern, then the well-known Langelier Saturation Index (*LSI*) is used to predict the directional tendency towards precipitation. Langelier (1939) developed a quantitative formula to predict if CaCO_3 is precipitated or dissolved in water. The equation for the Langelier Saturation Index, *LSI*, is based on *pH*, total alkalinity, hardness and temperature, which all affect the solubility of calcium carbonate in water:

$$LSI = pH - pH_s \quad (3.61)$$

pH is the actual system *pH* whereas *pH_s* is the computed saturation *pH* for calcium carbonate. It can be calculated from:

$$pH_s = pK_2 - pK_{sp} + pCa^{+2} + p(T.A.) \quad (3.62)$$

or

$$pH_s = 9.3 + A + B - (C + D) \quad (3.63)$$

where *A*, *B*, *C* and *D* are given in Table 3.5.

The Langelier Saturation Index is widely used in water conditioning practice as a control parameter. A negative value implies corrosive tendencies, whereas a positive *LSI* implies calcium carbonate supersaturation and scale-forming tendencies. If the acidified water is slightly corrosive, a corrosion inhibitor must be added, which may lead to increased deposition. The Langelier Saturation Index shows the direction of the driving force but does not indicate if the supersaturation is high enough to initiate crystallisation or how fast and where it will form. This means that this index indicates the tendency of a water to precipitate calcium carbonate, but it does not indicate the amount of precipitation.

It should be noted that all saturation predictions are based on some specific temperature. For most applications, the temperature that should be selected is the surface temperature, since calcium carbonate and calcium sulphate both have inverse solubility.

Table 3.5 Data for quick calculations of the Langelier Saturation Index (Nordell, 1951)

A		B		C		D	
TDS (ppm)	A	T (°F)	B	Calcium Hardness (ppm as CaCO ₃)	C	Alkalinity (ppm as CaCO ₃)	D
50-300	0.1	32-34	2.6	10-11	0.6	10-11	1.0
400-1000	0.2	36-42	2.5	12-13	0.7	12-13	1.1
		44-48	2.4	14-17	0.8	14-17	1.2
		50-56	2.3	18-22	0.9	18-22	1.3
		58-62	2.2	23-27	1.0	23-27	1.4
		64-70	2.1	28-34	1.1	28-35	1.5
		72-80	2.0	35-43	1.2	36-44	1.6
		82-88	1.9	44-55	1.3	45-55	1.7
		90-98	1.8	56-69	1.4	56-69	1.8
		100-110	1.7	70-87	1.5	70-88	1.9
		112-122	1.6	88-110	1.6	89-110	2.0
		124-132	1.5	111-138	1.7	111-139	2.1
		134-146	1.4	139-174	1.8	140-176	2.2
		148-160	1.3	175-220	1.9	177-220	2.3
		162-178	1.2	230-270	2.0	230-270	2.4
				280-340	2.1	280-350	2.5
				350-430	2.2	360-440	2.6
				440-550	2.3	450-550	2.7
				560-690	2.4	560-690	2.8
				700-870	2.5	700-880	2.9
				880-1000	2.6	890-1000	3.0
				1000-1200	2.7	1000-1200	3.1
				1200-1300	2.8	1200-1300	3.2

When Langelier proposed his methodology in 1939, certain reaction variables were assumed to have a negligible value. However, since then many other researchers have improved upon this equation for pH_s .

Modified Langelier Saturation Index

If the concentration of salt in water, such as for seawater, is high (>4000 ppm) a Modified Langelier Saturation Index must be used. The Modified Saturation Index is defined as (NIOC files);

$$MSI = pH - pCa^{2+} - p(TA) - K \quad (3.64)$$

Figure 3.9 Effect of temperature and ionic strength on K-value of Equation 3.64

where

MSI = Modified Langelier Saturation Index

pH = measured pH of water

$pCa^{2+} = -\log [Ca^{2+}]$

$p(TA) = -\log$ (total alkalinity)

k = constant the value of which depends on total salt concentration and temperature

At equilibrium MSI is zero, therefore, Equation (3.64) reduces to:

$$K = pH - pCa - p(TA) \quad (3.65)$$

The relationship between constant K , operating temperature and total ionic strength of the solution is given in Figure 3.9 (Stiff and Davis, 1952).

Ryznar Stability Index (1944)

A second widely used parameter to establish the $CaCO_3$ scale-forming tendency of a given water is the Ryznar Stability Index, RSI (1944). Ryznar suggested an index, which not only indicates the tendency of a water to precipitate calcium carbonate (or be corrosive if it is saturated with oxygen), it also gives a semi-quantitative estimate of the amount of scale which will form or the seriousness of the corrosion. The Ryznar Stability Index, RSI, is defined as:

$$RSI = 2pH_s - pH = 2(pK'_2 - pK'_s) - \log [Ca^{2+}] - \log [ALKY] + 9.3 + \frac{2.5\sqrt{I}}{1 + 5.3\sqrt{I} + 5.5I} - pH \quad (3.66)$$

where;

$[Ca^{2+}]$ = Calcium ion concentration, ppm

ALKY = $[CO_3^{2-}] + [HCO_3^-]$ concentration, ppm as $CaCO_3$

I = Molal ionic strength

pK'_2 and pK'_s = Empirical constants measured by Langelier

pH = Actual pH of the solution

pH_s = pH at saturation

Ryznar's stability index values always are positive. It can be interpreted as follows:

- i) Stability index < 5.5 indicates CaCO_3 scale formation. The smaller the index, the larger the amount of scale formation.
- ii) Stability index > 5.5 indicates corrosion. The larger the index, the more severe the anticipated corrosion.

Stiff and Davis Method (1952)

Stiff and Davis empirically extended the Langelier method to apply to oilfield brines. Their equation is as follows:

$$SI = pH - pH_s \quad (3.67)$$

$$pH_s = K + pCa + pALK \quad (3.68)$$

$$SI = pH - K - pCa - pALK \quad (3.69)$$

where

SI = Stability Index

K = a constant which is a function of salinity, composition and water temperature. Its values are obtained from a graphically as shown in Figure 3.9 with ionic strength and the temperature of the water.

$pCa = -\log$ (moles of Ca^{+2} per litre)

$pALK = -\log$ (equivalent carbonate alkalinity per litre)

Carbonate alkalinity = $\text{CO}_3^{2-} + \text{HCO}_3^-$

In order to calculate SI, temperature, pH, HCO_3^- and CO_3^{2-} concentrations should be known. In addition, a complete water analysis is necessary to enable calculation of the ionic strength. It should be noted that field measurements of pH values would not suffice when attempting to apply this method to high pressures and temperatures, i.e. downhole

conditions in producing or injection wells. Then the pH must be calculated. Equations are given in the following section which enable calculation of pH values at elevated pressures and temperatures.

The results of the calculation may be summarised as follows:

- i) If SI is negative, the water is subsaturated with CaCO_3 and scale formation is unlikely.
- ii) If SI is positive, the water is supersaturated with CaCO_3 and scale is likely to form.
- iii) If SI is zero, the water is at the saturation point.

Oddo and Tomson Method (1982)

More recently, Oddo and Tomson developed a method to calculate a saturation index, I_s , for calcium carbonate scale which includes the effect of pressure. The method enables the calculation of pH in two-phase systems (gas + water), and considers total pressure as well as varying CO_2 partial pressure. Its meaning is analogous to that of the Stiff and Davis index. The equations are given as follows:

- i) Two phases systems (gas and water) where the pH is unknown.

$$I_s = \log \left(\frac{[\text{Ca}^{2+}] \text{Alk}^2}{P_t X_{\text{CO}_2}} \right) + 5.89 + 1.549(10^{-2}) T - 4.26(10^{-6}) T^2 - 7.44(10^{-5}) P_t - 2.52 I^{0.5} + 0.919 I \quad (3.70)$$

- ii) Any system (single or multi-phase) where the pH is known or can be calculated

$$I_s = \log \left([\text{Ca}^{2+}] \text{Alk} \right) + \text{pH} - 2.78 + 1.143(10^{-2}) T - 4.72(10^{-6}) T^2 - 4.37(10^{-5}) P_t - 2.05 I^{0.5} + 0.727 I \quad (3.71)$$

- iii) Calculation of pH in a two-phase system

$$\text{pH}_c = -\log \left(\frac{P_t X_{\text{CO}_2}}{\text{Alk}} \right) + 8.68 + 4.05(10^{-3}) T + 4.58(10^{-7}) T^2 - 3.07(10^{-5}) P_t - 0.477 I^{0.5} + 0.193 I \quad (3.72)$$

where:

I_s = Saturation index

pH_c = Calculated pH

$[Ca^{2+}]$ = Ca^{2+} concentration, mol/l

Alk = HCO_3^- concentration, mol/l

P_t = Total pressure, psia

X_{CO_2} = Mole fraction of CO_2 in the gas phase

T = Temperature, °F

I = Ionic strength, mol/l

This method is valid over the following conditions:

Temperature: 0-200 °C

Pressure: 0-137823 kPa

Molar ionic strength: 0-4.0

Comparison of Indices for $CaCO_3$ Solutions

The predictions of the Langelier Saturation Index, Ryznar Stability Index and Saturation Index were compared for beginning scaling conditions, i.e. for S.I.= 1, L.S.I.= 0 and R.S.I.= 6 (Müller-Steinhagen and Branch, 1988). The results may be interpreted as the pH which has to be adjusted for a given composition and temperature to minimise scaling and corrosion. Figure 3.10 shows the prediction of the three indices as a function of the heat transfer surface temperature. Scaling occurs above the curves, corrosion is likely for conditions below the curves.

Generally, scaling tendency increases with increasing values of pH and surface temperature. As was expected, the Saturation Index and the Langelier Saturation Index give comparable values and trends. pH-values for incipient scaling predicted by the Ryznar Stability Index differ considerably from those predicted by the two saturation indices. For lower solution temperature, the Ryznar Stability Index predicts higher pH values than the two saturation indices, whereas Ryznar Stability Index predicts lower pH values than the others for higher solution temperature.

Figure 3.10 Comparison of scaling indices for CaCO_3 solutions

It should be noted that all these indices will underpredict scaling for nucleate boiling because of concentration effects in the bubble microlayer.

Chapter 4

EXPERIMENTAL EQUIPMENT AND PROCEDURE

It is generally believed that there are three methods in which data on fouling can be obtained. Experience-based data, laboratory studies data and plant data are three sources for achieving the needed information. Experimental investigation of the fouling phenomenon is one of the most important sources of acquiring data and understanding the processes that are involved. Therefore, the purpose of any laboratory technique is to simulate the conditions that are likely to occur in a heat transfer equipment. Laboratory investigation can provide insights into the fouling mechanisms and produce valuable data that may be useful in modeling of the fouling phenomenon.

The experimental set-up which was used in this study is shown in Figure 4.1.

Figure 4.1 Experimental set-up

4.1 TEST RIG

The measurements were performed in a flow circuit which included two parallel annular test sections as shown schematically in Figure 4.2. Each test section consisted of an electrically heated cylindrical stainless steel rod. This test heater, shown in Figure 4.3, was manufactured by Ashland Chemicals according to specifications by Heat Transfer Research Incorporated (HTRI). It was located concentrically within the surrounding vertical pipe and the test liquid was flowing through the annulus in upward direction. A miniature stainless steel sheathed resistance wire was fitted into the centre of the heater rod.

Figure 4.2 Schematic diagram of test rig

Figure 4.3 Schematic diagram of test heater

Four stainless steel sheathed E-type 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/m^2 .

The fluid was pumped from a temperature-controlled supply tank through the annular test sections. The flow velocities were measured by two magnetic flow meters; their calibration curves are given in Appendix A. The flow rates were controlled by two automatic control valves behind the test section, and with the bypass line. Varying the flow rate and the amount of bypass flow may affect the pressure. 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 K-type thermocouples located in mixing chambers before and after the test section.

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 μm and was 0.5 m long. It was made of polypropylene and polyethylene. Due to the corrosive nature of some of the electrolytes used in this investigation, all wetted parts were manufactured from stainless steel.

4.2 DATA AQUISITION

A data acquisition system was used to measure temperatures, velocities and heat fluxes at pre-selected time intervals. All data were recorded with an IBM compatible personal computer in connection with an OMEGA EXP-16 sixteen channels expansion multiplexer/amplifier board. The expansion board had built-in cold junction compensation and was connected to an OMEGA DAS 8 board. The DAS 8 board was connected to the computer, which controlled the data acquisition using purpose-written software. The different recorded and computed data were saved either as processed data (calculated values) or as raw data (directly measured voltages). The raw data included the electrical current and voltage of the heaters, the temperature of the thermocouples in the heater and the bulk temperatures. The processed data were the heat flux, the surface temperatures of the heaters, the velocity and the heat transfer coefficient.

The surface temperature of the test heater was calculated from the measured values $T_{\text{TC},i}$ of the thermocouples

$$T_{s,i} = T_{\text{TC},i} - \left(\frac{s_i}{\lambda} \right) \dot{q} \quad (4.1)$$

In this equation, s is the distance between the thermocouple location and the heat transfer surface and λ is the thermal conductivity of the heater material. The values of s/λ were determined by calibration of the test heaters, as given in Appendix B. The average surface temperature was the arithmetic average for all three thermocouples. The power supplied to the test heater was calculated from the measured current and voltage. The

local bulk temperature at the wall thermocouple plane in the experimental apparatus was calculated as:

$$T_b = T_b^{No.1} + \frac{82.6}{99.1} \cdot (T_b^{No.2} - T_b^{No.1}) \quad (4.2)$$

This assumes that the bulk temperature increases linearly from $T_b^{No.1}$, in mixing chamber 1, to $T_b^{No.2}$, in mixing chamber 2. For constant heat flux boundary conditions, this is a valid assumption.

Finally, the heat transfer coefficient α was calculated from

$$\alpha = \frac{\dot{q}}{(T_s - T_b)} \quad (4.3)$$

4.3 PREPARATION OF SOLUTIONS

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 solubilities of the electrolytes in water were determined 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.

Since calcium sulphate crystals do not dissolve easily in water, calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and sodium sulphate (Na_2SO_4) were dissolved, resulting in calcium sulphate crystallising on the heat transfer surface.

Similarly, calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and sodium carbonate (Na_2CO_3) were dissolved in water, resulting in crystallisation of calcium carbonate. The dissociation of the various ionic species of sodium carbonate in water is quite sensitive to the pH of the solution. In the present analysis, a low pH solution (i.e. $6.5 < \text{pH} < 7.5$) was adjusted, so that most of the dissolved carbonate ions are in the form of bicarbonate HCO_3^- (Wahl, 1977). Calcium

carbonate precipitation is usually caused by pressure drop releasing CO_2 from bicarbonate ions (HCO_3^-). When CO_2 is released from the water, the pH increases, the solubility of dissolved carbonate decreases and consequently the more soluble bicarbonates are converted to less soluble carbonate.

However, the primary cause of fouling is supersaturation. When the concentration product of Ca^{2+} and SO_4^{2-} or Ca^{2+} and HCO_3^- (CO_3^{2-}) ions exceeds the saturation value, calcium sulphate or calcium carbonate precipitates and forms scale.

All salts used in this work were Merck reagent grade. Solutions were prepared for each run by dissolving the respective salt in distilled water and allowing it to equilibrate in a stirred tank for about five hours. The range of salt concentrations used in this investigation is given in Table 4.1.

4.4 EXPERIMENTAL PROCEDURE

60 litres of salt solution with predetermined composition and concentration were added to the supply tank. The pump was then switched on and the test rig left to equilibrate at a selected bulk temperature and flow velocity. After steady state conditions were reached, a sample of the solution was taken. Then the selected heat flux, surface temperature or difference between bulk and surface temperature were adjusted and the experiment started. A large number of experiments has been performed in the forced convective heat transfer and sub-cooled flow boiling regions, with different contributions of nucleate boiling. The range of the experimental parameters in the present investigation is given in Table 4.1.

Table 4.1 Range of investigated operating parameters

Velocity (m/s)	Bulk Temp. (°C)	Heat Flux (kW/m ²)	CaSO ₄ Conc. (g/l)	T.A. as CaCO ₃ (g/l)
0.5-2	50-90	100-450	1-2.5	0.0-0.3

4.5 CONCENTRATION MEASUREMENTS

4.5.1 Hardness Measurements

A large number of metal ions can be determined by titration using a standard solution of complexing agent which is known as complex formation titration. Most metal ions form co-ordination complexes with molecules or anions which are referred to as ligands. These ligands contribute an unshared electron pair to the metal ion to form a metal-ligand bond. Ligands that contain two or more donor atoms are generally known as chelates.

A very popular molecule forming chelate which complexes with metal ions is Ethylene-Diamine-Tetra-Acetate, EDTA, $[(\text{HOOCCH}_2)_2\text{-NCH}_2\text{CH}_2\text{N-(CH}_2\text{COOH)}_2]$. EDTA always reacts with a metal in a 1:1 molar ratio so that the titration will be stoichiometric and quantitative. For example, the stoichiometric reaction of calcium ions with EDTA molecules is:

H_2Y^{2-} is disodium EDTA, H is the hydrogen atom and Y is the rest.

Hardness is defined as the total concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions contained in a solution. In this investigation, hardness was determined by EDTA titration (Skoog et al., 1992) using Calmegite Solution as an indicator. Both the sharpness of the end point and the tendency of CaCO_3 and Mg(OH)_2 to precipitate increase with increasing pH. Therefore, a pH value of 10.0 ± 0.01 is recommended as a satisfactory compromise. A buffer solution was prepared by mixing 142 ml of concentrated ammonia solution (specific gravity = 0.9) with 17.5 g ammonium chloride and then diluted to a volume of 250 ml with distilled water.

To prevent the interfering effect of some metal ions which cause an indistinct end point, 1.233 g of magnesium sulphate was dissolved in 500 ml of distilled water to prepare of a 0.01 mol/l solution of magnesium sulphate. Magnesium ions show the end point better than calcium ions during the titration.

To perform the titration, 2 ml of buffer, 3 ml of inhibitor and a few drops of indicator were added to a 25 ml sample which had already been diluted to 50 ml. This solution was then titrated with 0.01 M EDTA solution until the solution (indicator) colour changed from red to clear blue. Duration of titration should not exceed five minutes in order to prevent degradation of EDTA and precipitation of CaCO_3 at higher pH values. Using the following formula, the hardness (Ca^{2+}) was determined:

$$M_1V_1 = M_2V_2 \quad (4.5)$$

where V_1 is the volume of the titrant (ml), M_1 is the molarity of EDTA solution, V_2 is the volume of sample (ml) and M_2 is the calcium ion molarity.

4.5.2 Alkalinity Measurements

Total alkalinity (T.A.) of the solution was measured by titration with a dilute solution of hydrochloric acid using bromocresol green-methyl red mixed indicator which is more suitable for alkalinities below 500 mg/l. $\text{Na}_2\text{S}_2\text{O}_3$ was used as an inhibitor for the removal of residual chlorine that would otherwise impair the indicator colour changes. 0.02 N HCl was used as a titrant and the end point was determined by the indicator colour change and by a pH meter (Skoog et al., 1992).

To perform the titration, 1 drop of $\text{Na}_2\text{S}_2\text{O}_3$ and 3 drops of mixed indicator were added to 50 ml of sample. The blue sample was titrated with 0.02 N HCl to the appearance of a light pink which occurs at pH 4.5. Total alkalinity was then calculated using the following formula:

$$N_1V_1 = N_2V_2 \Rightarrow T.A. = \frac{V_1N_1 \times 50000}{V_2} \quad (4.6)$$

where V_1 is the volume of titrant (ml), N_1 is the normality of titrant, V_2 is the volume of sample (ml) and N_2 is the normality of the sample. The T.A. was calculated in ppm CaCO_3/l .

4.5.3 Sulphate Measurements

The quantitative determination of a substance by precipitation followed by isolation and weighing of the precipitate is called gravimetric analysis. Hence, gravimetric analysis, by definition, includes all methods of analysis in which the final stage of the analysis involves weighing. In the most basic case, this could involve simply heating a sample to dryness and weighing to determine the amount of volatile components. In this account, however, gravimetric methods which rely on the use of precipitation reactions were used.

The basic method of gravimetric analysis is fairly straightforward. A weighed sample is dissolved after which an excess of a precipitating agent is added. The precipitate which forms is filtered, dried or ignited and weighed. From the mass and known composition of the precipitate, the amount of the original ions can be determined.

There are several important steps and operations involved in a gravimetric analysis. They can be summarised as follows:

- Preparation of solution
- Precipitation
- Digestion
- Filtration
- Washing
- Drying or igniting
- Weighing
- Calculation

It is also important that the precipitate be sufficiently insoluble, hence the loss due to solubility will be negligible. Moreover, the precipitation should consist of large crystals so that they can be easily filtered.

For successful determinations, the following criteria must be met;

1. The desired substance must be completely precipitated. In most determinations, the precipitate is of such low solubility that losses from dissolution are negligible. An

additional factor is the "common ion" effect; this further reduces the solubility of the precipitate. For example, when SO_4^{2-} is precipitated out by addition of Ba^{2+} according to;

The low solubility of BaSO_4 is reduced still further by the excess of Ba^{2+} which is added, pushing the equilibrium to the right.

2. The weighed form of the product should be of known composition.
3. The product should be "pure" and easily filtered. It is usually difficult to obtain a product which is "pure", i.e. one which is free from impurities but careful precipitation and sufficient washing helps reduce the level of impurity.
4. One aspect that should be emphasised is weighing. All weightings must be done at room temperature, it is not allowed to weigh the sinters straight from the oven, it must first be cooled in a desiccator. This means drying the product, cooling to room temperature, weighing and returning the product to the oven. The process of heating, cooling and weighing should be repeated until a constant mass is obtained.

Conditions for Analytical Precipitation:

In an ideal situation, an analytical precipitate for gravimetric analysis should consist of perfect large crystals to be easily washed and filtered. The perfect crystal would be free from impurities and large enough so that it presented a minimum surface area onto which foreign ions could be adsorbed. The precipitate should also be "insoluble" (i.e. be of such low solubility that losses from dissolution would be minimal).

Drying of the solid:

Generally the solids are dried at about 120°C but conditions for drying can vary considerably. To determine the correct drying regime, a thermogravimetric balance should be used.

Procedure:

The sulphate in a sample was determined by precipitation as barium sulphate. The sulphate salt was dissolved in a dilute solution of hydrochloric acid and barium chloride was added slowly to it, resulting in precipitation of the sulphate salt. The precipitate was digested, filtered, dried before being weighed accurately.

To obtain high accuracy, care should be taken such that no precipitate (or no more than a tenth of a percent of the total precipitate) was lost. BaSO_4 is also susceptible to co-precipitation of foreign ions, so care should be taken to keep the supersaturation ratio as low as possible during precipitation.

To perform measurements, a set (three) of Gooch crucibles was prepared by putting a borosilicate-glass filter pad in each crucible. The pads should not have any holes and this was examined by holding them against the light. The crucible was placed in a suction filtration assembly and a vacuum was pulled. First the pad was moistened with a few drops of distilled water and then a few ml of dilute nitric acid was added. This removes any soluble material that may have been on the filter pad. The crucible was placed on the burner using a second crucible to place the Gooch crucible in and ignited for 10 to 15 min. The heating should be to the point that the crucible glows faintly red. Heating too intensely may result in melting of the pad. The crucible was allowed to cool to room temperature and then it was weighed. The HNO_3 rinsing and heating of the crucible was repeated till it reaches a constant weight (within 0.2 mg of the previous weight).

Sample preparation and precipitation:

About 0.5 gr of the dried sulphate sample was weighed. It was placed in a clean 400 ml beaker and dissolved in 250 ml of distilled water and 3 ml of 6M HCl. The solution was heated to near boiling. An excess (approximately 70 - 80 ml) of 0.05 M BaCl_2 solution was slowly added with efficient stirring. The precipitate was digested for about 30 min near the boiling point. Completeness of the precipitation could be tested by letting the precipitate settle, and adding a few drops of BaCl_2 to the clear liquid above the

precipitate. If cloudiness appears, it means that some sulphate is still in solution. An additional 5-10 ml of BaCl_2 needs to be added and the digestion procedure repeated.

Filtration and ignition of the precipitate:

The crucible was placed on the filtration assembly. The clear liquid was passed through the filter. The precipitate was completely transferred to the crucible. A stream of water from a wash bottle and a rubber policeman were used to scrape off any remaining precipitate sticking to the beaker wall or the stirring rod. The precipitate was washed several times with a few ml of water. The filtrate needs to be checked for the presence of soluble salts by checking for chloride. This was done by collecting a 5-10 ml portion in a test tube and then adding a 1 ml of 0.1 M HNO_3 and a few drops of AgNO_3 . If Cl^- is present, solid AgCl will precipitate out indicating that the precipitate in the crucible needs further washing with water. The crucible was ignited so that a constant weight was reached by following the procedure mentioned before.

It should be noted that HCl was added to the sulphate solution to prevent the precipitation of barium salts of weak acids such as CO_3^{2-} , PO_4^{3-} etc. It volatilises during ignition. Presence of excess of BaCl_2 reduces the amount of sulphate remaining in the solution by the common ion effect. Digestion of precipitate increases the average particle size and reduces co-precipitation.

The sulphate content of the sample was calculated using the following formula:

$$\% \text{SO}_4 = \text{precipitated BaSO}_4 \left(\frac{MW_{\text{SO}_4}}{MW_{\text{BaSO}_4}} \right) \left(\frac{1}{\text{Sample Weight}} \right) \times 100 \quad (4.8)$$

It is necessary to state that Ion Chromatography is another technique for measuring the sulphate content of any sample. Some of the samples were analysed using this method in the central laboratory of the National Iranian Oil Company (NIOC). The comparison of obtained results showed that the prediction of these two methods was almost equal. In this investigation, the gravimetric method was used for sulphate determination, because it was cheaper and more accessible.

Chapter 5

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 affected by active nucleation sites and the remaining area which is influenced by forced convection. 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 mechanisms.

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):

$$NBF = \frac{\alpha_{nb} S}{\alpha_{fb}} \quad (5.1)$$

where α_{fb} is the flow boiling heat transfer coefficient, S is a suppression factor and α_{nb} is the nucleate boiling heat transfer coefficient. 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.:

$$\alpha_{jb} = \alpha_c F + \alpha_{nb} S \quad (5.2)$$

Here, F is the enhancement factor and α_c is the convective heat transfer coefficient. For calculation of NBF, the predicted clean heat transfer coefficients at the beginning of each run can be used. Calculated values for NBF for the present experimental conditions at 80 °C are given in Table 5.1.

Table 5.1 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 5.1 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.

In what follows the effects of operating variables on the rate of crystallisation fouling are discussed.

5.1 CRYSTALLIZATION FOULING OF MIXED SALTS

5.1.1 Heat Transfer Coefficient

Figure 5.1 is a typical example for measured heat transfer coefficients as a function of time for mixed salt solutions. The shape of the measured heat transfer coefficient versus time curve is characterised by a decrease in heat transfer coefficient at the beginning of the operating time due to the formation of scale on the heater surface, followed by a short

increase and a subsequent gradual decrease. The increase in heat transfer coefficient at the early stage of fouling is thought to be due to the increase in the number of active bubble nucleation sites and the surface roughness generated by the deposit. Additional nucleation sites and surface roughness increase the turbulence level in the zone near the heat transfer surface and, therefore, improve the heat transfer coefficient until the insulation effect of the growing deposits becomes dominant.

There is usually a time interval between the start of the experiment and the detection of a thermal fouling resistance. This is called the *delay time* or *initiation period*. During this period certain conditions required for deposition, such as crystal nucleation and surface conditioning, are established. The delay time may vary from a very short time period to one which is relatively long ranging from seconds to hours depending on the degree of supersaturation, temperature and heat flux. In this investigation, because of the high degree of supersaturation, high surface temperature and high heat flux, the delay time was less than five minutes.

Figure 5.1 Typical variation of heat transfer coefficient with time

5.1.2 Fouling Curve

A fouling curve shows the relationship between the thermal resistance of the deposit and the time. The shape of fouling curves is representative of the phenomena occurring during the fouling process. In the present investigation, the fouling resistances were calculated from the measured heat transfer coefficients at the beginning of each experiment and the actual heat transfer coefficients after a certain operational period, according to the following equation:

$$R_f = \frac{1}{\alpha(t)} - \frac{1}{\alpha(t=0)} \quad (5.3)$$

The shape of the fouling curves may have linear, falling rate, asymptotic or saw-tooth profile. After a slight improvement at the beginning of the experiments, most measured fouling curves showed an almost linear increase in fouling resistance with time at the early stages. A linear relationship is generally characteristic of hard and adherent deposits and indicates that the deposition rate is either constant and there is no removal, or that the difference between deposition rate and removal rate is constant.

Figure 5.2 Variation of fouling resistance with time

In some experiments, a falling rate curve was observed. This type of fouling curve is characteristic of softer or more fragile deposits which tear off easily due to the shear force of the flow. It could also be the result of a retardation process such as reduction in heat flux or surface temperature during the experiment. In this study, the falling rate behaviour is thought to be due to the retardation process that will be discussed in the next chapter.

Figure 5.2 is an example for measured fouling resistances as a function of time, calculated from the data depicted in Figure 5.1. This figure shows the results of a typical run at an initial surface temperature of 111 °C and bulk temperature of 80 °C. The fouling process represents a falling rate behaviour during the course of the experiment. The rate of fouling is relatively low for about 3 hours, which is then followed by an almost linear and subsequently a falling rate of deposition. In addition, during the early stages of some experiments, the induced roughness by deposit increased the heat transfer coefficient as compared with the value for a clean surface and resulted in a negative fouling resistance while actually deposit was being formed on the surface.

5.1.3 Effect of Flow Velocity

In heat exchangers, the principle variable is the velocity of the fluid across the heat transfer surface. This parameter is the one over which the designer has the greatest control (Bott, 1995). Generally, in the design stage the designer has freedom to fix the velocity on both sides of the heat exchanger. It is usual to match this specification in terms of pressure drop at minimum capital cost.

As the velocity is increased, the heat transfer coefficient is also increased. This means that for a given temperature difference, the heat transfer area and hence the capital cost is decreased. On the other hand as the velocity is increased, the pressure drop is also increased. However, the problem which arises is that the optimum velocity for acceptable pressure drop may not be the same as that required for minimising the incidence of fouling.

Many investigations have been carried out to determine the effect of flow velocity on scale formation during forced convective heat transfer. The experimental data reported in the

literature show different effects of the fluid velocity. High velocities can sometimes reduce fouling (Hasson and Zahavi, 1970), while in other cases they accelerate fouling (Hatch, 1973). This depends on the thickness of the laminar sub-layer and on the mechanism which controls deposition. Fouling can be controlled by molecular diffusion through the laminar sub-layer, by chemical reaction at the heat transfer surface or by both mechanisms. If the fouling process is not mass transfer-controlled, then the deposition rate should be independent of the flow velocity as long as the surface temperature remains constant.

It is generally believed that the deposition term depends on the transport process and on the formation/attachment reaction. It is conceptually helpful to think of these as two processes acting in sequence, so a mass transfer coefficient, β , and a reaction rate constant k_r are involved. As will be discussed in the following chapter, if the formation/attachment reaction can be assumed, for simplicity, to be a first order reaction, the rate of formation, $\dot{m}_d$ of the fouling material can be expressed by

$$\dot{m}_d = \frac{C_b - C^*}{\frac{1}{\beta} + \frac{1}{k_r}} \quad (5.4)$$

where C_b and C^* are the concentration of fouling material in the bulk of the fluid and the saturation concentration respectively.

It is obvious that the relative magnitude of the mass transfer coefficient and reaction rate constant will decide whether one or both of these processes will control the rate of deposition. This means that, since the mass transfer coefficient depends on the fluid velocity, when mass transfer is slower than the formation/attachment reaction, then the rate of fouling will be sensitive to the fluid velocity. If the formation/attachment reaction is slower than the transport processes, then the rate of formation will be sensitive to a variable other than fluid velocity, such as the surface temperature. Therefore, if fouling is not influenced by diffusional mass transfer, the fouling rate should be independent of the flow velocity if the surface temperature remains constant. In certain circumstances this predominance of one process over the other may change with time and/or operating conditions.

According to the work of Ritter (1983), crystallisation fouling of calcium sulphate under forced convective conditions and flow velocities similar to those used in this investigation is mass transfer-controlled. However, Hasson and Zahavi (1970) claimed that crystallisation fouling of calcium sulphate is reaction-controlled, while Hasson et al. (1968) pointed out that the crystallisation fouling of calcium carbonate is mass transfer-controlled.

It should be noted that at constant heat flux conditions, velocity affects the deposit surface temperature. For a given heat flux, the level of turbulence increases with increasing velocity, and hence the heat transfer coefficient also improves with increasing velocity. Therefore, under constant bulk temperature and constant heat flux conditions, the surface temperature and consequently the deposition rate are significantly decreased.

However, increasing the fluid velocity increases the fluid shear stress, which may cause even more removal. This may yield lower fouling rates as well as lower ultimate values of the fouling resistance. For weak deposits, increasing the flow velocity may even completely eliminate fouling. For stronger deposits, increasing the flow velocity up to a particular point may not decrease fouling significantly. For very strongly adhering deposits like CaSO_4 and CaCO_3 , increasing the flow velocity may not have any effect at all.

The effect of fluid velocity on the fouling resistance for typical mixed salt fouling runs is shown in Figure 5.3 for constant solution composition, initial surface temperature and bulk temperature. Since the surface temperature has a significant effect on fouling conditions, it was decided to run all tests with an initial surface temperature of 101 °C to allow a better comparability. The flow velocity ranged from 20 cm/s up to 160 cm/s or expressed by dimensionless Reynolds number from 8,000 to 65,000. This means that the bulk flow was fully turbulent.

It is obvious that the fouling resistance is more pronounced at the higher velocities than at the lower velocities. For the investigated range of flow velocities, most of the fouling curves describe a process starting with clean surface having zero fouling resistance, which then develops at a constant rate with time. This form is generally characteristic of tough, hard, adherent deposits and indicates that the deposition rate is constant and there is no removal or that the difference between deposition rate and removal rate is constant.

Two of the fouling curves (i.e. at higher velocities) show an almost falling rate increase in fouling resistance with time after an initial linear rate of deposition. Falling rate behaviour may be obtained even though there is no removal, due to retardation mechanisms that increase as the deposit builds up. In the present investigation, falling rate fouling curve may be attributed to the reduction in heat flux and consequently deposit surface temperature, due to additional heat transfer area as a result of the fouling related increase in heater rod diameter. This concept will be more explained in Chapter 6.

Figure 5.3 Effect of flow velocity on the fouling resistance

To find the controlling mechanism, the fouling rates, i.e. the slopes of fouling curves in Figure 5.3, for constant degree of supersaturation and constant bulk and initial surface temperatures are plotted as a function of Reynolds number in Figure 5.4. It should be noted that heat transfer occurred by forced convection only for all five experiments. At lower fluid velocities, the fouling process is clearly affected by diffusion. With increasing flow velocity, the fouling rate is obviously not affected by the velocity which confirms that the mechanism is changing to reaction-controlled.

It is believed that the laminar sub-layer which forms next to the heat transfer surface has a strong effect on the fouling characteristics. The thickness of this layer is strongly affected by flow velocity. Temperature and degree of supersaturation are different in this region from those in the bulk of the solution. The mechanism of fouling on the heat transfer surface can be controlled either by molecular diffusion within this film or by chemical reaction at the heat transfer surface or by both mechanisms. At lower velocities, the mass transfer boundary layer is relatively thick and, therefore, molecular diffusion has some effect on the fouling rate. As the fluid velocity is increased, the boundary layer thickness is decreased and mass transfer across the boundary layer no longer affects the fouling rate, giving control to chemical reaction. Therefore, these results prove that the controlling mechanism could shift, depending upon the operating conditions for a given chemical fluid system. Since the initial surface temperatures were identical for all runs, the nucleate boiling fractions were negligible for all velocities.

Figure 5.4 Fouling rate as a function of Reynolds number

It is important to note that the above procedure for finding the controlling mechanisms is only valid during forced convective heat transfer. During sub-cooled flow boiling conditions, another parameter than the surface temperature, i.e. nucleate boiling fraction, is also influencing the deposition process. In other words, for finding the controlling mechanism, it is not possible to fix the surface temperature and nucleate boiling fraction simultaneously. Both these parameters are important for additional deposition during sub-cooled flow boiling conditions.

The effect of fluid velocity on the fouling resistances for typical mixed salt fouling runs during sub-cooled flow boiling conditions is shown in Figure 5.5. Similar to convective heat transfer, we may expect that, as the velocity is increased, the fouling resistance is also increased. The experimental data shows, however, that the opposite is true, i.e. as the velocity is increased, the fouling resistance is decreased at constant initial surface and bulk temperature. In this situation, the fouling resistance shows a falling rate behaviour due to the reduction in heat flux, nucleate boiling fraction and surface temperature. This concept will be more explained in Chapter 6.

It was previously mentioned that it is impossible to fix the surface temperature and the nucleate boiling fraction simultaneously. By increasing the velocity at constant surface temperature, the nucleate boiling fraction is decreased. The effect of this parameter is very strong and causes a reduction in the fouling resistance. *NBF* values at different velocities and heat fluxes are given in Table 5.2.

Table 5.2 NBF values at different velocities and heat fluxes

$\dot{q}$ (kW/m ²) V(cm/s)	250	295	375
50	NBF=0.292	NBF=0.3741	NBF=0.481
80	NBF=0.0821	NBF=0.161	NBF=0.285
120	NBF=0.0016	NBF=0.0189	NBF=0.099

Figure 5.5 Measured fouling resistances at different velocities during sub-cooled flow boiling conditions

It should be noted that as the deposition process continues at constant heat flux, the deposit temperature, adjacent to the heater surface, rises. For these higher temperature conditions, some processes of dehydration and reorientation of crystals are likely to occur (Taborek, 1972). The strength of the deposit may be affected by these additional processes.

5.1.4 Effect of Surface Temperature

Surface temperature can exert a considerable influence on the development of fouling layers. Supersaturation of inverse soluble salts at the heat transfer surface increases as a result of increased surface temperature, as well as the nucleation site density. In general, increasing the surface temperature can initiate and increase deposition rate of inverse soluble salts.

For convective heat transfer, the variation in fouling resistance with surface temperature for mixed salt solutions at constant velocity, bulk temperature and solution concentration is shown in Figure 5.6. As it was expected, the fouling resistance depends on the heat transfer surface temperature. As the temperature of the heat transfer surface increases, mass transfer coefficient, reaction rate constant and driving force for deposition increase. Therefore, the fouling resistance due to crystallisation by inverse soluble salts such as CaSO_4 and CaCO_3 increases.

Figure 5.6 Effect of surface temperature on the fouling resistance

It was mentioned that the surface temperature has a strong effect on the fouling rate. Its main effect on a mass transfer-controlled process is through the diffusivity of the depositing species, and on chemical reaction-controlled system through the reaction rate constant of the process. Since mass transfer coefficients are a linear function of temperature (Hasson et al., 1968), fouling rate should increase similarly with surface temperature for the mass transfer-controlled systems. This trend was indeed observed for liquid velocities below 80 cm/s during convective heat transfer, as discussed in the previous section and as shown in Figure

5.7. It is expected that for liquid velocities above 80 cm/s, the effect of surface temperature becomes increasingly stronger, approaching the Arrhenius relationship for reaction-controlled systems. In other words, the reaction-controlled system is strongly affected by the surface temperature, and this effect is more pronounced at higher surface temperature.

Figure 5.7 Fouling rate as a function of surface temperature for convective heat transfer

For sub-cooled flow boiling conditions, the variation in fouling resistance with surface temperature for mixed salt solutions at constant velocity, bulk temperature and solution concentration is shown in Figure 5.8. It is clear that the fouling resistance strongly depends on the heat transfer surface temperature. Different trends are observed during the fouling experiments under sub-cooled flow boiling conditions at different surface temperatures and hence different nucleate boiling fractions.

While the experiment with a surface temperature of 110 °C was basically in the sub-cooled flow boiling heat transfer regime (NBF=0.05), significant improvement in NBF values occurred for the two higher surface temperatures of 112 °C and 114 °C (NBF=0.08

and $NBF=0.16$). Therefore, the trend of scale formation during sub-cooled flow boiling is considerably different, due to the extra deposition created by bubble formation and micro-layer evaporation on the heat transfer surface.

Figure 5.8 Effect of surface temperature on the fouling resistance

The fouling rate for constant bulk temperature, fluid velocity and solution concentration under sub-cooled flow boiling conditions is plotted as a function of surface temperature in Figure 5.9. It is clear that the rate of crystallisation fouling increases with an increase in surface temperature, but this increasing is not linearly dependent to the surface temperature, at a velocity of 80 cm/s. In this velocity, the fouling rate should increase linearly with surface temperature, i.e. mass transfer-controlled system. Therefore, the results shown in this figure confirm that the fouling process during sub-cooled flow boiling is due to the extra deposition created by bubble formation and micro-layer evaporation on the heat transfer surface. This concept will be more explained in Chapter 6.

It is believed that the surface temperature affects predominantly the deposition rate and that the removal rate is affected more by flow velocity than by surface temperature. This means

that the temperature does not affect the removal rate directly, but higher surface temperatures may be associated with deposit phase transition, i.e. transformation of calcium sulphate dihydrate into hemihydrate and anhydrite (Wells, 1962). Both forms are much stronger than dihydrate (Gypsum).

Figure 5.9 Fouling rate as a function of surface temperature for sub-cooled flow boiling

5.1.5 Effect of Bulk Temperature

Bulk temperature is a key parameter with respect to the formation of deposits on heat transfer surface. For considering the effect of bulk temperature, the experiments can be carried out at constant surface temperature or constant heat flux. In constant heat flux conditions, the surface temperature and accordingly saturation concentration on the surface are depended on the bulk temperature, i.e. the surface temperature increases with increasing bulk temperature and the saturation concentration of inversely soluble salts decreases with increasing surface temperature. In other words, saturation concentration and consequently the degree of supersaturation are highly dependent on the bulk

temperature. Both surface temperature and degree of supersaturation will increase the rate of deposition.

For constant operating conditions, when the bulk temperature is increased, the surface temperature is also increased. Therefore, it is essential to reduce the heat flux to reach the desired constant surface temperature. As will be shown in Chapter 6, this leads to a significant improvement in the nucleate boiling fraction. Hence, the nucleate boiling fraction and accordingly enhancement factor are increased with increasing bulk temperature. In the present investigation, the initial surface temperature was kept constant by heat flux variation.

The effect of bulk temperature on the fouling resistance is shown in Figure 5.10 for constant surface temperature, solution concentration and fluid velocity, under sub-cooled flow boiling conditions. Since the surface temperature during fully developed sub-cooled flow boiling is almost independent of the bulk temperature, it was expected that the rate of fouling is also independent of the bulk temperature. However, the results show a considerable dependency of the rate of fouling on bulk temperature, which is indicative for the fact that fully-developed boiling did not exist for the present experimental conditions.

Figure 5.10 Effect of bulk temperature on the fouling resistance

With a substantial contribution from convective heat transfer to the total amount of heat transfer, both nucleate boiling fraction and number of nucleation sites will increase with increasing bulk temperature. Both will promote the occurrence of crystallisation fouling. It is also thought that for inverse solubility salts, if some precipitation may happen in the bulk of the solution, increasing the bulk temperature increases the concentration of suspended particles which enhance the rate of crystal deposition by providing additional nucleation sites on the heat transfer surface.

5.1.6 Effect of Solution Concentration

The effect of solution concentration on the fouling resistance at constant bulk temperature, surface temperature and fluid velocity is shown in Figure 5.11. Moreover, pure calcium sulphate and pure calcium carbonate fouling are compared with fouling of their mixture in this figure. The results show that the bulk composition has a strong effect on the fouling rates.

Figure 5.11 Effect of salt concentration on the fouling resistance

The fouling curves for all concentrations show an almost falling rate fouling curve. The fouling curves for the different solution concentrations approach different fouling resistances, with fouling for the higher concentration being considerably more severe than for the lower concentration. It is important to note that, for some concentrations, the solution is not supersaturated with respect to calcium sulphate or calcium carbonate ($[\text{CaSO}_4]=0.0$ g/l, $[\text{T.A.}]=0.25$ g/l and $[\text{CaSO}_4]=1.6$ g/l, $[\text{T.A.}]=0.25$ g/l). Scanning Electron Microscopy and X-Ray Diffraction analyses indicated that deposit from mixed salt solutions included a mixture of crystals of both dissolved salts in the solution. The supersaturation necessary for crystal nucleation and growth must, therefore, be created locally by the bubble growth mechanisms, i.e. $\text{NBF}=0.0821$.

It is believed that the important factor relevant to crystallisation fouling is the degree of supersaturation of the deposit forming species, rather than the molar concentration. Hence, the extent of supersaturation will generally determine the rate of the crystallisation or deposition process. In the next chapter, it will be shown that regardless of the mechanism of fouling the effect of concentration is strong and that it is more pronounced under boiling and reaction-controlled conditions.

5.1.7 Effect of Heat Flux

The variation of heat transfer coefficients and fouling resistances for different heat fluxes of mixed salt solutions at constant velocity, bulk temperature and concentration are shown in Figures 5.12 and 5.13 respectively. The results show that at constant bulk temperature, liquid velocity and bulk concentration, heat flux is one of the major parameters affecting the deposition rate.

As expected, the clean heat transfer coefficient at the beginning of each experiment increases with increasing heat flux. As long as the other operational parameters are kept constant, heat transfer coefficients at high heat fluxes decrease faster and to a greater extent than at low heat fluxes. In other words, since the surface temperature and bubble generation depend on heat flux, deposition rates in boiling heat transfer are strongly dependent on heat flux. Furthermore, the higher heat fluxes radically increase the number

of nucleation sites and microlayer evaporation, and as a consequence the character of the heat transfer surface.

Figure 5.12 Variation of heat transfer coefficient at different heat fluxes

Figure 5.13 shows that there is a direct relationship between the rate of fouling and the heat flux. If there is an increase in the heat flux, there will be a corresponding increase in the fouling rate, provided that the other operational parameters remain constant. Hence, the rate of fouling decreases with decreasing heat flux. To confirm the previous statement, dR_f/dt is plotted as a function of heat flux in Figure 5.14. Therefore, the dependency of the fouling rate on the heat flux can be approximated by a polynomial/power function.

Considering a solution which is saturated with respect to the principal scaling species at the bulk temperature and supersaturated at the heat transfer surface temperature, and assuming a linear inverse solubility curve over the supersaturated range, the Reitzer type model can be written as:

$$\frac{dR_f}{dt} = k_1 (T_s - T_b)^n \quad (5.5)$$

Since the heater surface temperature changes during fouling experiments, the deposit surface temperature should be used in the calculations. Equation (5.5) shows that the fouling rate versus temperature difference, $(T_s - T_b)$, can be plotted on a log-log paper. A linear dependency of fouling rate on the temperature difference (on a log-log paper) may be observed, which leads to the calculation of the diffusion-reaction coefficient and exponent, n .

Since

$$\dot{q} = \alpha(T_s - T_b) \quad (5.6)$$

it follows that,

$$\frac{dR_f}{dt} = k_1 \left(\frac{\dot{q}}{\alpha} \right)^n = \left(\frac{k_1}{\alpha^n} \right) \dot{q}^n = k_2 \dot{q}^n \quad (5.7)$$

This equation confirms that the fouling rate is highly dependent to the heat flux and it should be more pronounced at higher heat fluxes.

Figure 5.13 Effect of heat flux on the fouling resistance

Figure 5.14 Fouling rate as a function of heat flux

It is important to note that the surface temperatures for all heat fluxes in Figure 5.14 are higher than the saturation temperature. Therefore, sub-cooled flow boiling occurred. It is evident that bubble formation plays a significant role in the problem of scale formation during boiling heat transfer. When bubbles form on a heat transfer surface, the solution becomes supersaturated at the gas/liquid/solid interface and deposits form. If the foulant has a negative solubility, the deposit will stay on the heat transfer surface. If the foulant is highly soluble, it will re-dissolve as the bubble departs.

Jamialahmadi et al. (1989) have argued that heat transfer to the boiling liquid occurs by three mechanisms: forced convection to the liquid, conduction through and evaporation of a liquid micro-layer between bubble and heat transfer surface and heat transfer from the superheated liquid boundary layer to the vapour bubble. From these mechanisms, only micro-layer evaporation can cause the formation of deposit on the heat transfer surface. Evaporation at the base of the bubble increases the concentration of the ions in the liquid beneath the bubbles significantly. The concentration of ions beneath the bubbles can be expressed in terms of bulk concentration (Najibi et al., 1997):

$$C_{bb} = \gamma C_b \quad (5.8)$$

where γ is the concentration effect in the micro-layer. An estimation for the concentration of ions in the micro-layer can be made by assuming that all the vapour is supplied to the bubble by the vaporisation of liquid from the micro-layer. Al-Hayes et al. (1981) measured the bubble departure diameter in sub-cooled flow boiling of water and reported that it does not exceed 3 mm. Using this value for the bubble departure diameter and 2 μm for the thickness of the micro-layer, which is reported by Moore and Mesler (1961) for a hemispherical bubble, the concentration multiplier, γ will be 1.48. Accordingly, a value of 1.5 was used by Najibi et al. (1997). They suggested that the rate of crystallisation fouling in the boiling zone is expressed as:

$$\dot{m}_d = k_r (\gamma C_b - C^*)^2 \quad (5.9)$$

This equation predicts that the rate of deposition becomes more severe when boiling occurred.

5.1.8 Effect of Ionic Strength

In Chapter 3, it was stated that salts with inverse solubility behaviour are more soluble in electrolyte solutions than in water, provided that the electrolyte contains no common ions with the salt. For example, the data plotted in Figure 3.3 in Chapter 3 demonstrate the magnitude of this effect for Gypsum. At a specified temperature, a more than twofold increase in the solubility of calcium sulphate is observed when the sodium chloride concentration is increased from 0 to 5%. The effect of electrolytes on solubility arises from the electrostatic attraction between the sodium/chloride ions and the ions of opposite charge formed by calcium sulphate, i.e. calcium/sulphate ions. It is obvious that increasing CaSO_4 solubility in NaCl solutions reduces the fouling tendency of this salt on the heat transfer surface.

Figure 5.15 shows measured fouling resistances as a function of time for various ionic strengths at constant velocity, bulk and surface temperatures. To increase the ionic strength,

potassium nitrate was used in different concentrations. Increasing the ionic strength of the solution increases the solubility of the calcium sulphate and calcium carbonate, which produces a reduction in the driving force for deposition.

Figure 5.15 Effect of ionic strength on the fouling resistance

The ionic strengths for different compositions used in this investigation are given in Table 5.3. The respective ionic strength could be calculated with Equation (3.58) or using the SOLMINEQ88 software.

Table 5.3 Ionic strength of the solution

[CaSO ₄] g/l	[T.A.] g/l	[KNO ₃] g/l	Ionic Strength, mol/l	α_1 (W/m ² K)
2	0.2	1	0.098	6600
2	0.2	3	0.118	6660
2	0.2	6.5	0.150	6702

Moreover, ionic strength has a significant effect on clean heat transfer coefficients. The clean heat transfer coefficients of sparingly soluble salts with negative solubility are much lower than those of distilled water (Najibi et al., 1997). Increasing salt concentration increases this reduction and this must be attributed to the different physical properties and the changes in the mechanism of bubble formation. In the present experiments, some minor improvement in heat transfer coefficients to the calcium sulphate and calcium carbonate solutions were observed when the ionic strength of solution was increased by adding potassium nitrate salt with positive solubility to the system (Table 5.3).

5.1.9 Effect of Pressure

Pressure is the least studied parameter in heat exchanger fouling. It was previously stated that the solubility of calcium sulphate and calcium carbonate, like other scale forming species in water, increases with increasing pressure. Pressure may affect the physical properties of the solution, i.e. boiling point, density, etc., as well. Sub-cooled flow boiling and the loss of volatile fractions can change the composition of the test fluid in the vicinity of the heated wall. Therefore, pressure alters the fouling tendencies and can have a significant effect on the fouling rate, especially where multi-component fluids are involved.

In vaporisation processes, the boiling point of salt solutions can be affected by changing the system pressure. Therefore, bubble formation, detachment, micro-layer evaporation and consequently nucleate boiling fraction, which enhance scale formation, decrease with increasing pressure.

Figure 5.16 shows the effect of pressure on the fouling resistance. It is clear that the effects of pressure on the fouling resistance for these three test runs are considerable. The results show that the fouling resistance is more at the lower pressures than at the higher pressures. It should be noted that the heat transfer occurred by sub-cooled flow boiling mechanism for these three experiments. At the lower pressure (105 kPa), the nucleate boiling fraction was 0.083. With increasing operating pressure to 125 kPa and 150 kPa, the nucleate boiling fraction was reduced to 0.023 and 0.004 respectively. This decreases the contribution of boiling mechanism on the deposition process.

Figure 5.16 Effect of pressure on the fouling resistance

5.1.10 Effect of Surface Material

The formation of a deposit on a heat transfer surface can be considered as an interaction between the deposit and the heat transfer surface. While the surface properties are important only as long as the surface is not fully covered by deposit, deposit break off may still occur at a later stage. In other words, once the deposit crystals cover the heat transfer surface, the beneficial effect of surface material may be negligible, but deposit break off can still be affected by the surface material.

The initial fouling rate depends significantly on the surface material. Different materials may have different catalytic properties and may promote or reduce fouling of different processes. For example, the surface material is very important for corrosion fouling because of the potential to react and form corrosion products. The use of non-metallic surfaces for highly corrosive fluids is very successful. Teflon coatings are frequently used because of their excellent corrosion resistance and anti-fouling properties.

The adhesion force is dependent on the surface energy of the materials involved. It has long been known that maximum foulant adhesion occurs in systems with higher surface energy and poorest foulant adhesion should occur on materials that have low surface energy. Hence, the decrease of the surface energy may lead to a reduction of scale formation on that surface. Many attempts have been made to achieve this by coating the surface with Teflon, ceramic or polymer layers. However, these coatings must be very thin in order to avoid loss in heat transfer capacity due to their low thermal conductivity. As the layers have to be very thin, the adhesion between metal surface and coating is limited which results in a reduced ability to withstand mechanical stresses.

A novel solution to this problem has recently been suggested through Ion Beam Implanting or Unbalanced Magnetron Sputtering foreign ions into the metal surface (Müller-Steinhagen and Zhao, 1997, 1999). They found that ion implantation and unbalanced magnetron sputtering have the greatest potential for preparing low fouling surfaces. Unlike commonly used coatings, any additional heat transfer resistance of alloy layers is negligible, because the thickness of the alloy layer is only about 1-3 μm . The coating also meets wear resistance and welding requirements.

By implanting or sputtering foreign ions onto the metal surface, Müller-Steinhagen and Zhao (1997, 1999) achieved a substantial reduction in CaSO_4 scale formation during pool boiling. Therefore, it was necessary to extend these results toward formation of salt mixtures under convective heat transfer and sub-cooled flow boiling conditions.

The aim of this part of this investigation was to examine the effects of treated surfaces on the deposition of salt mixtures. Many experiments were performed to investigate whether the surface modifications prepared by Müller-Steinhagen and Zhao (1997, 1999) are also successful for mixed salt crystallisation fouling during forced convection and sub-cooled flow-boiling conditions. Experimental work included fouling tests with various heat fluxes, different concentrations and different velocities. Different surfaces were studied by comparing an untreated stainless steel test heater with a treated one. Generally, the effect of the modified heat transfer surface was a considerable reduction of the fouling

resistance. The observed reduction in scale formation must be attributed to the surface energy reduction due to the different surface treatments.

Seven test heaters with different surface treatments were used, i.e. an untreated, *DLC* sputtered, *CrNTiF* sputtered, *H* implanted, *F* sputtered, *Ni-P-PTFE* coated and *Ni-P-PTFE* porous coated surface. The surface energies of different treated surfaces are summarised in Table 5.4 (Müller-Steinhagen and Zhao, 1997). Preliminary experiments have shown that *DLC* and *CrNTiF* sputtered, *H* implanted and *Ni-P-PTFE* coated surfaces were the most effective treatments to mitigate crystallisation fouling. To limit the scope of work, the operational parameter study was restricted to the *DLC* sputtered surface.

Table 5.4 Surface energies of different treated surfaces

Surface	Surface Energy, mJ/m ²
Untreated	88.3
<i>DLC</i> , Sputtered	35
<i>CrNTiF</i> , Sputtered	40
<i>H</i> , Implanted	41
<i>F</i> , Sputtered	39
<i>Ni-P-PTFE</i> , Coated	30
<i>Ni-P-PTFE</i> , Coated, Porous	33

Figures 5.17 and 5.18 are typical examples for measured heat transfer coefficients and fouling resistances as a function of time for mixed salt solutions. For the untreated surface, a significant decrease in the heat transfer coefficient is observed which is caused by the formation of deposits. As the deposit layer grows in thickness, the heat transfer coefficient decreases and the fouling curve approaches an asymptotic value.

A similar behaviour for the initial phase of the fouling runs can be seen in the curves for the treated surface, i.e. *DLC* sputtered surface, which also show a first drop in heat transfer coefficient and a small increase to a certain constant value.

Figure 5.17 Variation of heat transfer coefficient for different surfaces

Figure 5.18 Effect of surface material on the fouling resistance

However, in comparison to the untreated surface, the decrease is not as sharply developed. Moreover, instead of continuing decrease, the heat transfer coefficient almost remains at a constant value obtained after the small increase. In other words, it remains fairly constant within the period of the measurements. The final value of the heat transfer coefficients of the DLC treated surface is significantly higher than that for the stainless steel surface. The asymptotic fouling resistance was lower than $1 \times 10^{-5} \text{ m}^2 \text{K/W}$ for the DLC treated surface, as compared to about $2.5 \times 10^{-4} \text{ m}^2 \text{K/W}$ for the untreated surface.

The surface energy of *DLC* surfaces is much lower than that of the untreated surface (35 mJ/m^2 as compared to 88 mJ/m^2). Therefore, the reduction of scale formation on the *DLC* sputtered surface must be attributed to the lower surface energy as a result of magnetron sputtering. It is clear that the fouling resistance values are scattered around $1 \times 10^{-5} \text{ m}^2 \text{K/W}$, this may show the alternating process of a small deposit formation and removal.

For other experiments with the *DLC* sputtered surface under different operating conditions, the heat transfer coefficients and thus the fouling resistance remained almost constant. The average of the asymptotic fouling resistance was about $1.5 \times 10^{-5} \text{ m}^2 \text{K/W}$. In contrast to the phenomena described for untreated surface, the *DLC* sputtered surface did not suffer from severe fouling for almost all-operational parameters. Even under extreme conditions such as a high heat flux of 400 kW/m^2 , flow velocity of 50 cm/s and high solution concentrations, hardly any fouling was observed for about 5000 minutes. It should be mentioned that the scale formation during convective heat transfer results in similar values of fouling resistance as under sub-cooled flow boiling conditions, for the *DLC* surface.

It was also observed that the extent of the reduction depends on the fluid velocity, i.e. Reynolds number. In other words, rather the low adhesion of deposits to the surface, their removal by the flow velocity seems to control the fouling rate. Due to the high efficiency of low energy surfaces, it was often not possible to take a sample of the deposit. For these cases, hardly any fouling layer was observed, which is of course the reason for the low fouling resistances.

More experimental results of the mixed salt fouling runs for different treated surfaces are given in Appendix C.

5.2 ERROR ANALYSIS

The difference between the actual value of a physical quantity and the measured value of the quantity is the error of the measurement. The amount of error associated with a particular measurement may be considered from the point of view of precision or the point of view of accuracy. The precision of a measured value expresses the deviation from the average of a large number of measurements of the same quantity, while the accuracy of a measured value expresses the deviation of the measurement from the true value of the quantity. Error is considered from the point of view of accuracy when the true value is known, but when the true value of a quantity is not known precision must be used in place of accuracy.

It is usual to obtain the precision of a measurement not by actually carrying out a large number of measurements but from knowledge of the limitations of the apparatus used to carry out the measurement procedure (Mortimer, 1985). For example, the precision of a thermometer is $\pm 0.2\text{ K}$. This precision can be obtained using proper measuring techniques and is a measure of the deviation expected in repetitive measurements.

Error can be expressed either as an absolute or a relative quantity; both forms of expression are commonly used. An absolute error has the same dimension as the measurement to which it relates, while a relative error is dimensionless. When mathematical operations are performed upon numbers which are the result of quantitative measurements, it is often necessary (and always desirable) to know the error of the calculated result. The error in the calculated result will depend upon the errors in the measurements from which the result is calculated. Since it is not reasonable to believe that the error of a calculated result can be less than the error in the least accurate number used in the calculation, scientists assume that errors always increase or propagate. The rules for propagation of error in arithmetic operations are simple:

1. When two values are added or subtracted, the absolute error of the calculated result is taken to be the sum of the absolute errors of the values.
2. When two values are multiplied or divided, the relative error of the calculated result is taken to be the sum of the relative errors of the values.

It should be noted that relative errors must be used in multiplication and division because the results of these operations have different units from those of the original values.

In this study, the experimental error for the measured heat transfer coefficients or fouling resistances may be due to errors of the measurement of the heat flux, bulk temperature, flow velocity, solution concentration and the surface temperature of the heaters. The heat transfer coefficient is dependent on the surface texture of the heat transfer surfaces. As treated heaters were sanded with grade 120 emery paper before treatment and then cleaned with tissue paper and untreated heaters were always cleaned with grade 120 emery paper, it was postulated that all surfaces were comparable in roughness. By repeating some fouling runs, almost the same fouling curves were obtained, which confirms the above assumption.

The error of the adjusted heat flux is due to errors in the measurements of electrical current and voltage. It was observed that the power delivered by the heater boxes showed small fluctuations depending on the time of the day. During the night and the weekends, a higher heat flux than during working days was observed. For example, it was intended to run the test with a heat flux of 250 kW/m^2 . The average of heat flux was 253 kW/m^2 . This magnitude corresponds to a deviation of 1.2% of the target value. It is clear that this phenomenon affects the values of heat transfer coefficients and subsequently the fouling resistance, i. e. as the heat flux decreases, the fouling resistance increases due to a reduction in heat transfer coefficient.

The variation of the deposit surface temperature when the fouling layer formed was assumed to be negligible. The fluid temperatures were measured with *K*-type thermocouples located in mixing chambers before and after the test sections. These thermocouples were initially checked against a quartz thermometer with an accuracy of about 0.02 K . The inaccuracy in temperature measurements is due to an error in calibration of thermocouples which leads to a deviation of approximately $\pm 0.2 \text{ K}$.

The flow velocity was measured with a magnetic flow meter that had an estimated measurement accuracy of 1% of the reading. The fluid pressure was measured with strain-gauge sensors having a factory calibrated accuracy of about 0.7% of the operating range, which was adequate for the fouling experiments.

The largest experimental errors for the heat transfer coefficients and fouling resistances would be expected at high heat fluxes with a small temperature difference between heat transfer surface and bulk of the liquid at high flow velocities. For fouling resistance measurements, the inaccuracy changes during the test run due to the change in temperature differences between the surface temperature and the bulk temperature. In this investigation, the smallest temperature differences for clean heat transfer coefficient measurements were at heat fluxes below 30 kW/m^2 where the experimental errors for the measured heat transfer coefficients were less or equal to $\pm 20\%$. The minimum heat flux in the fouling runs was 100 kW/m^2 and the temperature differences were more than 20°C . Hence this source of error was further reduced to less than $\pm 3\%$.

As an example, heat flux, flow velocity and bulk temperature are plotted for the whole duration of a typical experiment in Figures 5.19, 5.20 and 5.21 respectively. Only the heat flux shows a small fluctuation, but at the end of the experiment, it is almost constant at the adjusted value of 250 kW/m^2 . It can be concluded that a small fluctuation of this parameter does not cause significant deviation in measured values.

Figure 5.19 Fluctuation of heat flux during an experiment

Figure 5.20 Fluctuation of velocity during an experiment

Figure 5.21 Fluctuation of bulk temperature during an experiment

Chapter 6

MATHEMATICAL MODELLING

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 definitely necessary to investigate 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 be an effective tool to make decisions about the types of water treatment which may be applied to prevent scaling problems. It is also helpful 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. On the other hand, the unavailability of a reliable tool to predict the possibility of scale deposition and its severity sometimes may cause serious irreversible and costly damages.

It was previously stated that fouling is a time-dependent phenomenon. Using a constant value for the fouling resistance at the design stage, which is common practice in designing heat exchangers, one can estimate what may happen to the equipment performance but not when it will happen. In order to provide a satisfactory surface area for an acceptable period of operation, it is therefore, necessary to be able to predict the dependence of fouling resistance on both time and operational parameters. Moreover, the ability to carry out such mechanistic description would also help to determine optimum cleaning cycles and the interactive effects of physical and chemical parameters.

Several investigators have studied fouling 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. Mixed salt crystallisation fouling on heat transfer surfaces during convective heat transfer and sub-cooled flow boiling is a very complicated process. Its mechanisms are related to many subjects such as momentum, heat and mass transfer, chemical kinetics, material science, etc. which makes it difficult to be explained in purely mathematical terms. Hence, theoretical analysis alone can not provide a general equation for prediction of fouling rates. It is, therefore, essential to identify the fundamental processes and parameters that affect the rate of fouling on heat transfer surfaces experimentally, before developing a semi-empirical model. With better understanding of the chemical and physical processes associated with fouling and the different fouling mechanisms, it is believed that models for crystallisation fouling can be formulated to describe the rate-governing process.

The motivation for this study came from the need to identify the potential of common salt scales which can be deposited on heat transfer equipment surfaces and in oilfield production operations. Therefore, the main objectives of the present investigation were to study the mechanisms of mixed salt crystallisation fouling during convective heat transfer and sub-cooled flow boiling by measuring the overall heat transfer coefficient over a wide range of flow velocities, bulk and heat transfer surface temperatures and fluid bulk concentrations. After clarification of the effect of these parameters on the deposition process, a predictive model for crystallisation fouling of calcium sulphate and calcium carbonate mixtures which are the dominant foulants in most industrial systems, under convective heat transfer and sub-cooled flow boiling has been developed.

This chapter presents the development of a model for predicting the scale formation of calcium sulphate and calcium carbonate resulting from either mixing of two sources of water or from changes in physical conditions. In this model, the effects of important parameters on the scale formation phenomenon such as velocity, temperature, heat flux, concentration, pressure, mixing ratio, pH and etc. have been considered. Moreover, the influence of precipitation of each type of scale on the others and the competition of various minerals such as CaSO_4 and CaCO_3 to deposit have been taken into account for the case where the calcium ion is the common ion in formation of the scales. Therefore, the

proposed model represents the physical and chemical steps of the overall fouling process, and will have the following functions:

- Prediction of the trend of fouling (for a chemically defined system),
- Determination of the effects of bulk conditions (operating variables)

In what follows, 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. The analyses have been used for determination of the local rate of fouling for a given set of bulk conditions and wall temperatures (heat flux).

6.1 DEVELOPMENT OF THE DEPOSITION MODEL

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 Figure 6.1. The model calculations include the appropriate conservation equation 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 annular flow, the continuity equation applicable for a radial system is derived.

Figure 6.1 Elemental volume of fluid flow in an annulus

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

$$\text{Mass flow rate in} - \text{Mass flow rate out} = \text{Rate of accumulation} = \text{Rate of deposition} \quad (6.1)$$

or

$$\dot{m}_{in} - \dot{m}_{out} = \frac{dm_d}{dt} \quad (6.2)$$

where

$$\dot{m}_{in} = \dot{V} C \quad (6.3)$$

$$\dot{m}_{out} = \dot{V} (C - dC) \quad (6.4)$$

and

$$\frac{dm_d}{dt} = \frac{d(\rho_d V_d)}{dt} = \rho_d \frac{dV_d}{dt} = \rho_d \frac{\pi[(r+dr)^2 - r^2] dx}{dt} = \rho_d \frac{\pi[r^2 + (dr)^2 + 2rdr - r^2] dx}{dt} \quad (6.5)$$

In the above equations;

$\dot{V}$ = volumetric flow rate

C = concentration of reacting material

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

$$\frac{dm_d}{dt} = \rho_d \frac{2\pi r dr dx}{dt} \quad (6.6)$$

Substitution in Equation (6.2),

$$\dot{V} C - \dot{V} C + \dot{V} dC = \rho_d \frac{2\pi r dr dx}{dt} \quad (6.7)$$

Assuming that $\frac{dx}{dt} = v$, Equation (6.7) reduces to

$$\dot{V} dC = \rho_d (2\pi v r dr) \quad (6.8)$$

Since

$$\dot{V} = v \pi (r_o^2 - r^2) \quad (6.9)$$

therefore,

$$v \pi (r_o^2 - r^2) dC = \rho_d (2\pi r dr) \quad (6.10)$$

Consequently, the continuity equation for the considered system results in,

$$\frac{dC}{dr} = \frac{2\rho_d r}{r_o^2 - r^2} \quad (6.11)$$

It is clear 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, $\frac{dr}{dt}$; according to the chain rule;

$$\frac{dr}{dt} = \frac{dr}{dC} \cdot \frac{dC}{dt} \quad (6.12)$$

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:

$$\dot{m}_d = \frac{dC}{dt} \times \frac{\text{element volume}}{\text{element surface area}} = \frac{dC}{dt} \cdot \frac{V_e}{A_e} \quad (6.13)$$

Therefore,

$$\frac{dC}{dt} = \dot{m}_d \frac{A_e}{V_e} = \dot{m}_d \frac{2\pi r dx}{\pi (r_o^2 - r^2) dx} = \dot{m}_d \frac{2r}{r_o^2 - r^2} \quad (6.14)$$

By substitution of Equations (6.11) and (6.14) in Equation (6.12),

$$\frac{dr}{dt} = \frac{r_o^2 - r^2}{2\rho_d r} \dot{m}_d \frac{2r}{r_o^2 - r^2} = \frac{\dot{m}_d}{\rho_d} \quad (6.15)$$

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:

$$r_{d,n} = r_{d,n-1} + \frac{\dot{m}_{d,n-1}}{\rho_d} (t_n - t_{n-1}) \quad (6.16)$$

where n is time step number.

The resulting equation formulated in this section should be incorporated into the heat balance equation to calculate the fouling resistance. For this purpose, the cross-section of a deposited layer with inside radius r_i , outside radius (deposit radius) r_d and length L is considered, as shown in Figure 6.2. This deposit layer is assumed to be exposed to a temperature difference $T_s - T_d$. For a long cylinder (compared to its diameter), it may be assumed that the heat flows in the radial direction only, so that the only geometric coordinate needed to specify the system is r .

Figure 6.2 Radial heat transfer through a cylindrical system

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:

$$\dot{Q} = -\lambda_d A \frac{dT}{dr} \quad (6.17)$$

The area for heat transfer in the cylindrical system is $A = 2\pi rL$. Therefore,

$$\dot{Q} = -\lambda_d (2\pi rL) \frac{dT}{dr} \quad (6.18)$$

or

$$\frac{\dot{Q} dr}{2\pi rL} = -\lambda_d dT \quad (6.19)$$

The above first order ordinary differential equation can be solved with the following boundary conditions:

$$T=T_{s,n} \text{ at } r=r_i \quad (6.20)$$

$$T=T_{d,n} \text{ at } r=r_{d,n}$$

Assuming constant thermal conductivity of the deposit, the solution to Equation (6.19) is

$$\frac{\dot{Q}}{2\pi L} \ln \frac{r_{d,n}}{r_i} = \lambda_d (T_{s,n} - T_{d,n}) \quad (6.21)$$

Dividing by $(r_i \ln r_{d,n}/r_i)$,

$$q_i = \frac{\dot{Q}}{2\pi r_i L} = \frac{\dot{Q}}{A_i} = \frac{\lambda_d (T_{s,n} - T_{d,n})}{r_i \ln \frac{r_{d,n}}{r_i}} \quad (6.22)$$

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

$$R_f = \frac{r_i \ln \frac{r_{d,n}}{r_i}}{\lambda_d} \quad (6.23)$$

Consequently, combining Equations (6.16) and (6.23) results in:

$$R_f = \frac{r_i \ln \left[\frac{r_{d,n-1} + \frac{\dot{m}_{d,n-1}}{\rho_d} (t_n - t_{n-1})}{r_i} \right]}{\lambda_d} \quad (6.24)$$

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

6.2 CALCULATION OF THE DEPOSITION RATE

6.2.1 Calculation of the Maximum Deposition Rate

The maximum deposition rate of a slightly soluble salt is obtained when the concentrations of the cation and anion are equal and the system immediately approaches equilibrium. However, in most process solutions, the cation and anion concentrations are not equal. The actual concentration of a sparingly soluble salt in these solutions is equal to the smaller of the cation and anion concentrations in the solution of interest, since the smaller concentration limits the amount of scale, which can be formed. In this case, the difference between the two concentrations is called the excess common ion concentration and the species with lower concentration is called the limiting reactant. Hence, the presence of the limiting reactant determines the ultimate value of the deposition.

It is possible to estimate the maximum amount of scale which could form, by assuming that the system immediately reaches equilibrium. If a solution is supersaturated with a salt such as CaCO_3 , CaSO_4 , BaSO_4 or SrSO_4 , precipitation can be expected. In this situation, it is better to consider the general case of the formation of a mineral scale, MA . The general formula, which represents the reaction of two ions to form a product that is typical in crystallisation fouling, can be given as:

Assuming a solution that is supersaturated with respect to MA , therefore

$$(m)(a) > K_{sp} \quad (6.26)$$

where m = initial concentration of M^{2+} , mol/l

a = initial concentration of A^{2-} , mol/l

K_{sp} = solubility product constant

If the solution is assumed to reach equilibrium, MA will precipitate until the solution reaches its saturation point with respect to MA . Since one mole of M^{2+} and one mole of A^{2-} are required to produce one mole of MA , the concentration of both ions will be decreased

by one mole for each mole of scale which precipitates. Assuming that p is the number of moles per litre of MA which precipitate in the act of reaching saturation,

$$K_{sp} = (m - p)(a - p) \quad (6.27)$$

By rearranging:

$$p^2 - (m + a)p + ma - K_{sp} = 0 \quad (6.28)$$

It is obvious that it can not be physically possible to take the positive root of the resulting quadratic equation. Therefore, taking the negative root of the above equation yields:

$$p = \frac{m + a - [(m - a)^2 + 4K_{sp}]^{1/2}}{2} \quad (6.29)$$

Assuming $G = m + a$ and $X = m - a$, therefore,

$$p = \frac{G - (X^2 + 4K_{sp})^{1/2}}{2} \quad \text{mol/l} \quad (6.30)$$

The Equation (6.30) can be expressed in terms of kg/m^3 of precipitation, therefore

$$p = \frac{[G - (X^2 + 4K_{sp})^{1/2}] \cdot MW}{2} \quad \text{kg/m}^3 \quad (6.31)$$

This equation can be used to calculate the maximum amount of any scale which could precipitate. In order to solve this equation for the maximum amount of calcium sulphate and calcium carbonate which could precipitate, the appropriate substitution is required for the K_{sp} value.

In certain cases, especially for flow through tubular or annular systems, it may be desirable to express the results in $\text{kg/m}^2 \cdot \text{s}$. Therefore, for CaSO_4 and CaCO_3 , Equation (6.31) becomes:

$$\dot{m}_d|_{max} = \frac{p \ v \ A_{cs}}{A_h} \quad (6.32)$$

where

p = Maximum amount of precipitation, kg/m^3

v = Fluid velocity, m/s

A_{cs} = Cross-sectional area, m^2

A_h = Heat transfer surface, m^2

$\dot{m}_d|_{max}$ = Maximum deposition rate, $\text{kg/m}^2 \cdot \text{s}$

Equation (6.32) can be used for predicting the maximum deposition rate of any foulants in surface installations or subsurface facilities during production operations.

6.2.1.1 Interactive Model for Scaling Tendency Calculation

One of the primary causes of scale formation is mixing of two or more waters or solutions which are incompatible. For example, the water native to an oil-bearing rock formation is in chemical equilibrium with the rock, the hydrocarbons and any other materials present in the formation (e.g. CO_2 , N_2 , H_2S and etc.). The water chosen for injection is also in equilibrium with its own environment, which is normally quite different from that of the formation into which it is injected. Any injection automatically leads to readjustment of the components present in the mixture of two waters as soon as the injection water enters the formation. Therefore, once two water are mixed, interactions between ions dissolved in the individual waters may form insoluble products. When such precipitation occur, the waters are said to be incompatible.

In oilfields in the onshore region only calcium ions exist in the formation water. After injection of seawater into the oil reservoir for pressure maintenance, calcium sulphate and calcium carbonate are the possible forms of scale that might precipitate, because of the presence of sulphate and bicarbonate ions in the injected water. Therefore, there may be a competition between sulphate and bicarbonate ions to form scale with the calcium ions. In

these cases, sequential precipitation is predicted in the literature from the mineral with the lowest solubility product to the highest one (Vetter, 1979), and this sequence is always fixed and unchangeable regardless to the ionic concentrations. Of course this concept can not be fully correct and separate calculations for one type of scale without taking into account the effect of precipitation of various other scales, leads to incorrect results. To avoid this deficiency, the model should include a process for calculating the simultaneous scale precipitation of more than one mineral.

In the model proposed in this work, the path and sequence of precipitation is chosen based on the saturation index from the highest value of SI to the lowest one. Hence, in the development of simultaneous crystallisation fouling, three 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 and there is a competition between ions for deposition as scales, 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, it is concluded that solubility product values can not be the determining factor for the precipitation sequence.
3. There is a further shortcoming in the solubility concepts. In the literature, solubility product values that are needed to determine the amount of scale deposition are computed at the beginning of the calculations (Allen and Roberts, 1979). These values are used in all stages of the modelling calculations. This is not fully correct, because solubility product values are a function of ionic strength, and after each stage of scale precipitation, ionic strength of the solution changes, thus solubility product values change. Therefore, it is necessary to compute new values for solubility products after each stage of scale deposition

or to keep the ionic strength parameter constant. Otherwise incorrect amounts of scale will be predicted.

However, as it was previously stated, if more than one of the minerals are supersaturated in the same solution, simultaneous precipitation will occur until equilibrium between the scaling ions and their solid precipitates is reached, which may be expressed as follows:

where x , y and z are the initial concentrations of Ca^{2+} , SO_4^{2-} and HCO_3^- respectively. p_1 and p_2 are the amounts of CaSO_4 and CaCO_3 which precipitate, respectively. Here, Ca^{2+} is the common ion in the formation of scales. The solubility products may be expressed as follows:

$$K_{sp(\text{CaSO}_4)} = (x - p_1 - p_2) (y - p_1) \quad (6.35)$$

$$K_{sp(\text{CaCO}_3)} = (x - p_1 - p_2) (z - p_2) \quad (6.36)$$

As mentioned earlier in Chapter 3, since the second ionisation constant of carbonic acid is much smaller than the first ionisation constant, bicarbonate ions vastly outnumber the number of carbonate ions present under any circumstances. Hence, it is believed that Equation (6.34) is the main reaction of CaCO_3 scale deposition. All parentheses in the above equations are the ionic concentrations at the precipitation/dissolution equilibria.

Furthermore, saturation indices are related to K_{sp} values as follows:

$$SI_{(\text{CaSO}_4)} = \log \frac{x y}{K_{sp(\text{CaSO}_4)}} \quad (6.37)$$

$$SI_{(\text{CaCO}_3)} = \log \frac{x z}{K_{sp(\text{CaCO}_3)}} \quad (6.38)$$

It is clear from Equations (6.35) through (6.38) that the amounts of supersaturation and precipitation of various minerals are dependent on each other, can not be dealt with separately and hence must be solved simultaneously. The values of the solubility products used in the set of Equations (6.35) and (6.36) are related to equilibrium conditions and to p_1 and p_2 , which are the concentration changes to the final equilibrium condition after the overall stages of precipitation.

Values of p_1 and p_2 in Equations (6.35) and (6.36) are unknown and must be determined. The Gauss-Seidel (Gerald and Wheatly, 1989) method, the Newton-Raphson method or any other appropriate mathematical method can be used to solve the set of equations. For example, the Gauss-Seidel method begins by solving each equation for one of the variables (unknown values). Initial approximations to the values of the variables are guessed (each component might be taken as zero if no better initial estimates are known). Substituting these into the right-hand sides of the set of equations generates new approximations that are closer to the true values. The new values are substituted into the right-hand sides to generate a second approximation, and the process is repeated until successive values of each of the variables are sufficiently alike and convergence is achieved. The listing of the computer program for this method is given in Appendix D.

The maximum deposition rate model was obtained assuming an instantaneous chemical reaction at the wall surface and zero mass transfer resistance in the bulk of the fluid. It works based on thermodynamic concepts, only. Therefore, the deposition rate can be obtained from thermodynamic equations. Mass transfer and kinetic data are not needed and thermodynamic information alone is sufficient. Figure 6.3 is a typical example of the experimental data and the corresponding predictions of the maximum deposition rate model. The results show that the model predicts much higher fouling resistances than the experimental data. It is clear that experimental data and predicted values are not comparable.

The weakness of this model is the assumption that the ions which form the deposits arrive at the liquid/crystals interface, without any resistance and incorporate into the existing crystal lattice immediately. It is apparent however that the deposition process is not rapid

enough and a finite time is required to enable this process to be carried out. This is due to the presence of a resistance against the deposition process. These resistances may be expressed in terms of mass transfer and surface reaction of the reacting species. In other words, the deposition rate must be controlled by mass transfer and/or surface reaction phenomena.

Figure 6.3 Comparison of experimental data and predictions of the maximum deposition rate model

6.2.2 Calculation of the Actual Deposition Rate

In 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:

$$\dot{m}_d|_{net} = \dot{m}_d - \dot{m}_r \quad (6.39)$$

The calculation of the local deposition rate requires knowledge of the following parameters:

- Bulk composition,
- Bulk temperature,
- Wall temperature,
- Heat flux,
- Fluid velocity,
- Transport phenomena (correlations to calculate heat and mass transfer coefficients),
- Possible chemical reactions (reactants to product) and chemical kinetics,
- Interactive effects of chemical and physical processes,
- Fouling film characteristics,
- Solubility equilibria,
- Probability factor and adhesion criteria for foulant sticking, and
- Removal mechanism

A number of studies have been made on the mechanism of calcium sulphate crystal growth under forced convective conditions. A brief survey of these studies has been given in Chapter 2. Of the fouling models presented in the literature, the models developed by Bohnet (1985) and Najibi et al. (1997) provide an approach to a generalised fouling model in which chemical reaction and transport phenomena are properly integrated. Similarly, the critical review by Watkinson (1988) shows that organic fluid fouling includes a two-step mechanism. Crittenden et al. (1987) applied the same assumption to determine polystyrene deposition from a dilute solution of styrene in kerosene by considering the reaction zone to be at the wall surface. These previous studies provide useful information for the development of a comprehensive fouling model.

It should be noted that the complexity of the deposition process and the need for a multidisciplinary approach are the principal reasons generally offered by investigators for simplifying the fouling analysis. In the present investigation, to determine $\dot{m}_d$ and $\dot{m}_r$, the following steps and assumptions should be considered in order to simplify the fouling process and to develop a mathematical model for crystallisation fouling:

1. The fouling process consists of a two-step process. The ions forming deposits (reacting ions) diffuse from the bulk to the reaction zone because of a positive concentration driving force between the bulk and the surface. Once they reach the reaction zone, they react to form crystalline products at the surface-fluid interface, which form the deposits.
2. The deposit materials may adhere to the heat transfer surface or return to the bulk fluid, either due to solubility in the solvent or by back-diffusion. It is assumed that a negligible amount of deposits is re-dissolved since the solution is supersaturated, and negligible back diffusion occurs.
3. Re-circulation of the test fluid in the laboratory means that fouling reactants are continuously being removed from the solution. In the present investigation, it is assumed that the bulk fluid concentration remains constant and equal to the initial value during the course of an experiment. This is a valid assumption, since only a small portion of the present ions reacted, even in cases of heavy fouling. Moreover, for maintaining constant bulk concentration, some make-up chemicals were added to the solution tank, if it was required. Therefore, the properties of the fluid mixture do not change significantly during the formation of deposits. It should be noted that chemical analysis of the test fluid is essential to determine the amount of reactants, in order to re-adjust the solution concentration.
4. The deposit layer is homogeneous across its thickness and porosity.
5. The bulk temperature is constant.
6. In the present approach, the ageing process will not be considered, because it could be specific to the system and it requires a separate set of laboratory experiments to study the long-term kinetics associated with ageing.

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. Figure 6.4 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^* . It is clear that $(C_b - C^*)$ is the overall supersaturation. $(C_b - C_i)$ 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.

Figure 6.4 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. Based on the above assumptions, 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,

$$\dot{m}_d = \beta(C_b - C_i) \quad (6.40)$$

where β is the mass transfer coefficient, which is a function of the degree of liquid phase turbulence.

It was stated that in the fouling process, mass diffusion plays a key role. Estimation of the diffusivity constant and corresponding mass transfer coefficient are one of the better-understood stages of the fouling phenomenon. The mass transfer coefficient can be calculated using a heat transfer correlation (e.g. Gnielinski, 1986) and the Colburn analogy (1933):

$$Sh = \frac{\frac{f}{8} (Re - 1000) Sc}{1 + 12.7 \sqrt{\frac{f}{8} (Sc - 1)}} \left(1 + \frac{1}{3} \left(\frac{D}{x} \right)^{\frac{2}{3}} \right) \left(\frac{Sc}{Sc_w} \right)^{0.11} \left(0.86 \left(\frac{d_i}{d_o} \right)^{-0.016} \right) \quad (6.41)$$

Equation (6.41) is valid for $2300 < Re < 1000000$ and $0.6 < Sc < 2000$. For soluble species with known chemical structure, it is possible to estimate the diffusivity in a given carrier fluid. The diffusion coefficient of ions in the present solutions can be calculated from the appropriate equations for electrolyte solutions (Reid, et al., 1988), since this parameter is required for calculation of the mass transfer coefficient. These equations have been given in Appendix D. All physical properties were evaluated at the bulk temperature except when mentioned otherwise. These properties were either taken from the literature, when available, or evaluated using the SOLMINEQ88 computer code which is recommended for electrolyte solutions and extensively used in petroleum industry.

The second step in the formation of foulants is the incorporation of key components into the crystal structure, i.e. 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 these 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 dependent upon 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. The chemical reaction may be assumed to follow a linear growth law, i.e. the rate of chemical reaction is linearly related to the driving concentration difference.

$$\dot{m}_d = k_r (C_i - C^*) \quad (6.42)$$

where k_r is the reaction rate constant. It will be shown later that the linear growth law is not normally followed in actual systems, but it is a useful form for discussion purposes.

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:

$$k_r = k_o e^{-\frac{E}{RT}} \quad (6.43)$$

The reaction zone is considered to be the viscous sub-layer, the thickness of which can be determined by (Qufer and Knudsen, 1993):

$$\delta = \frac{5 d_h}{Re} \left(\frac{f}{2} \right)^{-0.5} \quad (6.44)$$

where d_h is the hydraulic diameter, Re is the Reynolds number and f is the friction factor. If β and k_r are known, it would be possible in principle to determine both C_i and $\dot{m}_d$ from Equations (6.40) and (6.42). These equations may be combined to give:

$$C_i = \frac{\beta C_b + k_r C^*}{\beta + k_r} \quad (6.45)$$

and

$$\dot{m}_d = \frac{C_b - C^*}{\frac{1}{\beta} + \frac{1}{k_r}} \quad (6.46)$$

Thus, if the mass transfer and chemical reaction processes are both linear with respect to the driving concentration difference, the rate of growth is also linear with respect to the overall supersaturation.

It is well known that the analogy between deposition process and electrical circuit is close; thus if $\dot{m}_d$ represents the current, $1/\beta$ and $1/k_r$ represent resistances, C_b , C_i and C^* represent voltages, then Equations (6.40) and (6.42) represent Ohm's law for the two individual resistances, and Equation (6.46) is Ohm's law for the two resistances in series. If an electric current flows through two resistances in series, and if one resistance is much larger than the other, the size of the current is determined by the larger resistance. Similarly, in the present case, if $\beta \ll k_r$, then;

$$\dot{m}_d = \beta(C_b - C^*) \quad (6.47)$$

In this equation, the mass transfer process is the slow one and will therefore, control the overall rate. This is often described by saying that the system is mass transfer-controlled and the interface concentration will approach the saturation value. On the other hand, if $k_r \ll \beta$, the overall rate is determined by the rate of surface reaction, and the system is said to be surface reaction-controlled. The interface concentration will then approach the bulk concentration, i.e.

$$\dot{m}_d = k_r(C_b - C^*) \quad (6.48)$$

Therefore, there are two possible limiting cases. In one case, where the reactant concentration at the interface is equal to its saturation value, mass transfer is the limiting step. In the other case, where the interfacial concentration is almost the same as the bulk value, the reaction rate at the interface is the limiting step, and the rate of deposition is controlled by the reaction rate. In real situations, however, it may not be possible to simplify the fouling model as described above. Both the chemical reaction and the mass transfer process may be important. As it was stated in Chapter 5, the results of this investigation prove that mass transfer effects have some influence on the rate of calcium sulphate and calcium carbonate deposition.

Turbulence, of course increases the rate of mass transfer; consequently when growth rate of crystals is plotted against velocity, Reynolds number or other measures of turbulence, the curve usually rises as the velocity is increased, but may flatten out to give a constant growth rate for very high velocities. This plateau growth rate will then be given by Equation (6.48). Under these experimental conditions, it should then be possible to determine directly the value of k_r . It should be noted that the removal rate may be neglected for crystallisation fouling process. This concept will be discussed at the end of this chapter.

It can be concluded that if the deposition process consists of a number of steps in series, it is the slowest step of the series that exerts the greatest influence and can be said to be the controlling step. A key problem is to find out which variables affect each of these steps and to what degree. Only when the magnitude of each factor is known, a clear picture of the effect of these variables on the rate of deposition is known. In this situation, it is possible to extrapolate these rates to new and different conditions.

In actual systems, it is believed that the crystal growth law is probably of an order higher than one. Therefore, a general order rate equation may be used in this situation.

$$\dot{m}_d = k_r (C_i - C^*)^n \quad (6.49)$$

where n is known as the order of the reaction and usually has a value greater than one. For chemical reactions with orders higher than one, Equations (6.40) and (6.49) can be combined to eliminate the interface concentrations, i.e.

$$\left(\frac{\dot{m}_d}{k_r} \right)^{1/n} + \frac{\dot{m}_d}{\beta} - (C_b - C^*) = 0 \quad (6.50)$$

However, the fouling model contains several kinetic and physical parameters that must be determined experimentally. Thus, for calculating the deposition rate using Equation (6.46) or (6.50), it is essential to obtain some information about the reaction order and the kinetic data of the proposed reactions, before finalising the mathematical model.

6.2.2.1 Determination of Kinetic Data

It was previously stated that the deposition process takes place in two successive steps, *mass transfer* and *chemical reaction*. The chemical reaction step is developed on the basis of knowledge of the possible reaction mechanism and the chemical structure of reactants and products. A fundamental question in the mathematical description of crystallisation fouling is identifying specific reactants and obtaining the kinetic data for their reaction to form insoluble deposits.

For calculating of the kinetic data, in order to develop a kinetic model, chemical reactions should be classified in different ways. In chemical reaction engineering, probably the most useful scheme is the breakdown according to the number and types of phases involved, the big division being between the homogeneous and heterogeneous systems. A reaction is homogeneous if it takes place in one phase alone. Therefore, in homogeneous reactions, all reacting materials are found within a single phase. A reaction is heterogeneous if it requires at least two phases to proceed.

Chemical reactions are also classified according to the stoichiometric equation contribution on the rate expression. Such reactions, in which the rate equation corresponds to a stoichiometric equation, are called elementary reactions. When there is no correspondence between stoichiometry and reaction rate, then chemical reaction will be a non-elementary one.

Many variables may affect the rate of a chemical reaction. In homogeneous systems, the temperature, pressure and composition are obvious variables. In heterogeneous systems more than one phase is involved, hence the problem becomes more complex. Material may have to move between two points or from one phase to another during reaction, hence the rate of mass transfer can become important. Thus, heat and mass transfer may play important roles in determining the rates of reactions.

For many reactions and particularly elementary ones, the rate expression can be written as a product of a temperature dependent term and a composition dependent term, or

$$r_i = f_1(\text{temperature}) \cdot f_2(\text{composition}) = k_r f_2(\text{composition}) \quad (6.51)$$

For such reactions, the temperature dependent term which is called the reaction rate constant has practically been found to be well represented by Arrhenius' law:

$$k_r = k_0 e^{-E/RT} \quad (6.43)$$

where k_0 is called the frequency factor and E is called the activation energy of the reaction. This expression fits experimental data well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency (Levenspiel, 1972). Therefore, the temperature dependency of reactions is determined by the activation energy and temperature level. From the Arrhenius law, it is obvious that;

1. A plot of $\ln(k)$ vs $1/T$ gives a straight line, with large slope for large E and small slope for small E .
2. Reactions with high activation energies are very temperature sensitive, reactions with low activation energies are relatively less temperature sensitive.
3. A given reaction is more temperature sensitive at low temperature than at high temperature.
4. The frequency factor k_0 does not affect the temperature sensitivity of a reaction. (In an actual reaction, there may be a slight temperature dependency of this term, however, this is rather minor and can be ignored) (Levenspiel, 1972).

However, the rate of a reaction may either be suggested by theoretical considerations or simply be the result of an empirical curve-fitting procedure. In any case the value of the constants of the equation can only be found by experiment. Equipment by which empirical information is obtained can be divided into two types, the batch and flow reactors. The batch reactor is simply a container to hold the contents while they react. All that has to be determined is the extent of reaction at various times, and this can be followed in a number of ways. For example:

1. By following the concentration of a given component.
2. By following the change in some physical property of the fluid such as the electrical conductivity or refractive index.

The experimental batch reactor is usually operated isothermally and at constant volume because it is easy to interpret the results of such runs. This reactor is a relatively simple device adaptable to small-scale laboratory setups, and it needs little auxiliary equipment or instrumentation. Thus it is used whenever possible for obtaining homogeneous kinetic data. The flow reactor is used primarily in the study of the kinetics of heterogeneous reactions, though in a number of instances it is used to complement and offers advantages over the batch reactor in the study of homogeneous reaction.

Moreover, there are two procedures for analyzing kinetic data, the integral and the differential methods. In the integral method of analysis, a particular form of rate equation is assumed and after appropriate integration and mathematical manipulations, the plot of a certain concentration function versus time should yield a straight line. The data are plotted, and if a reasonably good straight line is obtained then the rate equation is said to satisfactorily fit the data. The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted C versus t curve with the experimental C versus t data. If the fit is unsatisfactory, another rate equation is suggested and tested.

In the differential method of analysis, the rate expression is fitted to the data directly without any integration. However, since the rate expression is a differential equation, dC/dt must first be found from the data before attempting the fitting procedure. In general, it is suggested that integral analysis be attempted first, and if not successful, then the differential method be tried (Levenspiel, 1972).

It was previously mentioned that calcium, sulphate and bicarbonate ions are transported from the bulk to the heat transfer surface. The reaction of these ions to form calcium sulphate and calcium carbonate solid phase can be described by;

Since the mechanism of reaction was not known, it was attempted to fit the data with an n^{th} -order rate equation of the form;

$$\dot{m}_d = -\frac{dC_A}{dt} \frac{V}{A_h} = k_r (C_A - C_A^*)^n \quad (6.52)$$

where V is the volume of the reactor and A_h is the heat transfer area. By separation of variables and integration;

$$[(C_A - C_A^*)^{1-n} - (C_{A0} - C_A^*)^{1-n}] \frac{V}{A_h} = (n-1)k_r t \quad n \neq 1 \quad (6.53)$$

It is clear that the order n cannot be found explicitly from Equation (6.53), so a non-linear regression analysis should be used. Based on the above analysis, the reaction rate equations used for the crystallisation of calcium sulphate and calcium carbonate during convective heat transfer at high velocities, i.e. 2.5 m/s, are;

$$\dot{m}_{\text{CaSO}_4} = -\frac{dC_{\text{CaSO}_4}}{dt} \frac{V}{A_h} = k_r (C_b - C^*)^n = k_o e^{\frac{-E}{RT}} (C_b - C^*)^n \quad (6.54)$$

$$\dot{m}_{\text{CaCO}_3} = -\frac{dC_{\text{CaCO}_3}}{dt} \frac{V}{A_h} = k_r (C_b - C^*)^n = k_o e^{\frac{-E}{RT}} (C_b - C^*)^n \quad (6.55)$$

where the reaction rate constants, k_r , have been expressed in the Arrhenius type equation. It should be noted that mass transfer effects are negligible at high velocities, hence the chemical reaction can be assumed as the controlling mechanism.

In the present investigation, for development of an appropriate kinetic model for calcium sulphate and calcium carbonate, frequency factors, activation energies, and order of reactions were obtained from batch reactor experiments and/or fouling experimental data. In batch reactor experiments, determination of the rate equation was a two-step procedure. First the concentration dependency was found at fixed temperature and then the temperature dependency of the rate constants was found, yielding the complete rate equation.

In this experimental approach, the fouling test rig was used as the batch reactor system. Fluid with known concentrations of reactants was allowed to react in the batch reactor, i.e. test rig, which was maintained at uniform bulk temperature by constant stirring and heating/cooling. Fluid samples were analysed as a function of time, and kinetic constants were calculated by varying temperature and reactant concentration. The details of the experimental equipment and procedure are given in Chapter 4.

Many experiments were performed to determine the kinetic constant required in the above reaction rate equations. The kinetic constants for two proposed reactions between calcium/sulphate ions and calcium/bicarbonate ions were calculated from these experimental data. A non-linear regression analysis of the experimental data for convective heat transfer at high velocities, i.e. 2.5 m/s, gave the Arrhenius correlation parameters and reaction orders for the reaction rate constants.

Alternatively, the kinetic constants for the proposed chemical reactions were determined by non-linear regression analysis of the fouling experimental data. These kinetic constants can be used for comparing the experimental data with the model predictions and in analysing the parametric effects in Section 6.5. The results are summarised in Table 6.1.

TABLE 6.1 Batch reactor data and fouling experimental data

<i>CaSO₄</i>				<i>CaCO₃</i>			
Batch Reactor Data		Fouling Experimental Data		Batch Reactor Data		Fouling Experimental Data	
T (°C)	100-120	T (°C)	100-130	T (°C)	100-120	T (°C)	100-130
[CaSO ₄] g/l	1.6-2.5	[CaSO ₄]g/l	1.6-3.0	[CaSO ₄] g/l	1.6-2.5	[CaSO ₄] g/l	1.6-3.0
[T.A.] g/l	0.1-0.3	[T.A.] g/l	0.1-0.35	[T.A.] g/l	0.1-0.3	[T.A.] g/l	0.1-0.35
n	1.95	n	1.91	n	1.92	n	1.89
E (j/mol)	106747	E (j/mol)	124287	E (j/mol)	103437	E (j/mol)	137863
k ₀ (m ⁴ /kg.s)	3.2x10 ¹¹	k ₀ (m ⁴ /kg.s)	3.8x10 ¹¹	k ₀ (m ⁴ /kg.s)	9.22x10 ¹¹	k ₀ (m ⁴ /kg.s)	10.39x10 ¹¹

From the obtained results, it may be concluded that the order of two for the proposed chemical reactions is satisfactory. These results also agree with those of previous investigations which have been made by Bohnet (1985) and Najibi et al. (1997). Therefore, the chemical reactions can be assumed as elementary ones, since the order of the reactions with respect to ion concentrations are equal to their stoichiometric coefficients. Therefore, Equations (6.54) and (6.55) become

$$\dot{m}_{\text{CaSO}_4} = k_r (C_b - C^*)^2 = k_o e^{\frac{-E}{RT}} (C_b - C^*)^2 \quad (6.56)$$

$$\dot{m}_{\text{CaCO}_3} = k_r (C_b - C^*)^2 = k_o e^{\frac{-E}{RT}} (C_b - C^*)^2 \quad (6.57)$$

6.2.2.2 Prediction of Deposition Rate of CaSO_4 and CaCO_3

To develop a predictive model for calcium sulphate and calcium carbonate crystallisation fouling, attention should be paid to solubility characteristics or solution thermodynamics of these salts as well as the flow hydrodynamics. 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 the reactant 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.

In the present investigation, it must be emphasised that the calculations are on the basis of limiting reactant concept, because the reactions are controlled by the limiting reactants. It is clear that the calcium ion is the common ion and sulphate and bicarbonate ions are non-common ions. Hence, it is initially essential to find the limiting reactant ions. Subsequently, the deposition model must be solved for the limiting reactants. All these steps are compiled in the computer program, which has been written for the model calculations.

For chemical reactions with orders higher than one, Equations (6.40) and (6.49) were combined to give:

$$\left(\frac{\dot{m}_d}{k_r}\right)^{1/n} + \frac{\dot{m}_d}{\beta} - (C_b - C^*) = 0 \quad (6.50)$$

From the obtained results in the kinetic data determination section, it was concluded that the order of two for the proposed chemical reactions is satisfactory. Therefore Equation (6.50) becomes:

$$\left(\frac{\dot{m}_d}{k_r}\right)^{1/2} + \frac{\dot{m}_d}{\beta} - (C_b - C^*) = 0 \quad (6.58)$$

After some mathematical manipulations and taking the negative root of the resulting quadratic equation, Equation (6.58) can be expressed as:

$$\dot{m}_d = \beta \left[\frac{1}{2} \left[\frac{\beta}{k_r} \right] + (C_b - C^*) - \sqrt{\frac{1}{4} \left[\frac{\beta}{k_r} \right]^2 + \left[\frac{\beta}{k_r} \right] (C_b - C^*)} \right] \quad (6.59)$$

Therefore, the overall fouling rate during convective heat transfer conditions can be calculated using Equation (6.59) in conjunction with Equations (6.41) and (6.43).

a) Proposed Model for Calcium Sulphate

It was previously stated that the deposition process of calcium sulphate could be summarised into two steps. In the first step, due to the concentration gradient, calcium and sulphate ions are transported to the heat transfer surface by diffusion through the boundary layer, which is formed between the deposit surface and the solution. In the second step the ions transported to the surface will react to form the solid phase of calcium sulphate. The reaction between ions completes the precipitation of CaSO_4 scale on the heat transfer surface. This surface reaction can be described by:

Since no back diffusion of deposits is assumed, the mass flux of reactants is equal to the rate of deposition by reaction. Therefore, according to Equation (6.59), the deposition rate during forced convection becomes:

$$\dot{m}_d|_{CaSO_4} = \beta \left[\frac{1}{2} \left[\frac{\beta}{k_r} \right] + (C_b - C^*) - \sqrt{\frac{1}{4} \left[\frac{\beta}{k_r} \right]^2 + \left[\frac{\beta}{k_r} \right] (C_b - C^*)} \right]_{CaSO_4} \quad (6.60)$$

where k_r is

$$k_r|_{CaSO_4} = k_o e^{-E/RT} \quad (6.43)$$

The temperature term represents the contribution to fouling by chemical reaction. In the present investigation, it was assumed that the reaction occurs on the heat transfer surface, therefore the surface temperature is used. The frequency factor and activation energy required for evaluation of k_r in Equations (6.60) were obtained from non-linear regression analysis of the experimental data. The results were summarised in Table 6.1.

It should be noted that the speciation between sulphate and bisulphate is pH dependent. For pH levels above 3, the major ionic species is SO_4^{2-} (and Ca^{2+}), compared to HSO_4^- (and Ca^{2+}) at lower pH levels. Around pH value of 2.5, sulphate and bisulphate coexist in equal proportions (Moeller, et al., 1989). In this situation, HSO_4^- ions also diffuse through the boundary layer as well as SO_4^{2-} ions. Therefore sulphate and bisulphate ions will react with calcium ions to form calcium sulphate deposits. In the present investigation, pH values were above 5, hence HSO_4^- ions did not exist in the solution.

b) Proposed Model for Calcium Carbonate

Similar to calcium sulphate, it is assumed that the deposition of calcium carbonate on the heat transfer surface during convective heat transfer condition takes place by a two-step mechanism. In the first step, due to the concentration gradient, calcium and bicarbonate ions are transported from the bulk of the liquid to the heated surface by diffusion through the boundary layer, which is formed between the surface and the solution. In the second step the ions transported to the surface will react to form the solid phase of calcium carbonate. This surface reaction can be described by,

Therefore, according to Equation (6.59), the deposition rate for calcium carbonate during forced convection becomes,

$$\dot{m}_d|_{CaCO_3} = \beta \left[\frac{1}{2} \left[\frac{\beta}{k_r} \right] + (C_b - C^*) - \sqrt{\frac{1}{4} \left[\frac{\beta}{k_r} \right]^2 + \left[\frac{\beta}{k_r} \right] (C_b - C^*)} \right]_{CaCO_3} \quad (6.61)$$

where k_r is

$$k_r|_{CaCO_3} = k_o e^{-E/RT} \quad (6.43)$$

The frequency factor and the activation energy required for evaluation of k_r in Equation (6.61) were obtained from non-linear regression analysis of the experimental data. The results of this analysis were summarised in Table 6.1.

Thermal conductivities of pure calcium sulphate and pure calcium carbonate were determined from the measured fouling resistances and the measured deposit radii in the University of Surrey and University of Petroleum Industry laboratories. The foulant density was also determined using the measured deposit mass and thickness (e.g. volume). Although it is believed that there is some error in such methods, the results agree with the literature data for calcium sulphate and calcium carbonate. The measured values are given in Table 6.2. These two parameters are used in Equation (6.24) for calculating the fouling resistances.

Table 6.2 Density and thermal conductivity of $CaSO_4$ and $CaCO_3$

Parameters Salts	ρ_d (kg/m^3)	λ_d ($W/m.K$)
Calcium sulphate	1991	2.03
Calcium carbonate	2434	1.821

An inspection of the results in Table 6.2 shows that the density and thermal conductivity of calcium sulphate and calcium carbonate deposits are different. Therefore, an average

value for these properties should be used while using Equation (6.24). The following equations are recommended to calculate the average density and thermal conductivity of deposit mixtures (Buckingham, 1975).

$$\rho_{mix} = \left(\sum \frac{w_i}{\rho_i} \right)^{-1} \quad (6.62)$$

and

$$\lambda_{mix} = \left(\sum \frac{\rho_{mix}}{\rho_i} \frac{w_i}{\lambda_i} \right)^{-1} \quad (6.63)$$

where ρ , λ and w are density, thermal conductivity and mass fraction respectively.

6.2.3 Solubility Calculations Employing Activity Coefficients

The solubility of sparingly soluble salts in water is often expressed in terms of the molar solubility product, K_{sp} . The use of activities rather than molar concentrations in equilibrium constant calculations yields more accurate information, especially for concentrated and/or high ionic strength solutions (Skoog, et al., 1992). For example, for precipitation of CaSO_4 ,

The solubility product, based on activities, can be written as;

$$K_{sp} = a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}} = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] f_{\text{Ca}^{2+}} f_{\text{SO}_4^{2-}} \quad (6.64)$$

Therefore,

$$[\text{Ca}^{2+}] [\text{SO}_4^{2-}] = \frac{K_{sp}}{f_{\text{Ca}^{2+}} \cdot f_{\text{SO}_4^{2-}}} \quad (6.65)$$

Since, the bracketed terms are molar concentrations of Ca^{2+} and SO_4^{2-} , division of K_{sp} by the product of the activity coefficients of Ca^{2+} and SO_4^{2-} yields another constant, K'_{sp} ,

which is applicable to a solution of a particular ionic strength. This constant can then be employed in the equilibrium calculations. The same expression could be obtained for the precipitation of CaCO_3 .

It is possible to calculate the activity coefficients of ions, by the Debye-Hückel expression (Skoog, et al., 1992);

$$-\log f_A = \frac{0.5085 Z_A^2 \sqrt{I}}{1 + 0.3281 d_A \sqrt{I}} \quad (6.66)$$

or

$$f_A = 10^{-\left(\frac{0.5085 Z_A^2 \sqrt{I}}{1 + 0.3281 d_A \sqrt{I}} \right)} \quad (6.67)$$

where

f_A = activity coefficient of species A

Z_A = charge of species A

I = ionic strength of the solution, mol/l

d_A = effective diameter of the hydrated ion A in Angström units ($\text{\AA}$)

$$d_{\text{Ca}^{2+}} = 6 \text{ \AA}$$

$$d_{\text{SO}_4^{2-}} = 4 \text{ \AA}$$

$$d_{\text{CO}_3^{2-}} = 4.5 \text{ \AA}$$

It should be noted that the constants 0.5085 and 0.3281 are applicable to solutions at 25 °C, other values must be employed at different temperatures. In the present investigation, using the results obtained from the SOLMINEQ88 software, the following correlation was obtained.

$$f_A = 10^{-\left(\frac{m Z_A^2 \sqrt{I}}{1 + n d_A \sqrt{I}} \right)} \quad (6.68)$$

where

$$\begin{aligned} m &= 0.31 + 56/T \\ n &= 0.11 + 68/T \end{aligned} \quad (6.69)$$

with T being the absolute temperature in K . The activity coefficients have been used in mathematical modelling of the mixed salt crystallisation fouling process.

6.2.4 Effect of Boiling on Deposition Rate

It was previously mentioned that scale formation on heat exchanger surfaces causes degradation in performance and can give rise to complicated consequences. The previous sections in this chapter have largely focused on crystallisation fouling under convective heat transfer, but scale formation during boiling conditions occurs in equipments such as boiler and evaporators. This problem is more serious during nucleate boiling conditions because of the mechanisms of bubble formation, detachment and micro-layer evaporation.

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 bubble causes the local supersaturation of salts such as calcium sulphate and calcium carbonate in the liquid beneath the bubbles 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 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 equations (6.60) and (6.61) 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 Equation (6.59) by inclusion of a factor, termed the enhancement factor, E . The inclusion of this enhancement factor results in modifying Equation (6.59) which becomes:

$$\dot{m}_d = E \left\{ \beta \left[\frac{1}{2} \left(\frac{\beta}{k_r} \right) + (C_b - C^*) - \sqrt{\frac{1}{4} \left(\frac{\beta}{k_r} \right)^2 + \frac{\beta}{k_r} (C_b - C^*)} \right] \right\} \quad (6.70)$$

E is a multiplier that accounts 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. Therefore,

$$E = 1 + 80 NBF \quad (6.71)$$

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 Equation (6.70) 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 Equations (6.70) and (6.24).

6.2.5 Effect of Heat Flux on Deposition Rate

Reitzer (1964) presented the following mathematical relationship for crystal deposition under boiling conditions;

$$\dot{m}_d = KA(C_b - C^*)^n \quad (6.72)$$

It should be noted that Equation (6.72) is based on the assumption that the mass diffusion and the reaction can be lumped together. Referring to solubility-temperature curves

discussed in Chapter 3, it could be assumed that the equilibrium concentrations are almost linearly related to their respective temperatures. Hence, by considering a solution which is saturated with respect to the principal scaling species at the bulk temperature and supersaturated at the heat transfer surface temperature and assuming a linear inverse solubility curve over the supersaturated ranges, this model can be written as;

$$\dot{m}_d = k_1(T_s - T_b)^n \quad (6.73)$$

Since

$$\dot{q} = \alpha(T_s - T_b) \quad (6.74)$$

it follows that,

$$\dot{m}_d = k_1 \left(\frac{\dot{q}}{\alpha} \right)^n = \left(\frac{k_1}{\alpha^n} \right) \dot{q}^n = k_2 \dot{q}^n \quad (6.75)$$

The above equation confirms that the rate of deposition is highly dependent on the heat flux and that it should be more pronounced at higher heat flux.

One important concept which must be considered is the variation of heat flux during the course of a fouling experiment. In studying the fouling process on heater rods, it is usual to fix the power to the header rod, which means constant heat flow rate. When deposition occurs on the heat transfer surfaces, the heat transfer area is increased. As a result, the heat flux based on the new area is decreased. Since the surface temperature is proportional to the heat flux, the surface temperature is also decreased. Therefore, at the early stages of the fouling process, the rate of deposition is relatively high. In the later stages of the fouling process, because of a significant drop in the heat flux due to additional heat transfer area, the surface temperature is decreased.

The same analysis can be done for deposition during sub-cooled flow boiling conditions. During an experiment, when the heat flux is decreased as a result of additional heat transfer area, surface temperature and nucleate boiling fraction (*NBF*) are also decreased. In either case, the fouling resistances may change to a falling rate curve. The falling rate is

a special case of the asymptotic model where the fouling resistance, R_f , tends to an asymptotic value as time approaches infinity. Asymptotic fouling is said to occur when either the removal rate equals the deposition rate or auto-retardation mechanisms are present.

Therefore, it is important to take into account the time-dependent variation of the heat flux, as a result of the variation of heat transfer area. It should be noted that the effect of variation of heat flux is more pronounced for high heat fluxes, i.e. 450000 W/m^2 .

In the present investigation, quasi-steady state conditions were assumed in which the rate of foulant deposition can be determined for subsequent small time intervals. In other words, the quasi-steady state assumption allows $\dot{m}_d$ to be constant during a time interval, Δt . The calculations continue with the next cycle at time $(t + \Delta t)$, using the new values of the heat transfer area, heat flux, surface temperature, sub-cooled flow boiling heat transfer coefficient, nucleate boiling heat transfer coefficient, nucleate boiling fraction, fluid velocity, hydraulic diameter and deposition rate. The new value of heat flux at time $(t + \Delta t)$ can be obtained by the following equation:

$$q_{t+\Delta t} = \frac{q_t A_t}{A_{t+\Delta t}} \quad (6.76)$$

where

q_t = heat flux at time t ,

$q_{t+\Delta t}$ = heat flux at time $t + \Delta t$,

A_t = heat transfer area at time t

$A_{t+\Delta t}$ = heat transfer area at time $t + \Delta t$

The variations of heat transfer area, heat flux, surface temperature, nucleate boiling heat transfer coefficient, sub-cooled flow boiling heat transfer coefficient, nucleate boiling fraction, fluid velocity, hydraulic diameter and deposition rate have been incorporated into the proposed model and the corresponding computer program to predict the crystallisation fouling of mixed salts. Typical calculated variations of the above parameters with time (during an experiment) are shown in Figures 6.5 to 6.13 respectively. These figures show

that the variations of parameters with time is considerable. It is clear that heat flux, surface temperature, nucleate boiling heat transfer coefficient, sub-cooled flow boiling heat transfer coefficient, nucleate boiling fraction, hydraulic diameter and deposition rate are decreased with increasing heat transfer area. On the other hand, fluid velocity is increased with increasing heat transfer area. The variations of these parameters results in a falling rate fouling curve with time, i.e. Figure 6.14, under constant power input conditions *which is known as constant heat flux conditions in the literature*. It is clear that the fouling curve will be linear under constant heat flux conditions, assuming negligible removal rate.

Moreover, typical variations of heat transfer area, heat flux and fouling resistance with time (during an experiment) for forced convection heat transfer (NBF=0) are shown in Figures 6.15 to 6.16 and 6.17 respectively. It is clear that the variation of heat transfer area and consequently heat flux is very small. Therefore, the fouling curve will be linear during forced convection heat transfer, assuming negligible removal rate.

Figure 6.5 Typical variation of the heat transfer area with time

Figure 6.6 Typical variation of the heat flux with time

Figure 6.7 Typical variation of the surface temperature with time

Figure 6.8 Typical variation of the nucleate boiling heat transfer coefficient with time

Figure 6.9 Typical variation of the flow boiling heat transfer coefficient with time

Figure 6.10 Typical variation of the nucleate boiling fraction with time

Figure 6.11 Typical variation of the fluid velocity with time

Figure 6.12 Typical variation of the hydraulic diameter with time

Figure 6.13 Typical variation of the deposition rate with time

Figure 6.14 Predictions of the fouling resistance based on the variation of heat flux

Figure 6.15 Typical variation of the heat transfer area with time

Figure 6.16 Typical variation of the heat flux with time

Figure 6.17 Predictions of the fouling resistance based on the variation of heat flux

It is concluded that the nucleate boiling fraction, NBF , and consequently enhancement factor, E , are major parameters in the fouling process and has a considerable influence on the type of fouling curves, see Figures 6.10, 6.14 and 6.17. Therefore, the mathematical model should be sensitive to the nucleate boiling fraction. The effect of this parameter on the fouling process will be more discussed in section 6.5.

In all applications where constant heat flow rate (e.g. power) is applied, the wall temperature rises due to the added thermal resistance. The higher temperature may cause dehydration and reorientation of the crystals close to the wall surface, forming dehydrated and very compact crystalline products that are difficult to remove. This was confirmed by obtaining the porosity of deposited samples in the National Iranian Oil Company Central Laboratory. It was observed that for thick deposited layers, the porosity varies from 2.5% to 8% from internal to external direction. Scanning Electron Microscopy photographs of internal and external surfaces are shown in Figures 6.18 and 6.19.

Figure 6.18 SEM photograph of internal deposit surface at $\dot{q}_i = 250 \text{ kW/m}^2$

Figure 6.19 SEM photograph of external deposit surface at $\dot{q}_o = 210 \text{ kW/m}^2$

6.3 ATTACHMENT

After the reactants have been transported to the surface, they will react and stick to the surface. Comparing the transport and attachment mechanisms of deposition for both crystallisation and particulate fouling, it can be seen that diffusion is the mechanism of transport for both processes. Of course, for crystallisation it is the diffusion of ions, while for particulate fouling it is the diffusion of colloidal particulate matter to the surface. The attachment stage is controlled by crystalline lattice energy at the interface for precipitation fouling (i.e. ionic and electrostatic forces) and by Van der Waals forces and electric double layer forces for particulate fouling.

However, for both crystallisation and particulate fouling, the last step is the attachment process. Due to the presence of strong ionic and electrostatic forces, which cause the adherent nature of the crystalline deposits, it was assumed that all ions reaching the surface are attached to the surface. Consequently, a sticking probability of one was assumed.

6.4 CALCULATION OF THE REMOVAL RATE

The net deposition rate is a combination of the opposing effects of deposition and removal, i.e. the net deposition rate is given by the difference between the deposition rate and the removal rate;

$$\dot{m}_d|_{net} = \dot{m}_d - \dot{m}_r \quad (6.77)$$

Epstein (1987) has summarized the previous studies and proposed two basic mechanisms of fouling film removal. Fouling deposits can be removed by the action of turbulent flow or by dissolution in the fluid. The turbulent flow can reach to the interface and remove loosely attached particles or part of the deposit, although this material may re-deposit further downstream. In other words, individual particles that are not strongly attached to the surface can be removed by the simple shear stress at the interface. This theory has been applied to particulate fouling; however, for crystallisation fouling, it is believed that the removal of the deposit by such a mechanism is negligible.

The other process of deposit removal from the fluid/wall interface is by dissolution and back-diffusion. In some cases, the reactants diffuse to the surface, and the reaction can proceed to form the insoluble foulant, but part of the reactants may diffuse back to the bulk of the fluid. Hence, the resulting rate of fouling will be less than that predicted by assuming no back-diffusion of reactant in the carrier fluid. Because of relatively high surface temperature and solution supersaturation, it is assumed that no reactant ion diffuses back to the bulk of the fluid after it reached at the solid-liquid interface.

A removal mechanism, which depends on the strength of the deposit material and on the removing action of the fluid shearing forces, has been proposed by Taborek et al. (1972). In this case, the removal occurs due to fluid shear forces, which are a function of flow velocity,

$$\dot{m}_r \propto \tau \quad (6.78)$$

and is also proportional to deposit thickness, x_f (Bohnet, 1985). Hence

$$\dot{m}_r \propto x_f \quad (6.79)$$

This term is also dependent on the strength of the deposited material; i.e. the bond resistance,

$$\dot{m}_r \propto \frac{l}{R_b} \quad (6.80)$$

Therefore, the following relationship can be used to approximate the removal rate:

$$\dot{m}_r = C_l \frac{\tau}{R_b} x_f \quad (6.81)$$

where C_l is a constant which may be determined experimentally. The fluid shear stress at the wall, τ , is given by;

$$\tau = \frac{f \rho v^2}{2} \quad (6.82)$$

The friction factor, f , appearing in Equation (6.82) can be evaluated using the Blasius equation (Qufer and Knudsen, 1993),

$$f = 0.078 \text{Re}^{-0.25} \quad (6.83)$$

The bond resistance, R_b , can be expressed as a function of a strength parameter which depends on the deposit structure, i.e. types of attractive force in the crystalline structures.

$$R_b \propto F_{at} \quad (6.84)$$

As will be discussed in the next chapter, a crystal structure is a symmetrical array of atoms, ions or molecules arranged in a repeating three dimensional pattern. Crystals can be classified into four types according to the kind of particles that make up the crystal and the forces that hold them together. Ionic crystals, molecular crystals, network crystals and metallic crystals are four types of crystalline solids. Calcium sulphate and calcium carbonate crystals are examples of ionic crystals.

An ionic crystal must accommodate ions of opposite charge and different size in the proper stoichiometric ratio and in such a way that electrostatic attractions outweigh electrostatic repulsion. In this type of crystals, positive and negative ions are held in the

crystal arrangement by ionic and electrostatic attraction. Because these forces are strong, ionic substances are hard, brittle and have high melting points. It will be shown in the next chapter that the crystal breaks into fragments if an attempt is made to deform an ionic crystal. For example, during the course of the deposition process at very high heat fluxes, bubble growth and departure generate forces which may cause parts of the scale to detach from the heat transfer surface.

Ionic bonds and electrostatic forces can describe the role of attractive forces (strength of the deposit material). Ionic bonding results when electrons are transferred from one type of atom to another. The atoms of one of the reacting elements lose electrons and become positively charged ions. The atoms of the other reactant gain electrons and become negatively charged ions. The attraction, which exists between positive and negative ions and that holds them together in a crystal structure, is called *ionic bonding*. For electrostatic forces, the electrons are shared, not transferred. For this reason, the ionic bond is much stronger than electrostatic forces.

The interaction force between two ions is directly proportional to the product of the charges between the two ions and inversely proportional to the distance between the centres of the two ions (Resnick et al., 1992):

$$F = \frac{k q_1 q_2}{d^2} \quad (6.85)$$

where k is equal to $8.988 \times 10^9 \text{ J.m/C}^2$, if q_1 and q_2 are expressed in Coulomb (C) and d is expressed in meters. If the charges have the same sign (both positive or both negative), they will repel each other and the interaction force will have a positive value. On the other hand, if the charges have unlike signs, they will attract each other and the interaction force will be a negative value. The most stable structure for a given compound, therefore, is one in which the largest possible number of cation-anion attractions exist and one in which the positive and negative ions are as close together as possible. It should be emphasised that the ionic bonding, which exists between two ions, is much stronger than the electrostatic forces.

The purpose of this section is to calculate the ionic and electrostatic forces in the lattice structure of calcium sulphate and calcium carbonate and the shear force exerted by the fluid at the wall. A comparison between these forces predicts that the removal process may be occurred or not.

a) Attraction Force Between Ca^{2+} and SO_4^{2-} Ions

According to Coulomb's law:

$$F = \frac{k q_1 q_2}{d^2} \quad (6.85)$$

where

$$k = 8.988 \times 10^9 \text{ J.m/C}^2$$

$$q_1 = 2 \times 1.6 \times 10^{-19} \text{ C}$$

$$q_2 = -2 \times 1.6 \times 10^{-19} \text{ C}$$

The ionic radius of the present ions is:

$$r_{\text{Ca}} = 197 \text{ pm}$$

$$r_{\text{S}} = 103 \text{ pm}$$

$$r_{\text{O}} = 74 \text{ pm}$$

For SO_4^{2-} , the ionic volume and average radius can be calculated by,

$$V_{\text{SO}_4^{2-}} = \frac{4}{3} \pi r^3 \quad (6.86)$$

$$V_{\text{SO}_4^{2-}} = \frac{4}{3} \pi [(103)^3 + 4(74)^3]$$

$$\text{hence } r_{\text{SO}_4^{2-}} = 139.5 \text{ pm}$$

$$\text{and } d = d_{\text{Ca-SO}_4} = 139.5 + 197 = 336.5 \text{ pm}$$

Therefore, the attraction force between Ca^{2+} and SO_4^{2-} ions, i.e. two ions, is equal to;

$$F = -9 \times 10^9 \times \frac{(2 \times 1.6 \times 10^{-19})^2}{(336.5 \times 10^{-12})^2} = -8.14 \times 10^{-9} \text{ N}$$

b) Rod Heater and Ions Surface Area

For the investigated rod heater,

$$A = \pi d L = \pi (1.1/100) (0.1) = 3.456 \times 10^{-3} \text{ m}^2$$

For Ca^{2+} ion;

$$A = \pi r^2 = \pi (197 \times 10^{-12})^2 = 1.219 \times 10^{-19} \text{ m}^2$$

The number of ions, i.e. Ca^{2+} , which may be deposited on the rod heater surface =
 $3.456 \times 10^{-3} / 1.219 \times 10^{-19} = 2.84 \times 10^{16}$

Each ion may form four ionic bonds. To consider repulsion forces, only one ionic bond is assumed. Therefore, for one ionic bond per atom,

$$F_{\text{total}} = -2.84 \times 10^{16} \times 8.14 \times 10^{-9} = -23.1 \times 10^7 \text{ N}$$

Therefore, the total force that holds all ions on the surface together, is equal to 23.1×10^7 N.

c) Fluid Shear Force

$$\tau_w = f \frac{\rho v^2}{2} \quad (6.87)$$

If $v = 0.6 \text{ m/s}$, then $f = 2.5 \times 10^{-2}$,

$$\tau_w = 2.5 \times 10^{-2} \times \frac{1000 \times 0.6^2}{2} = 4.5 \frac{\text{N}}{\text{m}^2}$$

and

$$F_{\text{fluid}} = \tau_w A \quad (6.88)$$

$$F_{\text{fluid}} = 4.5 \times 3.456 \times 10^{-3} = 1.5 \times 10^{-2} \text{ N}$$

This force acts on the surface, by the fluid. A comparison between these forces indicates that the removal process can not take place.

d) Lattice Energy

The energy required to separate the ions of an ionic solid to an infinite distance is called the lattice energy of the solid. The lattice energy of an ionic solid is a measure of the force of attraction between the ions in the solid. The higher the lattice energy, the stronger the ionic bonds, and, in general the harder and higher the melting point of the solid.

Born-Haber cycles are usually used to calculate lattice energies, which are difficult to determine experimentally. The lattice energy depends on the charges and sizes of the ions involved. Increasing charge while size is kept constant increases the lattice energy. Increasing the size of the cations while charges are kept constant lowers the lattice energy. The same statement is true about the anions. Increasing the size of the anions also results in a decrease in lattice energy. Compounds, of 2+ and 2- charges have very high lattice energy and are very stable.

For CaSO_4 and CaCO_3 :

Lattice energy = 3000 KJ/mol = 3000000 J/mol

Assuming deposit thickness = 0.0005 m ($r_d = 0.005835$ m, $r_i = 0.005335$ m)

Scale Volume = $\pi [0.005835^2 - 0.005335^2] 0.1 = 1.755 \times 10^{-6} \text{ m}^3$

Mass of Scale = $\rho V = 2000 \times 1.755 \times 10^{-6} = 3.51 \times 10^{-3} \text{ kg} = 3.51 \text{ g}$

Lattice Energy for 3.51 g = $3.51 \times 3000000 / 136 = 77426 \text{ J}$

e) Kinetic Energy of the Fluid

$$K.E = \frac{1}{2} m v^2 = \frac{1}{2} (\rho V) v^2 = \frac{\rho v^2}{2} V \quad (6.89)$$

$$\tau_w = f \frac{\rho v^2}{2} \quad (6.87)$$

thus

$$\frac{\rho v^2}{2} = \frac{\tau_w}{f} \quad (6.90)$$

Combining Equations (6.89) and (6.90) results in:

$$K.E = \frac{\tau_w}{f} V \quad (6.91)$$

$$K.E = \frac{4.5}{2.5 \times 10^{-2}} \pi (0.0127^2 - 0.005835^2) 0.1$$

$$K.E = 7.195 \times 10^{-3} \text{ J}$$

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.

6.5 VALIDATION OF THE PROPOSED MODEL

In order to test the developed model, the fouling resistances predicted by the proposed model are compared with the experimental data during fouling runs of electrolyte solutions containing calcium, sulphate and bicarbonate ions. The fouling resistances were determined from Equations (6.24) and (6.70), by assuming the removal rate to be zero whereas the reaction rate constant, k_r , and the mass transfer coefficient of the reactant, β , are expressed by Equations (6.43) and (6.41), respectively.

To compare typical predictions of the proposed model with the experimental data, the predictions are compared with the results of two representative experiments, when CaCO_3 and CaSO_4 form and deposit on the heat transfer surface simultaneously, see Figures 6.20 and 6.21.

Figure 6.20 Comparison of measured and predicted fouling resistances

Figure 6.21 Comparison of measured and predicted fouling resistances

6.5.1 Effects of Operating Parameters

The main objective of mathematical modelling is to evaluate the fouling resistance and to investigate the effect of operational parameters on this process. It is possible to analyse the relative effects of these parameters on the rate of fouling by the suggested fouling model, and to compare the predicted values with the experimental data. In this section of the present investigation, several series of experiments were selected to consider the suggested model for characterising the effects of operational parameters. The essential parameters for interpretation of the fouling data are chemical composition and operating conditions for a given system.

Therefore, the major parameters analysed are:

- Fluid velocity,
- Surface temperature,
- Concentration of dissolved salts,
- Bulk temperature

6.5.1.1 Fluid Velocity

The fluid velocity is a key parameter for determining the fouling resistance and for optimising the fouling process in industrial installations by adjusting the operating conditions. The effects of fluid dynamics and associated heat and mass transfer processes on crystallisation fouling can be analysed by keeping the surface temperature, bulk temperature and bulk concentration constant and varying the fluid velocity.

The effects of fluid velocity on the fouling process have been predicted in Figure 6.22 for constant surface and bulk temperatures, during forced convective heat transfer. For all velocities, the fouling curves show an increase in fouling resistance with time. It is obvious that the effect of heat flux reduction is not considerable, because of the low deposition rate and consequently small fouling layer thickness during forced convective heat transfer.

Figure 6.22 Predicted fouling resistances at different velocities

Figure 6.23 Fouling rate as a function of Reynolds number

To identify the controlling mechanism, the fouling rates for constant bulk and surface temperature during convective heat transfer are plotted as a function of velocity, in Figure 6.23. The proposed model predicts that the process is mainly controlled by surface reaction above 80 cm/s; however, the effects of diffusion cannot be neglected for velocities less than 80 cm/s. This is in good agreement with the experimental results discussed in Chapter 5.

The fouling resistances predicted by the proposed model are compared with the experimental data during sub-cooled flow boiling in Figure 6.24, at three different velocities. Similar to convective heat transfer, we may expect that, as the velocity is increased, the fouling resistance is also increased. The experimental data and the predictions of the model show, however, that the opposite is true; i.e. as the velocity is increased, the fouling resistance is decreased at constant initial surface and bulk temperature. During sub-cooled flow boiling conditions, another parameter than the surface temperature, i.e. the nucleate boiling fraction, is also affecting the deposition process.

Figure 6.24 Predicted and measured fouling resistances at different velocities during sub-cooled flow boiling conditions

By increasing the velocity at constant surface temperature, the nucleate boiling fraction and hence the enhancement factor are decreased. The effect of these parameters is very strong and causes a reduction in the fouling resistance. *NBF* and *E* values at different velocities and heat fluxes are given in Table 6.3.

It should be noted that, it is not possible to fix the surface temperature and the nucleate boiling fraction simultaneously. However, Figure 6.24 clearly shows that the predictions of the proposed model are in good agreement with the experimental data.

Table 6.3 NBF and E values at different velocities

$\begin{matrix} \dot{q} \text{ (kW/m}^2\text{)} \\ V \text{ (cm/s)} \end{matrix}$	250	295	375
50	NBF=0.292 E=25.15	NBF=0.3741 E=31.66	NBF=0.481 E=40.02
80	NBF=0.0821 E=8.15	NBF=0.161 E=14.68	NBF=0.285 E=24.58
120	NBF=0.0016 E=1.16	NBF=0.0189 E=2.74	NBF=0.099 E=9.53

In this situation, the fouling resistance shows a falling rate behaviour due to the reduction in heat flux, nucleate boiling fraction and surface temperature.

6.5.1.2 Surface Temperature

The initial surface temperature is directly related to the heat flux for a given fluid velocity and bulk temperature. Therefore, the effect of surface temperature was determined by varying the heat flux while the bulk temperature and the flow velocity were kept constant. The predicted results show the fouling resistance as a function of surface temperature, without having the effect masked by other parameters.

To consider the effect of surface temperature, the fouling model was used to predict the fouling resistance for three surface temperatures. Because of the effect of fluid velocity and bulk temperature, only one set of results at fluid velocity of 80 cm/s and bulk temperature of 80 °C is shown in Figure 6.25. It is clear that there are significant changes

in the fouling resistances as the surface temperature is increased from 112 °C to 114 °C. In development of the model, it was assumed that the chemical reaction takes place at the surface; therefore, the surface temperature has a significant effect on the rate of fouling, as can be seen in Figure 6.25. Moreover, increasing the heat flux to reach the desired surface temperature also leads to a significant improvement in the Enhancement factor. This parameter further increases the fouling resistance.

The predicted fouling resistances are also compared with experimental data in Figure 6.25. While the prediction was higher than the experimental data for all surface temperatures, the fouling trend was predicted with reasonable accuracy and the results are encouraging.

Figure 6.25 Predicted and measured fouling resistances at different surface temperatures

The predicted fouling rate and nucleation boiling fraction (at $t=0$) for constant bulk temperature, fluid velocity and solution concentration are given in Table 6.4 and plotted as a function of surface temperature in Figure 6.26. It is clear that the rate of crystallisation

fouling and nucleate boiling fraction increase with an increase in surface temperature, but this increase is not linearly dependent on the surface temperature. Therefore, the fouling rate strongly depends on the surface temperature and nucleate boiling fraction.

Table 6.4 Fouling rate and NBF values for different heat fluxes and surface temperatures
($V=80$ cm/s, $T_b=80$ °C, $[CaSO_4]=1.8$ g/l, $[T.A.] = 0.2$ g/l)

$\dot{q}$ (kW/m ²)	T_s (°C)	$10^8 \times dR_f/dt$ (m ² K/W.min)	NBF
100	94	0.072	0.0
150	100	0.138	0.0
200	107	0.544	0.0125
250	112	9	0.0821
300	114	32.67	0.1699
350	116	61.66	0.2494
400	118	91.3	0.3169
450	119	120	0.3737

Figure 6.26 Initial fouling rate and NBF as a function of surface temperature

While the experiment with surface temperatures of 94 °C and 100 °C was basically in the convective heat transfer regime (NBF=0.0), significant increase in NBF values occurred for the higher surface temperatures of 107 °C, 114 °C and 119 °C (NBF=0.0125, NBF=0.17 and NBF=0.37). Therefore, the trend of scale formation during sub-cooled flow boiling is considerably different, due to the extra deposition created by bubble formation and micro-layer evaporation on the heat transfer surface.

6.5.1.3 Reactant Concentrations

The model predictions and experimental data shown in Figure 6.27 represent the effects of reactant concentration on the fouling resistance. Other parameters including fluid velocity, surface and bulk temperatures were kept at predetermined constant values. According to the proposed model, the effects of concentration of reactant ions are reflected by concentration driving force, diffusion and reaction processes. However, the results prove that the effect of reactant concentration is strong and that a good agreement exists between the experimental data and the model predictions.

Figure 6.27 Predicted and measured fouling resistances at different concentrations

6.5.1.4 Bulk Temperature

The bulk temperature is also a key parameter for evaluating the fouling resistance. In constant heat flux conditions, the surface temperature and accordingly the saturation concentration on the surface are highly dependent on the bulk temperature; i.e. the surface temperature increases with increasing bulk temperature and the saturation concentration of inverse soluble salts decreases with increasing surface temperature. Both of these parameters will increase the rate of deposition.

For constant surface temperature conditions, when the bulk temperature is increased, it is essential to reduce the heat flux to reach the desired constant surface temperature. This leads to a significant improvement in the nucleate boiling fraction and consequently the enhancement factor. The predicted nucleate boiling fractions and enhancement factors for constant surface temperature, fluid velocity and solution concentration are given in Table 6.5. It is clear that the nucleate boiling fraction and enhancement factor are increased with increasing bulk temperature. It should be noted that fully developed sub-cooled flow boiling does not exist for this situation.

Table 6.5 NBF and E values for different bulk temperatures

($V=60$ cm/s, $T_s=111$ °C, $[CaSO_4]=2.0$ g/l, $[T.A.]=0.2$ g/l)

T_b (°C)	$\dot{q}$ (kW/m ²)	NBF	E
70	250	0.0732	6.856
80	198	0.0902	8.216
90	142	0.1219	10.752

The measured effects of bulk temperature on the fouling resistance are shown in Figure 6.28. This figure also shows the predicted fouling resistances according to the proposed model. The initial surface temperature and the fluid velocity were maintained constant for both bulk temperatures. Therefore, the observed rate of fouling shows the effects of the

bulk temperature on the deposition process. This figure shows a significant increase in the fouling resistance for a fluid temperature change from about 70 °C to 90 °C. The predicted results and the experimental data clearly show that the bulk temperature must be considered along with other parameters in analysing the effects of operating variables on the rate of fouling.

Figure 6.28 Predicted and measured fouling resistances at different bulk temperatures

6.5.2 Concluding Remarks

The suitability of the suggested model for prediction of calcium sulphate, calcium carbonate, and calcium sulphate/calcium carbonate mixture fouling resistances during sub-cooled flow boiling is illustrated in Figure 6.29 where the experimental data (present investigation data and Najibi et al. data) obtained under various operational conditions are compared with those predicted by the proposed model. Visual analysis of the data

shows that the fouling resistances predicted by the proposed model are comparable with the measured values. Considering the uncertainties associated with heat transfer fouling experiments, deviations ranging from 6% to 25% are considered acceptable. It can be concluded that this model can be applied for mixed salt crystallisation fouling during convective heat transfer and sub-cooled flow boiling conditions.

Figure 6.29 Predicted versus measured fouling resistances at different conditions

6.6 COMPARISON WITH NAJIBI et al. MODEL

Several investigators have studied the fouling mechanisms in an effort to develop a predictive model. Most of the previously discussed models (in Chapter 2) have focused on crystallisation fouling under forced convective heat transfer. From the industrial point of view, pool boiling and sub-cooled flow boiling are important heat transfer modes, but little research work on fouling during these mechanisms can be found in the literature. Najibi et al. (1997) performed many experiments on calcium sulphate and on calcium carbonate scale deposition during convective heat transfer and sub-cooled flow boiling in a

vertical annulus. For the investigated range of flow velocity, an almost linear increase in fouling resistance with time has been observed, except during the initial period of the experiments.

Based on experimental results, Najibi et al. developed a mechanistic model for prediction of crystallisation fouling rates of calcium sulphate and calcium carbonate during sub-cooled flow boiling. This model was developed based on the initial deposition rate, and the removal rate was ignored. In this model, the heat transfer surface was divided into two separate zones, namely the area affected by vapour bubbles and the remaining area where forced convective heat transfer occurs. Therefore, the overall fouling rate was presented by the following equation:

$$\frac{dR_f}{dt}(\rho_f \lambda_f) = NBF \cdot \dot{m}_{nb} + (1 - NBF) \cdot \dot{m}_{fc} \quad (6.92)$$

where NBF is the nucleate boiling fraction, i.e. the fraction of the total heat transfer affected by bubble formation and detachment. The Chen (1966) model was used to calculate the fraction of heat transferred by nucleate boiling, NBF :

$$NBF = \frac{\alpha_{nb} S}{\alpha_{fb}} \quad (6.93)$$

Because of the high level of turbulence created by the departure of the vapour bubbles from the nucleation sites, it was assumed that crystallisation fouling in the boiling zones is reaction rate controlled and second order, and given by:

$$\dot{m}_{nb} = K_I (\gamma C_b - C_s^*)^2 \quad (6.94)$$

where

$$K_I = K_{I,0} \exp\left(\frac{-E}{RT_s}\right) \quad (6.95)$$

and γ is the concentration effect in the micro-layer beneath the vapour bubble. A value of 1.5 was obtained for this parameter.

According to this model, the fouling rate during forced convective heat transfer was assumed a second order reaction and represented by the following equation:

$$\dot{m}_{fc} = \beta \left[\frac{I}{2} \left(\frac{\beta}{K_2} \right) + (C_b - C_s^*) - \sqrt{\frac{I}{4} \left(\frac{\beta}{K_2} \right)^2 + \left(\frac{\beta}{K_2} \right) (C_b - C_s^*)} \right] \quad (6.96)$$

where

$$K_2 = K_{2,0} \exp \left(\frac{-E}{RT_s} \right) \quad (6.97)$$

The parameters and physical properties of calcium sulphate and calcium carbonate, which were used in this model, are given in Table 6.6.

Table 6.6 Parameters and physical properties used in the Najibi et al. (1997) model

Parameters Salts	$K_{1,0}$ ($\text{m}^4/\text{kg.s}$)	$K_{2,0}$ ($\text{m}^4/\text{kg.s}$)	E (kJ/kmol)	ρ_d (kg/m^3)	λ_d (W/m.K)
Calcium sulphate	2.9×10^{10}	5.7×10^{11}	112517	2165	2.23
Calcium carbonate	9.8×10^{11}	9.8×10^{11}	122150	2705	1.942

Comparing the measured fouling resistances for calcium sulphate with the predictions of the Najibi et al. model shows that there are considerable differences between experimental data and the prediction of this model (Figure 6.30). Although this is one of the most detailed models available in the literature, there are two concepts that should be considered. This model predicts a linear relationship between fouling resistance and time and does not include the variation of heat flux due to variation of heater rod diameter. As it was previously explained, when the deposit is formed on the surface of a heater rod, its diameter is increased. Consequently, the heat flux based on the new area is decreased.

Therefore, nucleate boiling fraction and surface temperature are reduced. Both these parameters will cause a reduction in fouling resistance, consequently the fouling process follows a falling rate behaviour. To modify the Najibi et al. model, it is essential to consider quasi-steady state conditions and variation of heat flux according to Equation (6.76).

Moreover, in this model, it has been assumed that the evaporation at the base of the bubble increases the local concentration of foulant in the liquid beneath the bubbles significantly. γ is the concentration effect in the micro-layer which was assumed equal to 1.5. Bubble formation is highly dependent on heat flux. At lower heat fluxes, bubbles may form on the heat transfer surface and detach from the surface separately. As the heat flux is increased, the number of bubbles is also increased. Therefore, interaction of the bubbles will be occurred. Consequently, the local concentration of foulant in the liquid beneath the bubbles is significantly increased. In other words, the concentration effect will be a function of heat flux, i.e. NBF . In this investigation, the effect of heat flux on concentration effect was obtained from non-linear regression analysis of the present experimental data. The result of this analysis can be written as:

$$\gamma = 1 + 3.875 \times NBF \quad (6.98)$$

It should be noted that Najibi has performed fouling experiments at lower heat fluxes. A value of 1.5 is a good approximation at these heat fluxes.

Typical measured fouling resistances for calcium sulphate fouling runs are compared with the predictions of the Najibi et al. model, the modified Najibi et al. model and the proposed model in Figure 6.30. The figure illustrates that the proposed model and the modified Najibi et al. model predict falling rate curves, while the Najibi et al. model predicts linear fouling behaviour. The results show that there are considerable differences between experimental data and the prediction of the Najibi et al. model. These results suggest that the proposed model and the modified Najibi et al. model are able to predict the effect of variation of heat flux on NBF as well as its effect on surface temperature.

It should be mentioned that the heat flux is reduced from an initial value of 200000 W/m^2 to a final value of 196000 W/m^2 for a typical experiment shown in Figure 6.30. The nucleate boiling fraction, NBF , is changed from 0.0126 (at the beginning of the experiment) to 0.009 (at the end of the experiment). The surface temperature is also changed from 380.3 K (at the beginning of the experiment) to 379.7 K (at the end of the experiment). It is concluded that the nucleate boiling fraction, i.e. NBF value, is the major parameter in the fouling process and its effect on the type of fouling curves is strong.

The proposed fouling model shows a better agreement than the Najibi et al. (1997) model at later stages but the predictions of the proposed model and the Najibi et al. model were comparable at the early stages of fouling. This could be attributed to the fact that the Najibi et al. model does not assume the variation of heat flux due to formation of fouling layer on rod heaters and that the effect of boiling in the micro-layer is assumed to be independent of heat flux.

Figure 6.30 Comparison of measured fouling resistances with three prediction models

6.7 COMPUTER PROGRAMMING

The fouling model was coded into a computer program to calculate the fouling resistance. The main program requires the following input data (Table 6.7) and calls thirteen different subroutines (STRENGTH, PHYSL, PHYSV, BOIL, FLAMI, FTURB, XDOT, TURB, LAMI, FS, BOX, INPUTSTR, and CACO3) for calculating of the fouling resistances.

It is important to note that, when the solution is supersaturated with respect to different ions, there is a competition between ions to react and deposit. In the constructed computer program, the path and sequence of precipitation is chosen based on the supersaturation ratios from the highest value to the lowest one. The limiting reactant is also found by comparing the key components. Moreover, the variation of heat flux, surface temperature, nucleate boiling fraction and enhancement factor are compiled in the proposed computer program. The resulting calculations give the curve of the fouling resistance as a function of time.

The list of input parameters required for running the computer program is shown in Table 6.7. The listing of the computer program is given in Appendix D.

TABLE 6.7 Input parameters required in computer code

Parameter	Computer Code Name	Typical Value
Velocity	U	80 cm/s
Bulk Temperature	T _b	80 °C
Heat Flux	$\dot{q}$	200 kW/m ²
Pressure	P	105 kPa
CaSO ₄ Concentration	[CaSO ₄]	2 g/l
pH	pH	7
Total Alkalinity	T.A.	0.2 g/l
Time Step	Δt	20 min.
Duration	t	2000 min.
Output File Name	B\$	RUN1

Chapter 7

CHARACTERISATION OF DEPOSITS

Solid deposits can be classified into crystalline or amorphous states. The crystalline state differs from the amorphous state by the regular arrangement of the constituting molecules, atoms or ions into some fixed locations known as lattice, which is the characteristic of the substance. Therefore, a crystal structure is a symmetrical array of atoms, ions or molecules arranged in a repeating three dimensional pattern. Crystals can exist in seven different lattice structures, namely Hexagonal, Tetragonal, Orthorhombic, Monoclinic, Triclinic, Trigonal and Regular (Bott, 1995 and Mullin, 1972). They are the most highly organised types of non-living matter.

Crystals are characterised by the repetition of their constituent building blocks in a three dimensional array, quite unlike liquids in which the molecules are randomly placed. The structural configuration of these crystals is largely determined by the size of their constituent atoms. The geometric configuration of these blocks, referred to as crystal lattices, is unique to the many chemical species we encounter in water treatment and individually characteristic of them.

7.1 TYPES OF CRYSTALLINE SOLIDS

Crystals can be classified into four types according to the kind of particles that make up the crystals and the forces that hold them together. Ionic crystals, molecular crystals, network crystals and metallic crystals are four types of crystalline solids.

1. Ionic Crystals. An ionic crystal must accommodate ions of opposite charge and different size in the proper stoichiometric ratio and in such a way that ionic and electrostatic attractions outweigh electrostatic repulsion. In ionic crystals, positive and negative ions are held in the crystal arrangement by ionic and electrostatic attractions. Because these forces are strong, ionic substances are hard, brittle and have a high melting points. Figure 7.1 shows what happens if an attempt is made to deform an ionic crystal

(Mortimer, 1985). Because of the movement of one plane of ions over another, ions with the same charge are brought next to each other. The crystal breaks into fragments. Ionic compounds are good conductors of electricity when molten or in solution but not in the crystalline state, where the ions are not free to move.

Figure 7.1 Effect of deformation on an ionic crystal (Mortimer, 1985)

Bott (1995) has commented that crystals are generally not perfect i.e. they contain various imperfections. A common defect is a missing unit from a lattice that leaves a pore in the structure. The pore space between the basic crystal units may be occupied by an impurity or by water. In petroleum engineering, the ratio of the pore volume to the bulk volume is called porosity. It is believed that the deposit strength is highly dependent on porosity. When the deposition rate is high, the crystal locations are more irregular, which causes more pores (e.g. higher porosity). In the other case, it is possible that ions or molecules other than the ions making the main crystal structure are incorporated into the structure. These modifications to the lattice structure probably lead to distortions in crystalline matter.

The presence of pore space in the lattice structure causes also dislocations of forming crystals which leads to a fault in the crystalline structure. When an external force is exerted to the crystal structure, it may be broken at the fault region. Moreover, the presence of pore spaces in the crystal structure prevents the individual crystals from

coming together to form a hard lattice structure. It can be concluded that the presence of pore spaces (e.g. porosity) or impurities in the pore structure causes the weakness of crystalline structures.

The interaction force between two ions is directly proportional to the product of the charges between the two ions (q_1 and q_2) and inversely proportional to the distance between the centres of the two ions, d (Resnick et al., 1992):

$$F = \frac{k q_1 q_2}{d^2} \quad (7.1)$$

where k is equal to $8.988 \times 10^9 \text{ J.m/C}^2$, if q_1 and q_2 are expressed in coulomb (C) and d is expressed in meters. If the charges have the same sign (both positive or both negative), they will repel each other and the interaction force will have a positive value. On the other hand, if the charges have unlike signs, they will attract each other and the interaction force will be negative. The most stable structure for a given compound, therefore, is one in which the largest possible number of cation-anion attractions exist and one in which the positive and negative ions are as close together as possible. It should be emphasised that the ionic bonding, which exists between two ions, is much stronger than the electrostatic forces.

2. Molecular Crystals. Molecules occupy positions in crystals of covalent compounds. The intermolecular forces that hold the molecules in the crystal structure are not nearly as strong as the electrostatic forces that hold ionic crystals together. Molecular crystals, therefore, are soft and have low melting points, usually below 300 °C. London forces hold non-polar molecules in the structure. In crystals of polar molecules, dipole-dipole forces as well as London forces occur. Therefore polar compounds generally melt at slightly higher temperatures than non-polar compounds of comparable molecular size and shape.

3. Network Crystals. In these crystals, atoms and molecules are joined by a network of covalent bonds. The entire crystal can be looked at as one giant molecule. In diamond, an example of this type of crystal, carbon atoms are bonded by covalent bonds into a three-dimensional structure.

4. Metallic Crystals. The outer electrons of metal atoms are loosely held and move freely throughout a metallic crystal. The remainder of the metal atoms, positive ions occupy fixed positions in the crystal. The negative cloud of the freely moving electrons, sometimes called an electron gas or a sea of electrons, binds the crystal together. This binding force is called a metallic bond.

The properties of the four types of crystals are summarised in Table 7.1.

Table 7.1 Types and properties of crystalline solids

Crystal	Particles	Attractive Forces	Properties	Examples
Ionic	Positive and negative ions	Ionic bonding and electrostatic attractions	High melting point, hard, brittle, good electrical conductor in molten state	NaCl, BaO, KNO ₃ , CaCO ₃ , CaSO ₄
Molecular	Polar molecules	London and dipole-dipole	Low melting point soft, non-conductor	H ₂ O, NH ₃ , SO ₂
	Non-polar molecules	London	or extremely poor conductor of electricity in liquid state	H ₂ , Cl ₂ , CH ₄
Network	Atoms	Covalent bonds	Very high melting point, very hard, non-conductor of electricity	C(diamond), SiC, AlN, SiO ₂
Metallic	Positive ions and mobile electrons	Metallic bonds	Fairly high melting point, hard or soft malleable and ductile, good electrical conductor	Ag, Cu, Na, Fe, K

7.2 IDENTIFICATION OF CRYSTALLINE SOLIDS

Identification of the above crystals by their structural configurations or physical properties can be accomplished by the following techniques:

1. Scanning Electron Microscopy (SEM)
2. Differential Thermal Analysis (DTA)
3. Polarised Light Microscopy (PLM)
4. X-Ray Diffraction (XRD)
5. Laser Light Scattering (LLS)

In the present investigation, calcium sulphate, calcium carbonate and mixed calcium sulphate/calcium carbonate solutions were used. After each run, deposits on the heat transfer surfaces were collected for analysis. According to the solubility curves shown in Figures 3.2 and 3.6, calcium sulphate and calcium carbonate deposits can occur in various ionic crystal structures. It was observed that nature and shape of deposits were a strong function of heat flux, concentration, ionic strength and other operating parameters, i. e. deposits formed under various conditions had different mechanical strength.

It was observed that CaSO_4 deposits were relatively soft and did not strongly adhere to the heat transfer surface, while CaCO_3 and mixed $\text{CaCO}_3/\text{CaSO}_4$ deposits were much harder and more adherent. Therefore, CaSO_4 deposits were poorly bonded and could easily be removed from the heat transfer surface, while it was very difficult to remove CaCO_3 and mixed $\text{CaCO}_3/\text{CaSO}_4$ deposits from the surface. During the experiments, it was observed that scales precipitated from mixed salt solutions could be more easily removed than those of pure calcium carbonate. Therefore, the occurrence of CaSO_4 crystals tends to weaken the crystalline structure of calcium carbonate and makes it more prone to removal than pure CaCO_3 .

To characterise the deposits of this study, samples were analysed using a high resolution Scanning Electron Microscope (SEM) and X-Ray Diffraction techniques. Examples of pure calcium sulphate, pure calcium carbonate and mixed calcium sulphate/calcium carbonate SEM photographs at two different conditions are shown in Figures 7.2 through 7.7. Moreover, X-ray analyses of CaSO_4 , CaCO_3 and a $\text{CaSO}_4/\text{CaCO}_3$ mixture are shown in

Figure 7.8, 7.9 and 7.10 respectively. Much of what is known about the structure of crystals has been learned from X-ray diffraction experiments.

Scanning Electron Microscopy and X-ray analysis indicated that deposits from mixed calcium sulphate/calcium carbonate solutions found in this investigation consisted of both calcium sulphate and calcium carbonate crystals, which means that both salts have precipitated simultaneously (Figures 7.6, 7.7 and 7.10). X-ray diffraction (XRD) analysis of the deposit of CaSO_4 fouling indicated the crystals are predominantly hemihydrate for surface temperatures higher than 105 °C, which is the gypsum-hemihydrate transition temperature. For CaCO_3 solutions, XRD analysis showed that most of the deposited crystals are aragonite.

SEM photographs also indicated that the deposit structure was not uniform and consists of different shapes and size fractions. Pure calcium sulphate deposits were rod-shaped crystals while mixed calcium sulphate/calcium carbonate deposits contain rod-shaped calcium sulphate crystals surrounded by compact calcium carbonate crystals. It is possible to recognise a few smaller crystals in among the larger crystals. The complexity of the crystalline structure is obvious.

Figure 7.2 Scanning Electron Microscope picture of CaSO_4 crystals

Figure 7.3 Scanning Electron Microscope picture of CaSO_4 crystals

Figure 7.4 Scanning Electron Microscope picture of CaCO_3 crystals

Figure 7.5 Scanning Electron Microscope picture of CaCO_3 crystals

Figure 7.6 Scanning Electron Microscope picture of $\text{CaSO}_4/\text{CaCO}_3$ crystals

Figure 7.7 Scanning Electron Microscope picture of $\text{CaSO}_4/\text{CaCO}_3$ crystals

Figure 7.8 X-ray analysis of CaSO_4 crystals

Figure 7.9 X-ray analysis of CaCO_3 crystals

Figure 7.10 X-ray analysis of $\text{CaSO}_4/\text{CaCO}_3$ crystals

7.2.1 Effect of Operating Parameters on Structure of Deposits

Operating conditions had a significant effect on the structure of deposits formed on the heat transfer surfaces. As shown in Figures 7.2 and 7.3, with increasing heat flux, the CaSO_4 crystals become smaller and their orientation changes from perpendicular to parallel to the bubble growth direction. In addition, the effect of boiling phenomena, i.e. nucleate boiling fraction, on the appearance of calcium sulphate crystals is shown in Figures 7.2 and 7.3. As the heat flux is increased, the nucleate boiling fraction is increased, subsequently the deposits appear to be fine-grained and rather compact. Similarly, for pure calcium carbonate and mixed salt solutions, heat flux had a significant effect on the strength of deposits. Deposits formed at high heat fluxes were harder, denser and more adherent than deposits formed at lower heat fluxes.

During some experiments, especially at higher concentrations and heat fluxes, CaSO_4 deposits broke off when the heater surface temperature exceeded 150 °C. The same results were obtained for a composition of 2.5 g/l of CaSO_4 and a total alkalinity of 0.15 g/l of the solution (i.e. presence of a high CaSO_4 concentration and low total alkalinity). This may be due to the presence of a large amount of calcium sulphate crystals in the forming deposit. It was probably caused by bubble formation underneath the deposit, shear forces induced by rising bubbles and thermal stresses between heat transfer surface and deposit. Re-formation of new scale resulted in a saw-tooth fouling curve which describes the breaking of the deposit layer after a certain time when a certain thickness of the fouling layer has been reached. The deposit fragments accumulated in the filters.

The saw-tooth fouling curve may also be the result of simultaneous crystallisation and particulate fouling, which weakens the lattice structure. It is well known that the presence of suspended particles increases the rate of crystallisation by providing additional nucleation sites (Bansal, 1993). When the concentration of the solution is 2 g/l or higher, reactions may occur in the bulk of the flowing liquid. The deposition on the heat transfer surface is then caused by simultaneous crystallisation and particulate fouling from the flowing solution even though a micro-filter has been installed in the test rig. For these conditions, the observed deposits were softer and more friable.

Figure 7.11 Scanning Electron Microscope picture of $\text{CaSO}_4/\text{CaCO}_3$ crystals

Figure 7.12 Scanning Electron Microscope picture of $\text{CaSO}_4/\text{CaCO}_3$ crystals

Furthermore, it was observed that with increasing bulk temperature and decreasing ionic strength, the deposit becomes more compact and more adherent. In these cases, it was more difficult to remove the deposit. With decreasing ionic strength, the deposit on the heat transfer surfaces was very dense and compact. Figures 7.11 and 7.12 show the SEM photographs of deposits for two different ionic strengths. For the higher ionic strength, it is possible to identify distinct crystals, while for the lower ionic strength, the crystal structure seems very compact.

7.2.2 Effect of Surface Material on Structure of Deposits

It was previously stated that during the fouling runs, a continuous crystal layer was formed on the untreated stainless steel heater surface, which had to be removed with emery paper. Contrary, the treated heaters showed an irregular and patchy thin deposit which could be cleaned with tissue paper. In some experiments, the amount of deposits on treated surfaces was negligible and it was not possible to collect any deposition samples.

As discussed in Chapter 5, the surface energy of the treated surfaces is lower than for the untreated surface. This decreases the number of activated nucleation sites, and hence results in irregular, patchy, less compact and lower fouling resistances. It was also observed that the distribution of calcium sulphate and calcium carbonate crystals on the DLC sputtered surface was different compared to the untreated surface, which leads to the assumption that the surface treatment also influences the kinetics of crystallisation, removal and hence the net deposition rate.

As shown in Figures 7.13 and 7.14, there is a clear difference in deposit structure under identical process conditions between the untreated and the DLC sputtered surfaces. For the treated surface, the deposition seems to be powder-like and less dense and it is not possible to identify individual crystals. As a result of the powder-like crystals, the deposit surface was very thin, porous and weak. This was in fact confirmed by the experimental results, where a very low and irregular fouling resistance for the whole experimental duration was observed. The untreated surface shows big and flat crystals, all aligned in the same direction.

Figure 7.13 Scanning Electron Microscope picture of crystals on untreated surface

Figure 7.14 Scanning Electron Microscope picture of crystals on treated surface

7.3 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.

After introducing this term by Mandelbrot, various attempts have been made to provide a mathematical definition of a fractal in a general context. Falconer (1997) pointed out that a set E in Euclidean space is a fractal if it has all or most of the following features:

1. E has a fine structure, that is irregular at arbitrarily small scales.
2. E is too irregular to be described by calculus or traditional geometrical language, either locally or globally.
3. Often E has some sort of self-similarity or self-affinity, perhaps in a statistical or approximate sense.
4. Usually the fractal *dimension* of E is strictly greater than its topological dimension.
5. In many cases of interest, E has a very simple, perhaps recursive, definition.
6. Often E has natural appearance.

This theory has been applied in many fields ranging from molecular physics to the large-scale structure of the universe, and provides new conceptual tools and insights. Fractal structures are often encountered in physical chemistry and transport phenomena involving solid materials i.e. catalysts, adsorbents, and porous media. Many materials such as aerogels and microporous adsorbents possess fractal properties (related to surface structure, to distribution of active reacting/adsorbing sites, or to pore-network topology) over a given range of length scales. Furthermore, cloud boundaries, mountain skylines, coastlines and many others natural objects have a form much better described in fractal terms than by the straight lines and smooth curves of classical geometry.

In engineering applications, fractal structures can be viewed as a limiting example of materials possessing complex geometry and topology. The study of transport and reaction phenomena on fractals permits to highlight and extrapolate physical laws of general

validity in engineering modelling and design. Furthermore, the development of a coherent and simple mathematical model of dynamic phenomena on the basis of fractal structures, capable of solving problems which can be addressed in closed form for Euclidean continua, is of great scientific importance. However, fractal phenomena in nature are often rather complicated to describe, and various assumptions and approximation may be required in setting up and analysing a mathematical model.

For example, a process of forming fractally distributed particles is fragmentation of larger, originally Euclidean-dimensioned bodies. While of obvious interest to geologists and engineers, fragmentation phenomena are also of significant relevance in the food processing and packaging industry. Another approach of generating fractal objects is of special concern to chemists, namely formation of fractal objects by aggregation of smaller, nearly identically sized particles, i.e. crystallisation.

7.3.1 Mass and Surface Fractals

There are two types of fractal objects, i.e. deterministic and random fractals. Deterministic fractals are generated iteratively in a deterministic way, while random fractals are generated using a stochastic process. 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. Laser Light Scattering experiments or photographic techniques give a value which describes the crystal behaviour.

Basically, it is necessary to distinguish between two different fractals (Jung, 1995). In systems without distinct surface, the fractal dimension, FD , relates mass, M , to radius of gyration, R , by

$$M(R) \propto R^{FD} \quad 1 < FD < 3 \quad (7.2)$$

Objects obeying Equation (7.2) are called mass or volume fractals and typically include polymers and percolation clusters. In contrast, objects that are more uniform, such that no scattering occurs from the bulk and only from the surface are called surface fractals. These objects obey Equation (7.3), where FD is the surface fractal dimension which relates the surface area, A , to size,

$$A(R) \propto R^{FD} \quad 2 < FD < 3 \quad (7.3)$$

In porous samples, where both the object and its surface can be thought of having fractal structure, it should be possible to distinguish between surface and mass fractals, depending on scattering parameters. However, as noted by Teixeira (1986), the crossover between the two regimes is not distinct if FD is between 2 and 3.

7.3.2 Fractal Dimension Measurements

A general measuring technique to obtain the fractal dimension is the box counting method. It is frequently used because it can be readily automated or even performed manually. Furthermore, its principle is clear and easily understood. The box counting or capacity measure is based on scaling principles. A cubic lattice with constant grid size ε for three dimensions or a square lattice with constant grid size ε in the case of two dimensions or in-plane projections is laid over the object of interest. The number of boxes, $N_B(\varepsilon)$, which cover any part of the object (the occupied or intersected boxes), are counted and each data couple $N_B(\varepsilon), \varepsilon$ is tabulated. This procedure is repeated with a set of successively smaller values of ε . $\log [N_B(\varepsilon)]$ is plotted versus $\log(\varepsilon)$, the slope of the resulting straight line will be the fractal dimension. The resulting $\log(N_B)$ vs. $\log(\varepsilon)$ can be illustrated as shown in Figure 7.15.

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 softwares 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 and strength of the deposits, i.e. their resistance against erosion by fluid shear forces. In the present investigation, 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 (Takayasu, 1990).

Figure 7.15 Log-Log plot of the number of occupied boxes versus box size

The results proofed 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}

($\text{m}^2 \cdot \text{K})/(\text{kW} \cdot \text{min})$), 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.

Fractal dimensions have been determined for deposits from about 30 experiments at different operating conditions with stainless steel and with modified heat transfer surfaces. For example, Figure 7.16 shows the deposit for a heat flux of 200 kW/m^2 whereas Figure 7.17 shows the deposit for a heat flux of 300 kW/m^2 . The corresponding fractal dimension were 2.72 and 2.55. 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 (Tables 7.2 and 7.3). 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.

Figure 7.16 Scanning Electron Microscope picture of mixed salt crystals

The measured fractal dimensions for treated and untreated surfaces show that this value is higher for treated surfaces than for untreated surface, at the same operating conditions. This agrees with the previous observations that the deposits which were rarely found on treated surfaces are more irregular and less compact.

Figure 7.17 Scanning Electron Microscope picture of mixed salt crystals

Tables 7.2 and 7.3 represent the measured values of fractal dimensions at different velocities, heat fluxes, bulk temperatures, ionic strengths, surface energy and deposit composition. Deposit composition was measured by ion chromatography and flame photometry techniques in the National Iranian Oil Company, NIOC, central laboratory.

From the measured fractal dimensions, it is clear that operating conditions and deposit composition have a significant effect on the surface texture of deposits, i.e. the fractal dimension is inversely proportional to heat flux, bulk temperature, fluid velocity, surface energy and proportional to ionic strength and $\text{CaSO}_4\text{-CaCO}_3$ ratio in crystalline structure.

Table 7.2 Measured fractal dimensions at different operating conditions

RUN-ID	V (cm/s)	$\dot{q}$ (kW/m ²)	T _b (°C)	I (mol/l)	FD
F-32	40	200	80	0.088	2.85
F-33	80	200	80	0.088	2.72
F-34	120	200	80	0.088	2.64
F-35	160	200	80	0.088	2.51
F-36	200	200	80	0.088	2.44
F-33	80	200	80	0.088	2.72
F-48	80	250	80	0.088	2.68
F-49	80	300	80	0.088	2.55
F-50	80	350	80	0.088	2.44
F-51	80	400	80	0.088	2.41
F-52	80	450	80	0.088	2.36
F-63	80	200	60	0.088	2.83
F-64	80	200	70	0.088	2.77
F-33	80	200	80	0.088	2.72
F-66	80	200	90	0.088	2.63
F-70	75	250	80	0.088	2.70
F-72	75	250	80	0.098	2.76
F-73	75	250	80	0.118	2.79
F-75	75	250	80	0.150	2.86
F-33 (Untreated)	80	200	80	0.088	2.72
T-12 (H, Implanted)	80	200	80	0.088	2.85
T-13 (DLC, Sputtered)	80	200	80	0.088	2.87
T-14 (Ni-P-PTFE)	80	200	80	0.088	2.90

Table 7.3 Measured fractal dimensions at different deposit composition

RUN-ID	T_b (°C)	Fluid Composition		Deposit Composition		FD
		[CaSO ₄] g/l	[T.A.] g/l	CaSO ₄ %	CaCO ₃ %	
F-21	80	2.2	0	100	0	2.98
F-25	80	2	0.2	92	8	2.85
F-26	80	2	0.25	82	18	2.72
F-28	80	1.9	0.25	65	35	2.64
F-31	80	0	0.25	0	100	2.56

The variations of fractal dimensions with the operating parameters, i.e. fluid velocity, heat flux, bulk temperature, ionic strength, surface energy and deposit composition are shown in Figures 7.18 to 7.23 respectively. These figures show that the effect of operating conditions on the surface texture, i.e. fractal dimension, is strong. It is clear that increasing calcium sulphate composition in the fouling layer and ionic strength and decreasing fluid velocity, heat flux and bulk temperature and surface energy were each found to increase the fractal dimension.

In Figures 7.19 and 7.20, it can be seen that the surface texture of the deposited material can be divided into two regions. At higher heat fluxes and bulk temperatures where the fouling rate is high, the crystals form and attach to the surface more regularly and more compact, although the higher fouling rate is attributed to a bridging mechanism during the crystallisation process, i.e. more open structure. It is believed that restructuring of crystals and compaction process occur at high heat fluxes and bulk temperatures. Reduction of the fractal dimension from 2.72 to 2.36 (as the heat flux is increased from 200 kW/m^2 to 450 kW/m^2), and 2.83 to 2.63 (as the bulk temperature is increased from 60 °C to 90 °C) suggests that the restructuring process is predominantly occurred when the heat flux or bulk temperature is increased. The effect is more noticeable at higher heat fluxes and bulk temperatures, where the boiling phenomenon is an important contributor to the deposition process. At lower heat fluxes and bulk temperatures, the deposition occurs slowly, more irregular and less compact. Therefore, the fractal dimension reasonably increases.

Figure 7.18 Fractal dimension as a function of fluid velocity

Figure 7.19 Fractal dimension as a function of heat flux

Figure 7.20 Fractal dimension as a function of bulk temperature

Figure 7.21 Fractal dimension as a function of ionic strength

Figure 7.22 Fractal dimension as a function of surface energy

Figure 7.23 Fractal dimension as a function of deposit composition

The effect of fluid velocity on surface fractal dimension follows the expected trend. The fractal dimensions of deposits formed in the presence of higher velocity were lower than the fractal dimensions of deposits obtained in the presence of lower velocity (Figure 7.18). It is believed that higher velocity results in erosion and removal of loose and fragile flocs and restructuring of crystals which is associated with more regular, more compact and lower surface roughness.

Figure 7.21 shows that increasing ionic strength of the solution increases the fractal dimension of the formed deposit layer. The increase of the fractal dimension suggests that the presence of impurities, i.e. ions such as K^+ or NO_3^- , causes heterogeneous crystallisation fouling. Heterogeneity produces rough, loose and irregular deposit layer (Figures 7.11 and 7.12). Hence, the fractal dimension considerably increases.

As shown in Figure 7.22, the surface texture of deposits prove that the fractal dimensions of fouling layers formed on surfaces that are coated with low surface energy molecules are higher than those obtained with higher surface energy molecules. It is believed that the lower fractal dimensions are due to regular deposition or restructuring within the forming crystals. At lower surface energies, regular deposition and restructuring does not occur, resulting in more irregular structures, with higher roughness and fractal dimensions. On the other hand, the aggregate structure formed on the untreated surface with higher surface energy is more regular and more compact than that formed on the treated surfaces. Therefore, the fractal dimension is lower for higher surface energies.

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.

Chapter 8

CONCLUSIONS AND FUTURE WORK

8.1 CONCLUSIONS

This investigation was concerned with the mechanisms of mixed salt crystallisation fouling on heat transfer surfaces. A substantial number of experiments were performed to investigate scale formation from solutions of calcium sulphate, calcium carbonate and calcium sulphate/calcium carbonate mixtures during forced convection and sub-cooled flow boiling in a vertical annulus. In addition, experiments were performed to study the effect of surface energy on fouling behaviour. From the theoretical and experimental studies of the present investigation, the following results are concluded:

- ❖ The experimental results showed that crystallisation fouling is dependent on operational parameters such as velocity, surface temperature, bulk temperature, solution concentration, heat flux, ionic strength, boiling phenomena and surface materials. It becomes stronger with increasing heat flux, surface temperature and boiling phenomena, i.e. enhancement factor.
- ❖ During convective heat transfer, it has been shown that the deposition rate is controlled by different mechanisms, depending on flow velocity and surface temperature. If mass transfer of the reactants to the heated surface is the controlling mechanism, higher velocity increases the fouling rate. On the other hand, if the chemical reaction on the surface is the controlling mechanism, higher velocity does not affect the fouling rate. Therefore, if the deposition process consists of a number of steps in series, it is the slowest step of the series that exerts the greatest influence and can be said to be the controlling step.
- ❖ The fouling characteristics during sub-cooled flow boiling conditions were significantly different and higher than those occurring under convective heat transfer conditions. During sub-cooled flow boiling, it may not be possible to find the

controlling mechanism as described for convective heat transfer. In this situation, both the chemical reaction and the mass transfer process may be important.

- ❖ For the investigated range of operational parameter, a falling rate of fouling resistance with time has been observed in most experiments. Falling rate behaviour could be the result of a retardation process such as reduction in heat flux, surface temperature or nucleate boiling fraction. In studying the fouling process on heater rods, one important concept is the variation of heat flux during the course of a fouling experiment. In this case, it is usual to fix the power to the header rod, which means constant heat flow rate. When deposition occurs on the heat transfer surfaces, the heat transfer area is increased, consequently the heat flux based on the new area is significantly decreased. Since the surface temperature and nucleate boiling fraction (NBF) are strongly dependent on the heat flux, these parameters are also decreased. Therefore, at the early stages of the fouling process, the rate of deposition is relatively high. In the later stages, the fouling resistances approach a falling rate curve.
- ❖ Calcium sulphate crystallisation fouling showed a saw-tooth fouling curve for heat transfer surface temperatures above 150 °C, while the calcium carbonate and mixed salt crystallisation fouling indicated a declining rate. It was also observed that calcium sulphate forms a weak deposit, which breaks off easily due to the shear force induced by bubble formation. For pure calcium carbonate, the deposits were more adherent. As soon as calcium sulphate and calcium carbonate were combined, the co-precipitated calcium carbonate seems to act as a cement, enhancing considerably the strength of the calcium sulphate scale layer, supporting the formation of an adherent deposit.
- ❖ The results of the measurements at different conditions were used to develop a mechanistic model for deposition from salt mixtures. It was assumed that the deposition of calcium sulphate/calcium carbonate mixtures on the heat transfer surface during convective heat transfer and sub-cooled flow boiling takes place in two successive steps. Due to the concentration gradient, Ca^{2+} , SO_4^{2-} and HCO_3^- will simultaneously be transported from the bulk of the liquid to the heat transfer surface.

HCO_3^- ions react with Ca^{2+} and SO_4^{2-} ions react with Ca^{2+} to form CaCO_3 and CaSO_4 , which precipitate on the heat transfer surface. 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 . The advantage of this correlation is the simplicity in form and the need for less parameters in comparison to other correlations. This model is able to predict all observed trends, i.e. the effect of variation in flow velocity, heat flux, bulk temperature, surface temperature, concentration, boiling phenomenon and variation of heat flux during the course of an experiment.

- ❖ 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 and associated correlations can be recommended for the prediction of fouling resistances for mixed salt solutions.
- ❖ For the co-precipitation process, the calculations must be performed on the basis of a limiting reactant concept, because the reactions are controlled by the limiting reactants. For example, during simultaneous precipitation of calcium sulphate and calcium carbonate, it is clear that the calcium ion is the common ion and sulphate and bicarbonate ions are non-common ions. Hence, it is initially essential to find the limiting reactant ions. Subsequently, the deposition model must be solved for the limiting reactants.
- ❖ Treated heat transfer surfaces have been tested successfully to reduce calcium sulphate, calcium carbonate and calcium sulphate/calcium carbonate mixture fouling, as a mitigation technique. The fouling runs on surfaces modified by Müller-Steinhagen and Zhao (1997, 1999) demonstrated that the treatment of the surface leads to a reduction of scale formation at the same operating conditions, due to a reduction of the surface energy. It was also observed that deposits formed on low energy surfaces were less adherent and less dense than for untreated surfaces.

- ❖ Despite the observed beneficial effects of Ion Implantation and Magnetron Sputtering, it should be noted that these treatments are expensive processes. Furthermore, their application is limited due to the size of the facilities and of the required vacuum chambers. In contrast to these costly methods, *Ni-P-PTFE* coating seems to be a promising surface treatment, providing very low surface energy. The process of *Ni-P-PTFE* coating is easy to realise and much cheaper. At the moment, there are some problems with corrosion and adhesion of the coating on the stainless steel surfaces (Müller-Steinhagen and Zhao 1997, 1999). Advancement of *Ni-P-PTFE* coating could lead to an industrial application suitable to reduce fouling.
- ❖ Scanning Electron Microscopy and X-Ray Diffraction are very useful techniques for identifying the crystal structure. These analyses indicated that deposits from mixed salt solutions included a mixture of crystals of both dissolved salts in the solution. These deposits had an adhesion strength approximately between that of CaSO_4 and CaCO_3 .
- ❖ 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 fluid velocity, heat flux, bulk temperature, surface energy 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.

8.2 FUTURE WORK

- Nomographs are accepted as an extremely useful tool in many fields of science and engineering. They are simple to use and can reduce lengthy calculations enormously. Constructing nomographs for studying solubility equilibria and fouling phenomena can be considered in future works.

- Artificial Neural Networks have recently become the focus of more attention, because of their wide range of applicability and the ease with which they can handle complex and non-linear problems. It is expected that Neural Network analysis will be a useful method for describing and studying fouling phenomena. The results of the performed experiments can be used to model fouling of heat transfer surfaces using Neural Network analysis.
- The key technical objective is to develop a methodology for applying the experimental data to industrial conditions. There may be some differences between field and laboratory data. For example, corrosion products found in process streams in the field might contribute to differences between laboratory and field data. Hence a fluid that does not foul in the laboratory can easily foul in the field due to the presence of ex-situ corrosion products. It is recommended to develop a methodology for matching the experimental data with field data.
- Ageing of the deposits causes continuous changes in chemical and physical parameters of the fouling deposit. It has been observed that a long-exposed fouling layer shows two distinct surfaces (i.e. internal and external surfaces), each possibly with different physical and chemical characteristics. In the present technical approach, the ageing process has not been considered, because it could be specific to the system and because it requires a separate set of laboratory installations to study the long-term kinetics associated with ageing. It is recommended that the ageing process is studied in the future.

NOMENCLATURE

A	Area, m^2
ALK	Bicarbonate ion concentration, mol/l
ALKY	Total alkalinity, ppm as CaCO_3
a	Activity
a	Constant
b	Constant
B	Time constant in Watkinson et al. model
C	Concentration, kg/m^3
D	Diffusion coefficient, m^2/s
DFI	Driving force index
d	Diameter, m
E	Activation energy, J/mole
E	Enhancement factor
F	Enhancement factor
f	Friction factor
f	Activity coefficient
g	Acceleration due to gravity, m/s^2
h	Latent heat of vaporisation, J/kg
I	Ionic strength, mol/l
IP	Ionic product
I_s	Oddo and Tomson saturation index
K	Combined diffusion-reaction coefficients
K	Dissociation constant
K	Stiff & Davis constant
K_{sp}	Solubility product
k	Reaction rate constant
L	Length, m
LSI	Langelier saturation index
M	Mass, kg

meq	Milliequivalent
$\dot{m}$	Rate of mass deposited, $\text{kg/m}^2 \cdot \text{s}$
NBF	Nucleate boiling fraction
N	Number of fault points within fouling layer
n	Constant
n	Order of reaction
P	Intercrystalline adhesion force
P	Pressure
P	Sticking probability
Pr	Prandtl number
PALK	-Log (equivalent total alkalinity per litre)
PCa^{2+}	-Log (mole of Ca^{2+} per litre)
PK'_2	Empirical constant
PK'_s	Empirical constant
$\dot{Q}$	Heat transfer rate, W
$\dot{q}$	Heat flux, W/m^2
R	Solubility product pressure effect factor
R	Thermal resistance
R	Universal gas constant
Re	Reynolds number
R_f	Fouling resistance, $\text{m}^2\text{K/W}$
R_f^*	Asymptotic fouling resistance, $\text{m}^2\text{K/W}$
RSI	Ryznar saturation index
S	Solubility
S	Suppression factor
Sc	Schmidt number
SG	Specific gravity
SI	Saturation index
SR	Supersaturation ratio
s	Distance between thermocouple location and heater surface, m
T	Temperature, K

T.A.	Total alkalinity, g/l
TDS	Total dissolved solids
t	Time, s
U	Overall heat transfer coefficient, W/m ² .K
V	Volume, m ³
$\dot{V}$	Flow rate, m ³ /s
v	Fluid velocity, m/s
x	Thickness, m
Z	Valence of the ion
z	Constant

Subscript and Superscript

b	Bulk
bb	Beneath the bubble
c	Calculated
c	Convection
c	Clean
D	Delay
d	Deposit
eq	Equivalent
f	Fault
f	Fouled
fb	Flow boiling
h	Heat transfer
i	Inside
i	Interface
nb	Nucleate boiling
o	Outside
o	Reference
ONB	Onset nucleate boiling
p	Particle

p	Precipitated
r	Reference
r	Removal
r	Reaction
s	Saturation
s	Surface
t	Total
tot	Total
TC	Thermocouple
w	Wall
*	Saturation

Greek symbols

α	Heat transfer coefficient, $\text{W/m}^2\cdot\text{K}$
β	Mass transfer coefficient, m/s
Δ	Difference operator
δ	Linear expansion coefficient
ε	Edge length of cubes or grids
ϕ	Rate of formation or removal
γ	Concentration effect
λ	Thermal conductivity, $\text{W/m}\cdot\text{K}$
ΔE	Interaction energy, J/m^2
μ	Dynamic viscosity, $\text{kg/m}\cdot\text{s}$
θ	Time constant
θ	Induction period
ρ	Density, kg/m^3
σ	Shear strength of the fouling layer, N/m^2
τ	Fluid shear stress, N/m^2
ψ	Empirical structural parameter
Ω	Water quality

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Appendix A

CALIBRATION OF MAGNETIC FLOW METERS

In this investigation, the flow velocities are measured by two magnetic flow meters. These magnetic flow meters have a 15 mm internal bore and are manufactured by ABB Kent Taylor Industries Ltd.

Both flow meters were calibrated by measuring the weight of the water passed through them in a certain period of time. The flow velocity can be calculated by knowing the dimensions of the test sections. For each flow rate, the data acquisition program records the output voltage from the flow meters. Figure A.1 shows the relationship between velocity and voltage for each magnetic flow meter.

Figure A.1 Calibration of magnetic flow meters

Appendix B

CALIBRATION OF ANNULAR TEST HEATERS

The electrical test heaters used for fouling measurements were described in section 4.1. The temperature profile from the thermocouple of the heating element to the fluid is shown schematically in Figure B.1.

Figure B.1 Temperature profile of the test heaters

Accurate surface temperature measurement, T_s , is essential for calculation of heat transfer coefficients. Thermocouples are embedded a small distance beneath the heater surface and surface temperatures are obtained from these thermocouple temperature.

A steady state energy balance from the thermocouple to the fluid results in:

$$\dot{q} = U (T_{TC} - T_b) = \alpha (T_s - T_b) = \frac{\lambda}{s} (T_{TC} - T_s) \quad (\text{B.1})$$

This equation can be rearranged to give the overall heat transfer coefficient, U , in terms of α , s and λ .

$$\frac{1}{U} = \frac{1}{\alpha} + \frac{s}{\lambda} \quad (\text{B.2})$$

The purpose of calibration of test heaters is to calculate s/λ , shown in Equation (B.2). A simple rearrangement of Equation (B.1) results in the following equation for the overall heat transfer coefficient, U .

$$U = \frac{\dot{q}}{(T_{tc} - T_b)} \quad (\text{B.3})$$

It can be seen that U is a function of the thermocouple and bulk temperature, which are measurable quantities. The only remaining quantity to be measured in Equation (B.2) is the convective heat transfer coefficient, α , which depends on the properties of the flowing fluid, the geometry of the flow path and the fluid velocity. It is normally calculated from empirical correlations, i.e.

$$\alpha = C Re^m Pr^n \left(\frac{Pr}{Pr_w} \right)^d \quad (\text{B.4})$$

For a given fluid and flow path, the heat transfer coefficient is principally dependent on the fluid velocity. Since the calibration runs are performed at constant surface and bulk temperatures for different velocities, the convective heat transfer coefficient would be a function of liquid velocity only. Consequently, the following relationship for the convective heat transfer coefficient under fully developed turbulent flow conditions can be written.

$$\alpha = C' v^m \quad (\text{B.5})$$

Substituting Equation (B.5) into Equation (B.2) results in:

$$\frac{1}{U} = \frac{1}{C'v^m} + \frac{s}{\lambda} \quad (\text{B.6})$$

Therefore, a plot of $1/U$ versus $1/v^m$, for each thermocouple, gives a straight line with s/λ as the intercept. However there remains some confusion as to what exponent of v to use. A simple rearrangement of the Dittus and Boelter correlation for convective heat transfer under fully developed turbulent flow conditions results in $v^{0.8}$. Based on the Gnielinski correlation for fully developed turbulent flow through the pipe, the exponent is a function of Reynolds number and Prandtl number and varies from 0.78 to 0.9. Wilson (1915) in the original paper suggested using $v^{0.82}$. Branch (1991) and Najibi (1997) used $v^{0.75}$ with good success. Knudsen (1981) suggested using non-linear regression with C' , the velocity exponent, m , and the term s/λ as the fitted parameter.

For this investigation, the method of non-linear regression, suggested by Knudsen (1981), was used. The value of m for which the least mean square error in the regression occurs is employed in the calculation of λ/s . The values of λ/s and velocity exponent, m , for each heaters used in this investigation are shown in Table B.1. Figures B.2, B.3, B.4 and B.5 show Equation (B.6) plotted for each thermocouple of the test heaters in Wilson plot form, which involves measuring U for various velocities and determining s/λ using an exponent for the velocity.

Table B.1 λ/s values for the test heaters used in this investigation

Heater Number	$(\lambda/s)_1$	$(\lambda/s)_2$	$(\lambda/s)_3$	m
435	17030	13530	19470	0.8
516	9226	11910	9566	0.86
552	14850	6679	8984	0.85
637	4466	6551	5621	0.81

Figure B.2 Wilson plot for the test heater 435

Figure B.3 Wilson plot for the test heater 516

Figure B.4 Wilson plot for the test heater 552

Figure B.5 Wilson plot for the test heater 637

Appendix C

FIGURES OF SOME FOULING RUNS

The figures shown in this Appendix are the results of the calcium carbonate fouling runs, calcium sulphate fouling runs and salt mixture fouling runs for treated surfaces, i.e. *DLC* sputtered, *CrNTiF* sputtered, *H* implanted, *F* sputtered, *Ni-P-PTFE* coated and *Ni-P-PTFE* porous coated surfaces, and untreated surface which were not given in the main part of the present report.

Figure C.1 Variation of heat transfer coefficient with time

Figure C.2 Variation of fouling resistance with time

Figure C.3 Variation of heat transfer coefficient with time

Figure C.4 Variation of fouling resistance with time

Figure C.5 Variation of heat transfer coefficient with time

Figure C.6 Variation of fouling resistance with time

Figure C.7 Variation of heat transfer coefficient with time

Figure C.8 Variation of fouling resistance with time

Figure C.9 Variation of heat transfer coefficient with time

Figure C.10 Variation of fouling resistance with time

Figure C.11 Variation of heat transfer coefficient with time

Figure C.12 Variation of fouling resistance with time

Figure C.13 Variation of heat transfer coefficient with time

Figure C.14 Variation of fouling resistance with time

Figure C.15 Variation of heat transfer coefficient with time

Figure C.16 Variation of fouling resistance with time

Figure C.17 Variation of heat transfer coefficient with time

Figure C.18 Variation of fouling resistance with time

Figure C.19 Variation of heat transfer coefficient with time

Figure C.20 Variation of fouling resistance with time

Figure C.21 Variation of heat transfer coefficient with time

Figure C.22 Variation of fouling resistance with time

Figure C.23 Variation of heat transfer coefficient with time

Figure C.24 Variation of fouling resistance with time

Figure C.25 Variation of heat transfer coefficient with time

Figure C.26 Variation of fouling resistance with time

Figure C.27 Variation of heat transfer coefficient with time

Figure C.28 Variation of fouling resistance with time

Figure C.29 Variation of heat transfer coefficient with time

Figure C.30 Variation of fouling resistance with time

Appendix D

LISTING OF COMPUTER PROGRAMS

```

' *****
' *
' *      MODELLING OF MIXED SALT      *
' *
' *      CRYSTALLISATION FOULING      *
' *
' *      (main program)                *
' *
' *      BY: ABBAS HELALIZADEH         *
' *****

```

```

DECLARE SUB STRENGTH (CCA!, CB!, ION!)
DECLARE SUB PHYSL (K0$, t!, Ts!, C!, VIS!, DEN!, CP!, TC!)
DECLARE SUB PHYSV (K0$, TSN!, BPR!, C!, P!, VISV!, DENV!, Ts!, HV!, SIG!, DENL!)
DECLARE SUB BOIL (K0$, P!, QB!, ANB!)
DECLARE SUB FLAMI (FI1!, RE!, DH!, RR!)
DECLARE SUB FTURB (F1!, RE!, DH!)
DECLARE SUB XDOT (HV!, CP!, QN!, Md!, DS!, RE!, PR!, XD!, NB!, DH!)
DECLARE SUB TURB (PR!, PHI!, GR!, RE!, NUT!, DH!, RR!)
DECLARE SUB LAMI (PR!, PHI!, GR!, RE!, NUL!, DH!, RR!)
DECLARE SUB FS (XD!, DENB!, DENV!, VISB!, VISV!, RE!, fl, sl, RETP!, DH!)
DECLARE SUB BOX (I1%, I2%)
DECLARE SUB INPUTSTR (int$, legal$)
DECLARE SUB CACO3 (ca!, TA!, PH!, ION!, TB!, Tw!, Ts!, DH!, U!, NBF!, gama!, Mc!)

CLEAR
N = 2000
DIM CBF(N), UF(N), QF(N), TBF(N), PF(N), AM(N), ACB(N)
DIM time(N), Rf(N), EE(N), EE1(N)

CLS
mm = 0

```

ii = 1

time = 0

OD = 2.54

ID = 1.067

Ro = (OD / 2) / 100 'm

Ri = (ID / 2) / 100 'm

EPS = 10^{-5}

RR = .4200787402#

DH = 2 * (Ro - Ri)

XT = .08255

XH = .216 + XT

'UF(1) = 50

'TBF(1) = 80

'QF(1) = 200

'PF(1) = 102

'CBF(1) = 2

'PH = 7

'TA = .2

'deltat = 100

'final = 2000

LOCATE 4, 1: COLOR 11, 4: BOX 7, 37

LOCATE 5, 2: COLOR 14, 4

INPUT " FLUID VELOCITY (cm/s)= "; UF(1)

LOCATE 7, 2

INPUT " BULK TEMPERATURE (C)= "; TBF(1)

LOCATE 9, 2

INPUT " HEAT FLUX (kW/m^2)= "; QF(1)

LOCATE 11, 2

INPUT " SYSTEM PRESSURE (kPa)= "; PF(1)

LOCATE 4, 41: COLOR 12, 1: BOX 7, 38

LOCATE 5, 42: COLOR 14, 1

INPUT " CaSO4 CONCENTRATION (gr/l)= "; CBF(1)

LOCATE 8, 42

INPUT " PH OF THE SOLUTION = "; PH

LOCATE 11, 42

INPUT " TOTAL ALKALITY AS CaCO₃ (gr/l)= "; TA

ca = TA

LOCATE 14, 22: COLOR 15, 2: BOX 5, 37

LOCATE 15, 27: COLOR 14, 2

INPUT " TIME STEP (min)= "; deltat

LOCATE 17, 27

INPUT " DURATION (min)= "; final

LOCATE 19, 27: INPUT " OUTPUT FILE NAME ="; B\$

OPEN B\$ FOR OUTPUT AS #2

'LOCATE 20, 31

'INPUT " EXPERIMENTAL HEAT TRANSFER COEFFICIENT (W/m².K)= "; AM(1)

AM(1) = 7000

CB = CBF(1); CCA = ca

FOR i = 1 TO final

IF (final / deltat) / 20 = i THEN final = final + deltat

NEXT i

qst = QF(1) 'first q

Ust = UF(1) / 100 'first U

CA0 = ca / 100.0892

ca = ca / 100.0892 '+ CBF(1) / 136.1376

TA = TA / 100.0892

COLOR , 8

19 mm = 0: CLS

LOCATE 1, 1: COLOR 11, 12: BOX 21, 78

LOCATE 1, 1: COLOR 11, 6: BOX 1, 78

LOCATE 2, 2: COLOR 14, 6

PRINT " t(min) q(W/m²) NBF Md (kg/m².s) Rd (m) Rf(m².K/W) "

LOCATE , 2

'PRINT

17 mm = mm + 1

CALL STRENGTH(CCA, CB, ION)

LOCATE 2, 30

9 'INPUT "Number of Data="; n

N = 1

IF N <= 0 THEN 9

IF N > 100 THEN 9

LOCATE , 10

'INPUT "INPUT (NACL) OR (KNO3) OR (NA2SO4) OR (H2O) OR (CASO4)="; K0\$

IF CBF(1) = 0 THEN K0\$ = "h2o" ELSE K0\$ = "caso4"

IF K0\$ = "NACL" OR K0\$ = "nacl" THEN

'PRINT " 0<CBF(I)<=396.63 "

END IF

IF K0\$ = "NA2SO4" OR K0\$ = "na2so4" THEN

'PRINT " 0<CBF(I)<=420.32 "

END IF

IF K0\$ = "KNO3" OR K0\$ = "kno3" THEN

'PRINT " 0<CBF(I)<=3706.7 "

END IF

IF K0\$ = "H2O" OR K0\$ = "h2o" THEN

FOR i = 1 TO N

CBF(i) = 0

NEXT i

END IF

FOR i = 1 TO N

IF K0\$ = "H2O" OR K0\$ = "h2o" THEN 80

'PRINT

LOCATE , 29

1 'CBF(i) = 2: 'PRINT " Cb("; i; ")(gr/lit)="; : INPUT CBF(i)

IF K0\$ = "NACL" OR K0\$ = "nacl" THEN

IF CBF(i) > 396.63 THEN 1

```
IF CBF(i) < 0 THEN 1
END IF
IF K0$ = "NA2SO4" OR K0$ = "na2so4" THEN
IF CBF(i) > 420.32 THEN 1
IF CBF(i) < 0 THEN 1
END IF
IF K0$ = "KNO3" OR K0$ = "kno3" THEN
IF CBF(i) > 3706.7 THEN 1
IF CBF(i) < 0 THEN 1
END IF
PRINT
LOCATE , 31
80
NEXT i
FOR i = 1 TO N
U = UF(i) / 100
q = QF(i) * 1000
CB = CBF(i)
TB = TBF(i)
P = PF(i) / 100
CALL PHYSV(K0$, TSN, BPR, CB, P, VISV, DENV, Ts, HV, SIG, DENL)
CALL PHYSL(K0$, TB, Ts, CB, VISB, DENB, CPB, TCB)
Md = DENB * U
PR = CPB * VISB / TCB
RE = DENB * U * DH / VISB
T1 = TB
T2 = T1 + 100
Tw = (T1 + T2) / 2
TF = (TB + Tw) / 2
DS = Ts - TB
DI = DS
10 CALL XDOT(HV, CPB, q, Md, DI, RE, PR, XD, NB, DH)
PWSB = (CB / (DENB - CB))
PWSI = PWSB / (1 - XD)
IF PWSI >= 1 THEN PWSI = 1
CI = PWSI * (DENB - CB)
```

```
CALL PHYSV(K0$, TSN, BPR, CI, P, VISV, DENV, TI, HV, SIG, DENL)
DIN = TI - TB
TOL = ABS(DIN / DI - 1)
IF TOL <= EPS GOTO 20
DI = DIN
GOTO 10
20 DI = DIN
CALL FS(XD, DENB, DENV, VISB, VISV, RE, f, s, RETP, DH)
30 DT = Tw - TB
TFS = (TB + Ts) / 2
CALL PHYSL(K0$, TF, TFS, CB, VISF, DENF, CPF, TCF)
CALL PHYSL(K0$, Tw, Ts, CB, VISW, DENW, CPW, TCW)
PHI = VISB / VISW
GR = DH ^ 3 * 9.81 * DENF ^ 2 / VISF / VISF * (DENB - DENW) / DENW
CALL LAMI(PR, PHI, GR, RETP, NUL, DH, RR)
CALL TURB(PR, PHI, GR, RETP, NUT, DH, RR)
NU = (NUL ^ 3 + NUT ^ 3) ^ (1 / 3)
AC = NU * TCB / DH
QC = AC * DT
QB = (q - QC) / s
IF QB <= 0 THEN AB = 0
IF QB > 0 THEN
CALL BOIL(K0$, P, QB, ANB)
AB = ANB * (1 - DI / DT) * s
IF AB <= 0 THEN AB = 0
END IF
ACB(i) = AC + AB
QI = ACB(i) * DT
TOL = ABS(QI / q - 1)
IF TOL <= EPS THEN
GOTO 50
END IF
IF QI < q THEN
T1 = Tw
Tw = (T1 + T2) / 2
TF = (TB + Tw) / 2
```



```

GOTO 40
END IF
IF QI > q THEN
  T2 = Tw
  Tw = (T1 + T2) / 2
  TF = (TB + Tw) / 2
  GOTO 40
END IF
40 GOTO 30
50 Tw = q / ACB(i) + TB
NBF = AB / ACB(i)

```

```

NEXT i

```

```

'SYSTEM MODELLING (CaSO4 and CaCO3)

```

```

=====
RHOs = 1991      'kg/m^3
LAMDA s = 2.03   'W/m.K
RHOc = 2434
LAMDA c = 1.821
gama = 1 + 3.875 * NBF

```

```

'SATURATION CONCENTRATION CALCULATION

```

```

*****

```

```

a = 2.047 - .01136 * (Tw + 273.15)
B = -6.5832 + .0226 * (Tw + 273.15)
'PRINT "a="; a, "b="; b
z = ION ^ .5 / (1 + 1.5 * ION ^ .5)
Csat = 10 ^ (a + B * z) * 136.1376      'saturation concentration
KSP = (Csat / 136.1376) ^ 2
'PRINT "z="; z, "Csat="; Csat

```

```

'PARAMETERS FOR Nfc

```

```

*****

```

```

K10 = 3.5 * 10 ^ 11
E = 115517

```

```

R = 8.314
K1 = K10 * EXP(-E / R / (Tw + 273.15))
Kr = K1
Tsats = Ts
f = (1.82 * LOG(RE) / 2.302585 - 1.64) ^ (-2)
IF RE < 2300 OR RE > 1000000 THEN GOTO 12 ELSE
TB = TB + 273.15      'K
dif = 1.0633 * 10 ^ -9 * TB / 355.65 * EXP(3.8 * (Tsats + 273.15) * (1 / 355.65 - 1 / TB))
SC = VISB / DENB / dif
IF SC < .6 OR SC > 2000 THEN GOTO 22 ELSE
Sh = (f / 8) * (RE - 1000) * SC / (1 + 12.7 * (f / 8) ^ .5 * (SC ^ (2 / 3) - 1))
Sh = Sh * (1 + 1 / 3 * (DH / XT) ^ (2 / 3))
Tw = Tw + 273.15
difw = 1.0633 * 10 ^ -9 * Tw / 355.65 * EXP(3.8 * (Tsats + 273.15) * (1 / 355.65 - 1 / Tw))
Scw = VISW / DENW / difw
Sh = Sh * (SC / Scw) ^ .11
Sh = Sh * .86 * (ID / OD) ^ -.16
beta = Sh * dif / DH
LOCATE , 25
'PRINT "beta (m/s)="; beta

'PRINT
'COLOR 14, 13
GOTO 32
12 : 'PRINT : 'PRINT : COLOR 20
'PRINT TAB(30); " WARNING!!"
'PRINT TAB(20); " REYNOLDS NUMBER IS OUT OF RANGE": END
22 : 'PRINT : 'PRINT : 'COLOR 20
'PRINT TAB(30); " WARNING!!"
'PRINT TAB(20); " SCHMIDT NUMBER IS OUT OF RANGE": END

32 'CLS : 'SCREEN 9

COLOR 1, 15
'LOCATE 6, 20: PRINT "1- CONTROLLING MECHANISM IS MASS TRANSFER"
'LOCATE 8, 18: PRINT "2- CONTROLLING MECHANISM IS CHEMICAL REACTION"

```

```
'LOCATE 9, 5: PRINT "3- CONTROLLING MECHANISMS ARE MASS TRANSFER AND
CHEMICAL REACTION SIMULTANEOUSLY"
```

```
COLOR 14, 0
```

```
'LOCATE 14, 20: INPUT "Please choose one of the above options"; chois
```

```
COLOR 15, 13
```

```
chois = 3
```

```
SELECT CASE chois
```

```
CASE 1
```

```
!*****
```

```
!* MASS TRANSFER CONTROL SYSTEM *
```

```
!*****
```

```
!*****
```

```
!* PREDICTION OF Nnb *
```

```
!*****
```

```
nnb = beta * (gamma * CB - Csat)
```

```
'PRINT "nnb="; nnb
```

```
!*****
```

```
!* PREDICTION OF Nfc *
```

```
!*****
```

```
nfc = beta * (CB - Csat)
```

```
'PRINT "nfc="; nfc
```

```
!*****
```

```
!* PREDICTION OF DEPOSIT RADIUS *
```

```
!*****
```

```
INPUT "time (min)="; time
```

```
t = time * 60
```

```
Ms = nnb * NBF + nfc * (1 - NBF)
```

```
Rd = (Ro ^ 2 - (Ro ^ 2 - Ri ^ 2) * EXP(-Ms / RHOs * t)) ^ .5
```

```
'PRINT "Cb="; Cb, "Csat="; Csat, "Ms="; Ms
```

```
'PRINT "DEPOSIT RADIUS (m)="; Rd
```

```
!*****
```

```
'* PREDICTION OF Rf      *
```

```
*****
```

```
Rf = 1 / LAMDAs * (Rd - Ri)
```

```
'PRINT "Rf (m^2.K/W) ="; Rf
```

```
q = q * .005335 / Rd
```

```
'PRINT "q (W/m^2) ="; q
```

```
END
```

```
CASE 2
```

```
*****
```

```
'* CHEMICAL REACTION CONTROL SYSTEM *
```

```
*****
```

```
*****
```

```
'* PREDICTION OF Nnb     *
```

```
*****
```

```
nnb = Kr * (gamma * CB - Csat) ^ 2
```

```
'PRINT "nnb="; nnb
```

```
*****
```

```
'* PREDICTION OF Nfc     *
```

```
*****
```

```
nfc = Kr * (CB - Csat) ^ 2
```

```
'PRINT "nfc="; nfc
```

```
*****
```

```
'* PREDICTION OF DEPOSIT RADIUS *
```

```
*****
```

```
INPUT "time (min) ="; time
```

```
t = time * 60
```

```
Ms = nnb * NBF + nfc * (1 - NBF)
```

```
Rd = (Ro ^ 2 - (Ro ^ 2 - Ri ^ 2) * EXP(-Ms / RHOs * t)) ^ .5
```

```
'PRINT "Kr="; Kr, "Cb="; Cb, "Csat="; Csat, "Ms=", Ms
```

```
'PRINT "DEPOSIT RADIUS (m) ="; Rd
```

```
*****
```

```
'* PREDICTION OF Rf *
```

```
*****
```

```
Rf = 1 / LAMDA * (Rd - Ri)
```

```
'PRINT "Rf (m^2.K/W) ="; Rf
```

```
q = q * .005335 / Rd
```

```
'PRINT "q (W/m^2) ="; q
```

```
END
```

```
CASE 3
```

```
'CLS
```

```
'LOCATE 2, 23: PRINT "IONIC STRENGTH (mole/L) ="; ION
```

```
'LOCATE 4, 35: PRINT "NBF ="; NBF:
```

```
t = time * 60
```

```
IF CB = 0 THEN 490
```

```
*****
```

```
'* SIMULTANEOUS MASS TRANSFER AND CHEMICAL REACTION *
```

```
*****
```

```
*****
```

```
'* PREDICTION OF Nnb *
```

```
*****
```

```
nnb = Kr * (gamma * CB - Csat) ^ 2
```

```
'COLOR 0, 10: LOCATE 7, 33: PRINT "nnb ="; nnb
```

```
*****
```

```
'* PREDICTION OF Nfc *
```

```
*****
```

```
IF Csat > CB THEN Csat = CB
```

```
nfc = beta * (.5 * beta / Kr + (CB - Csat) - (.25 * (beta / Kr) ^ 2 + (beta / Kr) * (CB - Csat)) ^ .5)
```

```
'LOCATE 9, 33: PRINT "nfc ="; nfc
```

```
480
```

```
*****
```

```
'* PREDICTION OF DEPOSITION RATE *
```

```
*****
```

COLOR 1, 7

LOCATE 11, 33

'Ms = nnb * NBF + nfc * (1 - NBF)

Ms = nfc

490

* PREDICTION OF CACO3 DEPOSITION RATE *

IF CA0 > 0 THEN 500 ELSE 510

500

CALL CACO3(ca, TA, PH, ION, TB, Tw, Ts, DH, U, NBF, gama, Mc)

'LOCATE 12, 12: PRINT "Mc="; Mc

510

* PREDICTION OF DEPOSIT RADIUS *

EN = 1 + 78.8 * NBF ^ .96

Md = EN * (Ms + Mc)

IF Md <= 0 THEN LOCATE , 25: COLOR 26, 13: PRINT "WARNING: THE SOLUTION IS
SUBSATURATED": END

Xs = EN * Ms / Md

Xc = EN * Mc / Md

RHod = (Xs / RHOs + Xc / RHOc) ^ -1

Rd = Ri + Md / RHod * t

'Rd = (Ro ^ 2 - (Ro ^ 2 - Ri ^ 2) * EXP(-Md / RHod * t)) ^ .5

IF Rd <= Rdo THEN 515

Rdo = Rd

LOCATE 12, 13

'PRINT "Kr="; Kr; " Cb="; Cb, "Csat="; Csat

COLOR 14, 8: LOCATE 14, 25

'PRINT "DEPOSITION RATE (kg/m^2.s)="; Ms

LOCATE 16, 28

'PRINT "DEPOSIT RADIUS (m)="; Rd

* PREDICTION OF Rf *

$K_d = X_s * RHO_d / RHO_s / LAMDA_s + X_c * RHO_d / RHO_c / LAMDA_c$

$LAMDA_d = 1 / K_d$

$R_f = 1 / LAMDA_d * (R_d - R_i)$

LOCATE 19, 32

'PRINT "Xs="; Xs; "Xc="; Xc; "RHOD="; RHOD; "LAMDA d (m.K/W) ="; LAMDA d

'PRINT "Rf (m^2.K/W) ="; Rf

LOCATE 21, 36

LOCATE 23, 28: PRINT "Surface Temperature="; Tw

LOCATE mm + 3, 4: COLOR 15, 12

PRINT USING "#####.###.#####.#####.#####.##### "; time;
q; NBF; Md; Rd; Rf

PRINT #2, USING "#####.###.####.#####.#####.##### "; time; q;
NBF; Md; Rd; Rf

'PRINT USING "#####.###.#####.#####.#####.##### ";
time; U; DH; Md; Rd; Rf

$DH = 2 * (R_o - R_d)$

$U = U_{st} * (R_o^2 - R_i^2) / (R_o^2 - R_d^2)$

$RR = R_d / R_o$

$q = q_{st} * 1000 * .005335 / R_d$

'PRINT "q (W/m^2)="; q

$QF(1) = q / 1000$

$UF(1) = U * 100$

time(ii) = time

Rf(ii) = Rf

time = time + deltat

ii = ii + 1

COLOR 1, 8

IF time > final THEN GOTO 18

IF mm = 20 THEN GOTO 19

GOTO 17

18 IF mm = 21 THEN mm = 20

515 LOCATE mm + 5, 14: COLOR 26, 14

INPUT "DO YOU LIKE TO SEE THE PLOT OF Rf vs TIME (Y/N)"; K10\$

IF K10\$ = "Y" OR K10\$ = "y" THEN GOTO 220 ELSE

END

END SELECT

220 CLS

k = time(ii - 1)

l = Rf(ii - 1)

SCREEN 12, 2

LOCATE 1, 1

COLOR 11

BOX 26, 75

COLOR 10

VIEW (70, 50)-(550, 400)

WINDOW (0, 0)-(k, l)

LINE (0, 0)-(k, 0)

LINE (0, 0)-(0, l)

LINE (0, 0)-(time(5) * ii, Rf(5) * ii)

ll = time(ii - 1) / 100

FOR j = 1 TO ii

COLOR 13

CIRCLE (time(j), Rf(j)), ll

NEXT j

LOCATE 26, 4: COLOR 10: PRINT Rf(1)

LOCATE 13, 5: COLOR 14: PRINT "Rf"

LOCATE 4, 2: COLOR 10: PRINT USING "#.#####"; 1

LOCATE 27, 8: COLOR 10: PRINT time(1)

LOCATE 27, 35: COLOR 14: PRINT "time";

LOCATE 27, 68: COLOR 10: PRINT k

COLOR 15

SUB BOIL (K0\$, P, QB, ANB)

QO = 20000

IF K0\$ = "H2O" OR K0\$ = "h2o" THEN

AO = 6000

END IF

IF K0\$ = "KNO3" OR K0\$ = "kno3" THEN

AO = 5600

END IF

IF K0\$ = "NA2SO4" OR K0\$ = "na2so4" THEN

AO = 5600

END IF

IF K0\$ = "NACL" OR K0\$ = "nacl" THEN

AO = 5600

END IF

IF K0\$ = "CASO4" OR K0\$ = "caso4" THEN

AO = 4800

END IF

'IF K0\$ = "CACO3" OR K0\$ = "caco3" THEN

'AO = 4800

'END IF

PC = 221.2

PS = P / PC

FD = $1.73 * PS^{.27} + (6.1 + .68 / (1 - PS)) * PS^2$

NP = $.9 - .3 * PS^{.15}$

ANB = AO * (QB / QO) ^ NP * FD

END SUB

SUB BOX (I1%, I2%)

' BOX : BOX

' ===== Notes =====

' ===== Purpose =====

' Draws a box with 11% rows and 12% columns. Location and color
' should be already set by caller.

' ===== Interface =====

' Routines called: NONE.

'

' Calling routines : Message\$.

'

' Globals: NONE.

'

' Global Consts: NONE.

'

' Arguments:

' 1. 11% as INTEGER Number of Rows

' 2. 12% as INTEGER The Row number of top
' left corner of the BOX

' 2. Col as INTEGER The Column number of top
' left corner of the BOX

'

" ===== Code =====

'

' Get current locations

'

Row% = CSRLIN

COL% = POS(0)

'IF Col% + 12% > 80 THEN EXIT SUB

'IF Row% + 2 + 11% > 24 THEN EXIT SUB

LOCATE , COL%

PRINT CHR\$(218); STRING\$(12%, 196); CHR\$(191)

FOR i% = 1 TO 11%

LOCATE , COL% ' Locate and print side bars.

PRINT CHR\$(179); SPACE\$(12%); CHR\$(179)

NEXT i%

LOCATE , COL%

```
PRINT CHR$(192); STRING$(12%, 196); CHR$(217)
```

```
'
```

```
'=====
```

```
END SUB
```

```
SUB CACO3 (ca, TA, PH, ION, TB, Tw, Ts, DH, U, NBF, gama, Mc)
```

```
R = 8.314
```

```
DJ = 1.145632 * .000000001#
```

```
T0 = 336
```

```
D1 = DJ * (TB / T0) * EXP(3.8 * (Ts + 273.15) * (1 / T0 - 1 / TB))
```

```
T1 = TB - 273.15
```

```
CB = (1.3272 * (20 - T1) - .001053 * (T1 - 20) * (T1 - 20))
```

```
CB = CB / (T1 + 105)
```

```
F1 = 1.002 / 1000
```

```
CB = CB + LOG(F1) / LOG(10)
```

```
AMU = 10 ^ (CB)
```

```
ROH = 999.83952# + 16.945176# * T1 - .0079870401# * T1 ^ 2
```

```
ROH = ROH - .0000461705# * T1 ^ 3 + 105.56302# * 10 ^ -9 * T1 ^ 4
```

```
ROH = ROH - 208.54253# * (10 ^ -12) * T1 ^ 5
```

```
ROH = ROH / (1 + 16.87985 * 10 ^ -3 * T1)
```

```
RE = (ROH * U * DH) / AMU
```

```
SC = AMU / (ROH * D1)
```

```
beta = .023 * RE ^ .85 * SC ^ .33
```

```
beta = beta * (D1 / DH)
```

```
'LOCATE , 20: PRINT TB; AMU; ROH; beta
```

```
FI = (ION ^ .5) / (1 + ION ^ .5) - .3 * ION
```

```
FM = 10 ^ (-.51 * FI)
```

```
FD = 10 ^ (-2.04 * FI)
```

```
Kw = (10 ^ (-4787.3 / TB - 7.1321 * LOG(TB) / LOG(10) - .01037 * TB + 22.801)) / FM ^ 2
```

```
H = (10 ^ (-1 * PH))
```

```
AOH = Kw / H
```

```
'LOCATE , 1: PRINT Kw; H; AOH
```

```
AK1 = 10 ^ (-17052 / TB - 215.21 * LOG(TB) / LOG(10) + .12675 * TB + 545.56)
```

```
AK2 = 10 ^ (-2902.39 / TB - .02379 * TB + 6.498)
```

```
AK1 = AK1 / FM ^ 2
```

```

AK2 = AK2 / FD / FM
HCO3 = (TA + H - AOH) / ((2 * AK2 / H) + 1)
CO2 = (H * (TA + H - AOH)) / (AK1 + 2 * AK1 * AK2 / H)
AKR = 7.1 * 10 ^ 11 * EXP(-110250 / 8.314 / Tw)
'AKR = 10 ^ -5 * EXP(41.04 - 20700 / (1.987 * Tw))
AKSP = 10 ^ (-.01183 * (Tw - 273.15) - 8.03)
AKSP = AKSP / (FD * FD)
BKSP = AKSP ^ .5
'PRINT AKSP; BKSP
a = 1 - 4 * AK2 * AKR * ca / (beta * AK1)
B = CO2 / ca + 4 * AK2 * AKR * HCO3 / (AK1 * beta) + AKSP * AKR / (beta * ca)
C = AK2 * AKR * HCO3 ^ 2 / (AK1 * beta * ca) - AKSP * CO2 * AKR / (ca ^ 2 * beta)
CC = (1 + 4 * a * C / B ^ 2) ^ .5 - 1
'nfc = .5 * beta * ca * B * CC / a

nfc = beta * (.5 * beta / AKR + (HCO3 - BKSP) - (.25 * (beta / AKR) ^ 2 + (beta / AKR) *
(HCO3 - BKSP)) ^ .5)
nfc = nfc * 100.0892

E2 = 122150 / 8.314
AKO = 9.806 * 10 ^ 11 * EXP(-122150 / 8.314 / Tw)

nnb = AKO * (gama * ca - BKSP) ^ 2
nnb = nnb * (100.0892) ^ 2
'Mc = nnb * NBF + nfc * (1 - NBF)
Mc = nfc
'LOCATE , 1: PRINT AKR; AKO; nnb; nfc; NBF; Mc
END SUB

SUB FLAMI (FI1, RE, DH, RR)

Ro = .0127: Ri = RR * Ro
XT = .08255: XH = .216 + XT
RML = SQR(((1 - RR ^ 2) / (2 * LOG(1 / RR))))
DR = (1 + RR ^ 2 - 2 * RML ^ 2) / ((1 - RR) ^ 2)
f = 16 / (RE * DR)

```

```
FR = (1 + RR) / RR * (RML ^ 2 - RR ^ 2) / (1 - RR ^ 2)
```

```
FI1 = f * FR
```

```
DEL = 2.11 * DH / SQR(RE * DH / XH)
```

```
PHI = (RML - RR) * Ro / DEL
```

```
IF PHI <= 1 THEN
```

```
PHI = 1
```

```
END IF
```

```
FI1 = FI1 * PHI
```

```
END SUB
```

```
SUB FS (XD, DENB, DENV, VISB, VISV, RE, f, s, RETP, DH)
```

```
XT = .08255: XH = .216 + XT
```

```
IF XD <= 0 THEN
```

```
f = 1
```

```
GOTO 6
```

```
END IF
```

```
XTT = ((1 - XD) / XD) ^ .9 * SQR(DENV / DENB)
```

```
XTT = XTT * (VISB / VISV) ^ .1
```

```
f = 2.35 * (1 / XTT + .213) ^ .736
```

```
IF f <= 1 THEN f = 1
```

```
6 RETP = RE * (1 - XD) * f ^ 1.25
```

```
s = 1 / (1 + 2.53 * 10 ^ (-6) * RETP ^ 1.17)
```

```
END SUB
```

```
SUB FTURB (F1, RE, DH)
```

```
XT = .08255: XH = .216 + XT
```

```
F1 = 1 / (1.5635 * LOG(RE / 7)) ^ 2
```

```
END SUB
```

```
SUB INPUTSTR (int$, legal$)
```

```
int$ = ""
```

```
DO
```

```
s$ = INPUT$(1)
```

```
IF s$ = CHR$(13) THEN
```

```
EXIT DO
ELSEIF s$ = CHR$(8) AND LEN(int$) <> 0 THEN
xz = POS(0)
yz = CSRLIN
LOCATE yz, xz - 1
PRINT " ";
xz = POS(0)
yz = CSRLIN
LOCATE yz, xz - 1
int$ = LEFT$(int$, LEN(int$) - 1)
ELSE
FOR i = 1 TO LEN(legal$)
IF s$ = MID$(legal$, i, 1) THEN
int$ = int$ + s$
PRINT s$;
EXIT FOR
END IF
NEXT i
END IF
LOOP WHILE s$ <> CHR$(13)
END SUB
```

```
SUB LAMI (PR, PHI, GR, RE, NUL, DH, RR)
'R = .4200787402#: Ro = .0127: Ri = R * Ro
XT = .08255: XH = .216 + XT
RES = SQR(RE ^ 2 + GR / 2.5)
GZ = RES * PR * DH / XT
CALL FLAMI(FI, RES, DH, RR)
FIRE = FI * RES
NUD = 6.487912
NUP = 6.547736
M = .5 - .3 / (1 + .8 * PHI ^ .413)
NU1 = 6 * (NUP - NUD) * M + 3 * NUD - 2 * NUP
NU2 = .517 * FIRE ^ (1 / 3)
NU2 = NU2 * GZ ^ M
NUL = (NU1 ^ 3 + NU2 ^ 3) ^ (1 / 3)
```

END SUB

SUB PHYSL (K0\$, t, Ts, C, VIS, DEN, CP, TC)

TI = t

IF t >= Ts THEN t = Ts

IF K0\$ = "H2O" OR K0\$ = "h2o" THEN 100

b0 = 1.78456: b1 = -.057112: b2 = 1.148143 * 10 ^ (-3)

b3 = -1.39809 * 10 ^ (-5): b4 = 9.42404 * 10 ^ (-8)

b5 = -3.010709 * 10 ^ (-10): b6 = 2.94707 * 10 ^ (-13)

VIS = b0 + b1 * t + b2 * t ^ 2 + b3 * t ^ 3 + b4 * t ^ 4 + b5 * t ^ 5

VIS = (VIS + b6 * t ^ 6) / 1000

100 IF K0\$ = "KNO3" OR K0\$ = "kno3" THEN

e0 = 1.006857: e1 = .002698: E2 = -1.797861 * 10 ^ (-4)

e3 = 5.399037 * 10 ^ (-4): e4 = -3.251041 * 10 ^ (-6)

DEN = e0 + e1 * (C * 100 / 958.1) + E2 * t + e3 * (C * 100 / 958.1) ^ 2

DEN = (DEN + e4 * t ^ 2) * 999.8

a0 = .964456: a1 = -.050786: a2 = .001176: a3 = .023156

a4 = 1.286 * 10 ^ (-5)

FV = a0 + a1 * (1000 * C / ((DEN * 101) - (C * 101))) + a2 * t

FV = FV + a3 * (1000 * C / ((DEN * 101) - (C * 101))) ^ 2 + a4 * t ^ 2

VIS = FV * VIS

CP = 4.172 - .0443 * (C * 100 / DEN)

CP = (CP + 421.2 * 10 ^ (-6) * (C * 100 / DEN) ^ 2) * 1000

TC = (1 - .00347 * (C * 100 / DEN))

TC = TC * (.5672 + .001934 * t - 7.9146 * 10 ^ (-6) * t ^ 2)

t = TI

END IF

IF K0\$ = "NA2SO4" OR K0\$ = "na2so4" THEN

a0 = 1.010099: a1 = .260567: a2 = 4.4472 * 10 ^ (-4)

a3 = .28488: a4 = -5.43514 * 10 ^ (-6)

e0 = 1.006917: e1 = .005204: E2 = -1.341766 * 10 ^ (-4)

e3 = 5.386546 * 10 ^ (-4): e4 = -3.143231 * 10 ^ (-6)

DEN = e0 + e1 * (C * 100 / 958.1) + E2 * t + e3 * (C * 100 / 958.1) ^ 2

DEN = (DEN + e4 * t ^ 2) * 999.8

FV = a0 + a1 * (1000 * C / ((DEN * 142) - (C * 142)))

FV = FV + a2 * (1000 * C / ((DEN * 142) - (C * 142))) ^ 2

```

FV = FV + a3 * (1000 * C / ((DEN * 142) - (C * 142))) ^ 3
FV = FV + a4 * (1000 * C / ((DEN * 142) - (C * 142))) ^ 4
VIS = FV * VIS
CP = 4.167 - 47.36 * 10 ^ (-3) * (C * 100 / DEN)
CP = (CP + 675 * 10 ^ (-6) * (C * 100 / DEN) ^ 2) * 1000
TC = (1 - .0002 * (C * 100 / DEN))
TC = TC * (.5672 + .00193 * t - 7.9146 * 10 ^ (-6) * t ^ 2)
END IF
IF K0$ = "NACL" OR K0$ = "nacl" THEN
a0 = .977479; a1 = .057527; a2 = .001331; a3 = .021254
a4 = -7.121041 * 10 ^ (-6)
e0 = 1.007913; e1 = .003451; E2 = -1.531018 * 10 ^ (-4)
e3 = 3.838497 * 10 ^ (-4); e4 = -2.991744 * 10 ^ (-6)
DEN = e0 + e1 * (C * 100 / 958.1) - E2 * t + e3 * (C * 100 / 958.1) ^ 2
DEN = (DEN + e4 * t ^ 2) * 999.8
FV = a0 + a1 * (1000 * C / ((DEN * 58.5) - (C * 58.5))) + a2 * t
FV = FV + a3 * (1000 * C / ((DEN * 58.5) - (C * 58.5))) ^ 2 + a4 * t ^ 2
VIS = FV * VIS
e20 = 4.66065; e21 = -.194571; e22 = .001355
e23 = .010072; e24 = -3.411203 * 10 ^ (-6)
CP = e20 + e21 * (C * 100 / DEN) + e22 * t + e23 * (C * 100 / DEN) ^ 2
CP = (CP + e24 * t ^ 2) * 1000
TC = (1 - .00248 * (C * 100 / DEN))
TC = TC * (.567 + .0019344 * t - 7.915 * 10 ^ (-6) * t ^ 2)
END IF
IF K0$ = "CASO4" OR K0$ = "caso4" THEN
CNA = 142 * C / 136
CCA = 164 * C / 136
a0 = 1.010099; a1 = .260567; a2 = 4.4472 * 10 ^ (-4)
a3 = .28488; a4 = -5.43514 * 10 ^ (-6)
e0 = 1.006917; e1 = .005204; E2 = -1.341766 * 10 ^ (-4)
e3 = 5.386546 * 10 ^ (-4); e4 = -3.143231 * 10 ^ (-6)
a50 = -.0041873286#; b50 = 4.109862 * 10 ^ (-5); c50 = .0073115705#
d50 = 1.0053825# * 10 ^ (-5); e50 = 1.1523134# * 10 ^ (-5)
f50 = -1.8730408# * 10 ^ (-7)
a60 = -.00551639943#; b60 = -7.3519229000000001D-02; c60 = .22923618#

```


$d60 = .013011551\#; e60 = .013462082\#$
 $a70 = -3.838 * 10^{(-1)}; b70 = 5.254 * 10^{(-3)}; c70 = -6.369 * 10^{(-6)}$
 $a51 = a50 + c50 * (CCA * 100 / 958.1) + e50 * (CCA * 100 / 958.1)^2$
 $a52 = 1 + b50 * (CCA * 100 / 958.1) + d50 * (CCA * 100 / 958.1)^2$
 $a52 = a52 + f50 * (CCA * 100 / 958.1)^3$
 $DENH = 999.83952\# + 16.945176\# * t - 7.9870401\# * 10^{(-3)} * t^2$
 $DENH = DENH - 46.170461\# * 10^{(-6)} * t^3 + .00000010556302\# * t^4$
 $DENH = DENH - 208.54253\# * 10^{(-12)} * t^5$
 $DENH = DENH / (1 + 16.87985 * 10^{(-3)} * t)$
 $CPH = (4.216 - 1.25142 * 10^{(-3)} * t + 1.2469442\# * 10^{(-5)} * t^2)$
 $CPH = CPH * 1000$
 $TCH = (.5672 + .00193 * t - 7.9146 * 10^{(-6)} * t^2)$
 $DENNA = e0 + e1 * (CNA * 100 / 958.1) + E2 * t$
 $DENNA = (DENNA + e3 * (CNA * 100 / 958.1)^2 + e4 * t^2) * 999.8$
 $DENCA = EXP(a51 / a52) * DENH$
 $FV = a0 + a1 * (1000 * CNA / ((DENNA * 142) - (CNA * 142)))$
 $FV = FV + a2 * (1000 * CNA / ((DENNA * 142) - (CNA * 142)))^2$
 $FV = FV + a3 * (1000 * CNA / ((DENNA * 142) - (CNA * 142)))^3$
 $FV = FV + a4 * (1000 * CNA / ((DENNA * 142) - (CNA * 142)))^4$
 $VISNA = FV * VIS$
 $VISCA = EXP((a60 + c60 * (CCA / 164) + e60 * (CCA / 164)^2) / (1 + b60 * (CCA / 164) + d60 * (CCA / 164)^2))$
 $VISCA = VISCA * VIS$
 $CPNA = 4.167 - 47.36 * 10^{(-3)} * (CNA * 100 / DENNA)$
 $CPNA = (CPNA + 675 * 10^{(-6)} * (CNA * 100 / DENNA)^2) * 1000$
 $CPCA = 4.185 - 37.61 * 10^{(-3)} * (CCA * 100 / DENCA)$
 $CPCA = (CPCA + 29.04 * 10^{(-6)} * (CCA * 100 / DENCA)^2) * 1000$
 $TC = a70 + b70 * 293 + c70 * 293^2 + ((CNA / 142) * 1.163 * 10^{(-5)})$
 $TC = TC + ((CCA / 164) * 2 * (-6.978 * 10^{(-5)}))$
 $TC = TC + ((CCA / 164) * (-.5815 * 10^{(-5)}))$
 $TC = TC * (a70 + b70 * (t + 273) + c70 * (t + 273)^2)$
 $TC = TC / (a70 + b70 * 293 + c70 * 293^2)$
 $DDENNA = ABS(DENNA - DENH)$
 $DDENCA = ABS(DENCA - DENH)$
 $DEN = DDENNA + DDENCA + DENH$
 $DVISNA = ABS(VISNA - VIS)$

```

DVISCA = ABS(VISCA - VIS)
VIS = VIS + DVISNA + DVISCA
DCPNA = ABS(CPNA - CPH)
DCPCA = ABS(CPCA - CPH)
CP = CPH - DCPNA - DCPCA
END IF
IF K0$ = "H2O" OR K0$ = "h2o" THEN
C1 = (EXP(4.502 * (C / 958.1) ^ 1.46) - EXP(-4.502 * (C / 958.1) ^ 1.46)) / 2
C2 = (EXP(4.801 * (C / 958.1) ^ 1.482) + EXP(-4.801 * (C / 958.1) ^ 1.482)) / 2
CB1 = (1.3272 * (20 - t) - .001053 * (t - 20) ^ 2) / (t + 105)
CB1 = CB1 + (LOG(1.002) / LOG(10))
VIS = 10 ^ (C1 + C2 * CB1) / 1000
DEN = 999.83952# + 16.945176# * t - 7.9870401# * 10 ^ (-3) * t ^ 2
DEN = DEN - 46.170461# * 10 ^ (-6) * t ^ 3 + .00000010556302# * t ^ 4
DEN = DEN - 208.54253# * 10 ^ (-12) * t ^ 5
DEN = DEN / (1 + 16.87985 * 10 ^ (-3) * t)
DEN = DEN * (1 + (C / 958.1) * (.571 + .00008 * t))
CP = 4.216 - 1.25142 * 10 ^ (-3) * t + 1.2469442# * 10 ^ (-5) * t ^ 2
CP = (CP - (C / DEN) * (2.58962 - .00482 * t)) * 1000
TC = .577 + 1.57947 * 10 ^ (-3) * t - 5.7944545# * 10 ^ (-6) * t ^ 2
TC = TC - (C / DEN) * (.344 - .00105 * t)
END IF
t = TI
END SUB

SUB PHYSV (K0$, TSN, BPR, C, P, VISV, DENV, Ts, HV, SIG, DENL)
R1 = 8.314: MR = 18.02: TC = 647.25: PC = 221.19: PN = 1.01325
IF K0$ = "NA2SO4" OR K0$ = "na2so4" THEN
a01 = 4.06521: b01 = -.8922: C01 = -3.604: d01 = .26357: e01 = 1.06176
x = (C / 142) / ((C / 142) + (1000 / 18))
n1 = C / 142
BPR = x * EXP((a01 + C01 * n1 + e01 * n1 ^ 2) / (1 + b01 * n1 + d01 * n1 ^ 2))
END IF
IF K0$ = "KNO3" OR K0$ = "kno3" THEN
a01 = 48.517932#: b01 = -.75847819000000001#: C01 = -38.880019#: d01 = .14531608#
e01 = 8.6742366#: f01 = 8.2512149999999999D-03

```

```

x = (C / 101) / ((C / 101) + (1000 / 18))
n1 = C / 101
BPR = (a01 + C01 * LOG(n1) + e01 * (LOG(n1)) ^ 2) / (1 + b01 * LOG(n1) + d01 * (LOG(n1))
^ 2 + f01 * (LOG(n1)) ^ 3)
BPR = x * BPR
END IF
IF K0$ = "NACL" OR K0$ = "nacl" THEN
a01 = 30.417723#: b01 = 14.580338#: C01 = -.35317605#
d01 = -9.529851499999999#: e01 = 10.120849#
x = (C / 58.5) / ((C / 58.5) + (1000 / 18))
n1 = C / 58.5
BPR = x * (a01 + b01 * n1 + C01 * n1 ^ 2 + d01 * (LOG(n1)) ^ 2 + (e01 / n1))
END IF
IF K0$ = "CASO4" OR K0$ = "caso4" THEN
CNA = 142 * C / 136
CCA = 164 * C / 136
a001 = 69.827414#
b001 = 111.59911#
C001 = 6.0830647#
d001 = -2.0568267#
xCA = (CCA / 164) / ((CCA / 164) + (957.0452 / 18))
nCA = CCA / 164
BPR1 = xCA * (a001 + (b001 / (1 + (nCA / C001) ^ d001)))
a002 = 4.06521
b002 = -.8922
c002 = -3.604
d002 = .26357
e002 = 1.06176
xNA = (CNA / 142) / ((CNA / 142) + (957.0452 / 18))
nNA = CNA / 142
BPR2 = xNA * EXP((a002 + c002 * nNA + e002 * nNA ^ 2) / (1 + b002 * nNA + d002 * nNA ^
2))
BPR = BPR1 + BPR2
END IF
IF K0$ = "H2O" OR K0$ = "h2o" THEN
BPR = 0

```

```

END IF
TSN = 100 + BPR
VISV = 11.072725# + 1.437297 * P - .28868544# * P ^ 2
VISV = (VISV + .024571084# * P ^ 3) * 10 ^ (-6)
HV = (2.0935 * (LOG(PC) - 1)) / (.93 - (TSN + 273.15) / TC)
HV = HV * (TSN + 273.15) * 4.184 / MR * 1000
F1 = (273.15 + TSN) * LOG(P / PN) * (.041 * P / PN + .942)
F2 = HV * MR / 1000 / (R1 * (TSN + 273.15))
F2 = F2 - .15 * LOG(P / PN)
Ts = TSN + F1 / F2
F3 = ((1 - (Ts + 273.15) / TC) / (1 - (TSN + 273.15) / TC)) ^ .32
HV = HV * F3
DENV = P / (R1 * 10 * (Ts + 273.15)) * MR * 1000
IF K0$ = "H2O" OR K0$ = "h2o" THEN 90
a11 = .075638354#: b11 = -.00011762489#: c11 = -4.4935482# * 10 ^ (-6)
d11 = -2.2612554# * 10 ^ (-9): e11 = -3.175688 * 10 ^ (-5)
SIG = a11 + b11 * Ts + c11 * Ts ^ 1.5 + d11 * Ts ^ 2.5 + e11 * Ts ^ .5
90 IF K0$ = "KNO3" OR K0$ = "kno3" THEN
e0 = 1.006857: e1 = .002698: E2 = -1.797861 * 10 ^ (-4)
e3 = 5.399037 * 10 ^ (-4): e4 = -3.251041 * 10 ^ (-6)
DENL = e0 + e1 * (C * 100 / 958.1) + E2 * Ts + e3 * (C * 100 / 958.1) ^ 2
DENL = (DENL + e4 * Ts ^ 2) * 999.8
a12 = 1.9034319# * 10 ^ (-5): b12 = .01564662#
c12 = 11.478203#: d12 = -1.0923545#
SIG = SIG + a12
SIG = SIG + (b12 / (1 + ((1000 * C / ((DENL * 101) - (C * 101)))) / c12) ^ d12))
END IF
IF K0$ = "NA2SO4" OR K0$ = "na2so4" THEN
e0 = 1.006917: e1 = .005204: E2 = -1.341766 * 10 ^ (-4)
e3 = 5.386546 * 10 ^ (-4): e4 = -3.143231 * 10 ^ (-6)
DENL = e0 + e1 * (C * 100 / 958.1) + E2 * Ts + e3 * (C * 100 / 958.1) ^ 2
DENL = (DENL + e4 * Ts ^ 2) * 999.8
a12 = .0027301863#: b12 = 1.00609
SIG = SIG + a12 * (1000 * C / ((DENL * 142) - (C * 142))) ^ b12
END IF
IF K0$ = "NACL" OR K0$ = "nacl" THEN

```

```

e0 = 1.007913; e1 = .003451; E2 = -1.531018 * 10 ^ (-4)
e3 = 3.838497 * 10 ^ (-4); e4 = -2.991744 * 10 ^ (-6)
DENL = e0 + e1 * (C * 100 / 958.1) - E2 * Ts + e3 * (C * 100 / 958.1) ^ 2
DENL = (DENL + e4 * Ts ^ 2) * 999.8
a12 = 8.0414105# * 10 ^ (-6); b12 = .0016329249#
c12 = -2.4698565# * 10 ^ (-8); d12 = -5.003138 * 10 ^ (-8)
e12 = 1.1741137# * 10 ^ (-8)
SIG = SIG + a12 + b12 * (1000 * C / ((DENL * 58.5) - (C * 58.5)))
SIG = SIG + c12 * (1000 * C / ((DENL * 58.5) - (C * 58.5))) ^ 3
SIG = SIG + (d12 / ((1000 * C / ((DENL * 58.5) - (C * 58.5)))) ^ 1.5)
SIG = SIG + (e12 / ((1000 * C / ((DENL * 58.5) - (C * 58.5)))) ^ 2)
END IF
IF K0$ = "CASO4" OR K0$ = "caso4" THEN
CNA = 142 * C / 136
CCA = 164 * C / 136
e0 = 1.006917; e1 = .005204; E2 = -1.341766 * 10 ^ (-4)
e3 = 5.386546 * 10 ^ (-4); e4 = -3.143231 * 10 ^ (-6)
a50 = -.0041873286#; b50 = 4.109862 * 10 ^ (-5); c50 = .0073115705#
d50 = 1.0053825# * 10 ^ (-5); e50 = 1.1523134# * 10 ^ (-5)
f50 = -1.8730408# * 10 ^ (-7)
a51 = a50 + c50 * (CCA * 100 / 958.1) + e50 * (CCA * 100 / 958.1) ^ 2
a52 = 1 + b50 * (CCA * 100 / 958.1) + d50 * (CCA * 100 / 958.1) ^ 2
a52 = a52 + f50 * (CCA * 100 / 958.1) ^ 3
DENLH = 999.83952# + 16.945176# * Ts - 7.9870401# * 10 ^ (-3) * Ts ^ 2
DENLH = DENLH - 46.170461# * 10 ^ (-6) * Ts ^ 3 + 105.56302# * 10 ^ (-9) * Ts ^ 4
DENLH = DENLH - 208.54253# * 10 ^ (-12) * Ts ^ 5
DENLH = DENLH / (1 + 16.87985 * 10 ^ (-3) * Ts)
DENLNA = e0 + e1 * (CNA * 100 / 958.1) + E2 * Ts + e3 * (CNA * 100 / 958.1) ^ 2
DENLNA = (DENLNA + e4 * Ts ^ 2) * 999.8
DENLCA = EXP(a51 / a52) * DENLH
DDENLNA = DENLNA - DENLH
DDENLCA = DENLCA - DENLH
DDENL = DDENLNA + DDENLCA
DENL = DENLH + DDENL
F4NA = 52.1 * (1 - .456 * (CNA / 958.1) ^ .377)
SIGNA = .001 * (F4NA * (DENLNA / (1000 * MR) - DENV / (1000 * MR))) ^ 4

```

```

F4CA = 52.1 * (1 - .456 * (CCA / 958.1) ^ .377)
SIGCA = .001 * (F4CA * (DENLCA / (1000 * MR) - DENV / (1000 * MR))) ^ 4
SIGH = .001 * (52.1 * (DENLH / (1000 * MR) - DENV / (1000 * MR))) ^ 4
DSIGNA = SIGNA - SIGH
DSIGCA = SIGCA - SIGH
DSIG = DSIGNA + DSIGCA
SIG = SIGH + DSIG
END IF
IF K0$ = "H2O" OR K0$ = "h2o" THEN
DENL = 999.83952# + 16.945176# * Ts - 7.9870401# * 10 ^ (-3) * Ts ^ 2
DENL = DENL - 46.170461# * 10 ^ (-6) * Ts ^ 3 + 105.56302# * 10 ^ (-9) * Ts ^ 4
DENL = DENL - 208.54253# * 10 ^ (-12) * Ts ^ 5
DENL = DENL / (1 + 16.87985 * 10 ^ (-3) * Ts)
DENL = DENL * (1 + (C / 958.1) * (.571 + .00008 * Ts))
F4 = 52.1 * (1 - .456 * (C / 958.1) ^ .377)
SIG = .001 * (F4 * (DENL / (1000 * MR) - DENV / (1000 * MR))) ^ 4
END IF
END SUB

SUB STRENGTH (CCA, CB, ION)
*****
!* THIS PROGRAM CALCULATES THE CONCENTRATIONS OF IONS *
!* *
!* IN THE SOLUTION AND IONIC STRENGTH OF THE SOLUTION AS *
!* *
!* AN INPUT TO SOLMINEQ88 SOFTWARE *
!* *
*****

xx = CB
yy = HCO3
zz = 0      'KNO3 Concentration
cal = 1.7346 * .1697 * xx
no31 = 1.7346 * .5251 * xx
na1 = 1.0433 * .3237 * xx
so41 = 1.0433 * .6763 * xx

```

```
ca2 = 2.3594 * .1697 * yy
no32 = 2.3594 * .5251 * yy
na2 = 1.0589 * .4338 * yy
co32 = 1.0589 * .5662 * yy
```

```
k = .38672 * zz
no33 = .61328 * zz
```

```
ca = ca1 + ca2
no3 = no31 + no32 + no33
na = na1 + na2
so4 = so41
co3 = co32
```

```
ION = .5 * (4 * ca / 40.08 + no3 / 62.0049 + na / 22.98977 + 4 * so4 / 96.0576 + 4 * co3 /
60.0092 + k / 39.0983)
```

```
'PRINT : PRINT
'PRINT "CaSO4 (gr/l)="; x
'PRINT "CaCO3 (gr/l)="; y
'PRINT "KNO3 (gr/l)="; z
'PRINT "Ca (gr/l)="; ca
'PRINT "NO3 (gr/l)="; no3
'PRINT "Na (gr/l)="; na
'PRINT "SO4 (gr/l)="; so4
'PRINT "CO3 (gr/l)="; co3
'PRINT "K (gr/l)="; k
'LOCATE 2, 20: PRINT "Ionic Strength (mol/l)="; ION
'PRINT : PRINT : PRINT
END SUB
```

```
SUB TURB (PR, PHI, GR, RE, NUT, DH, RR)
'R = .4200787402#: Ro = .0127: Ri = R * Ro
XT = .08255: XH = .216 + XT
RES = SQR(RE ^ 2 + GR / 2.5)
CALL FTURB(f, RES, DH)
```

```
NUT = f / 2 * RES * PR
NUT = NUT / (1 + 12.7 * SQR(f / 2) * (PR ^ (2 / 3) - 1))
NUT = NUT * (1 + (1 / 3) * (DH / XT) ^ (2 / 3))
NUT = NUT * .86 * (1 / RR) ^ .16
NUT = NUT * PHI ^ .11
END SUB

SUB XDOT (HV, CP, QN, Md, DS, RE, PR, XD, NB, DH)
'R = .4200787402#: Ro = .0127: Ri = R * Ro
XT = .08255: XH = .216 + XT
NB = QN / (Md * HV)
PHO = -CP * DS / HV
DL = -PHO * DH / (4 * NB)
C = 1 / SQR((455 / (RE * PR)) ^ 2 + .0065 ^ 2)
PHN = -C * NB
DTH = DL - XT
PH = -4 * NB * DTH / DH
IF (PHN - PH) >= 0 THEN
XD = 0
GOTO 5
END IF
XD = PH - PHN * EXP(PH / PHN - 1)
5 END SUB
```



```

1 SCREEN 0: WIDTH 80: CLS : KEY OFF
5 PRINT "*****"
10 PRINT "*"
20 PRINT "*"
25 PRINT "          THE GAUSS SEIDEL METHOD"
30 PRINT "*"
35 PRINT "      FOR SIMULTANEOUS LINEAR ALGEBRAIC EQUATIONS"
40 PRINT "*"
44 PRINT "*"
50 PRINT "*"
90 PRINT "*****"

100 ***** Main Program *****

120 'Enter the number of equations, the coefficients, and constants
140 PRINT : PRINT "NUMBER OF EQUATIONS"; : INPUT N
150 DIM A(N, N + 1), B(N, N + 1), X(N), NPIVROW(N, 2), NPIVCOL(N, 2)
160 PRINT : PRINT "ENTER COEFFICIENTS AND CONSTANT FOR EACH EQUATION"
170 FOR K = 1 TO N
180 PRINT : PRINT "EQUATION "; K: PRINT
190 FOR J = 1 TO N
200 PRINT "  COEFFICIENT ("; K; ", "; J; ") = "; : INPUT B(K, J)
210 NEXT J
220 PRINT : PRINT "  CONSTANT "; K; " = "; : INPUT B(K, N + 1)
230 NEXT K
240 NC = N + 1
250 PRINT
260 PRINT "GIVE THE MIN. ALLOWABLE VALUE OF THE PIVOT ELEMENT"; : INPUT
EPS
270 PRINT CHR$(12)
280 DET = 1
290 FOR K = 1 TO N
300 FOR J = 1 TO NC
310 A(K, J) = B(K, J)
320 NEXT J: NEXT K
330 PRINT : PRINT

```

```
340 PRINT "*****"
350 PRINT "AUGMENTED MATRIX:"
360 GOSUB 2000
370 PRINT : INPUT "IS THE AUGMENTED MATRIX CORRECT(Y/N)"; Q$: PRINT
380 IF Q$ = "Y" OR Q$ = "y" THEN 450
390 PRINT "GIVE THE POSITION OF THE ELEMENT TO BE CORRECTED:": PRINT
400 INPUT "  ROW NUMBER"; NROW: INPUT "  COLUMN NUMBER"; NCOL
410 PRINT : INPUT "  CORRECT VALUE OF THE ELEMENT"; B(NROW, NCOL): PRINT
420 GOTO 270
430 '
440 'Beginning of the Gauss elimination procedure
450 INPUT "DO YOU WANT TO SEE STEP-BY-STEP RESULTS(Y/N)"; Q2$: PRINT
460 PRINT "*****"
470 FOR K = 1 TO N
480 'Apply complete pivoting strategy
490 MAXPIVOT = ABS(A(K, K))
500 NPIVROW(K, 1) = K: NPIVROW(K, 2) = K
510 NPIVCOL(K, 1) = K: NPIVCOL(K, 2) = K
520 FOR I = K TO N
530 FOR J = K TO N
540 IF MAXPIVOT >= ABS(A(I, J)) GOTO 580
550 MAXPIVOT = ABS(A(I, J))
560 NPIVROW(K, 1) = K: NPIVROW(K, 2) = I
570 NPIVCOL(K, 1) = K: NPIVCOL(K, 2) = J
580 NEXT J: NEXT I
590 IF MAXPIVOT >= EPS GOTO 610
600 PRINT "PIVOT ELEMENT SMALLER THAN"; EPS; "MATRIX MAY BE SINGULAR"
602 GOTO 910
610 IF NPIVROW(K, 2) = K GOTO 690
620 IF Q2$ = "Y" OR Q2$ = "y" THEN PRINT "PIVOTING ROWS:"
630 IF Q2$ = "Y" OR Q2$ = "y" THEN PRINT "INTERCHANGE ROWS "; NPIVROW(K, 2);
  " AND "; K
640 FOR J = K TO NC
650 SWAP A(NPIVROW(K, 2), J), A(K, J)

660 NEXT J
```

```
670 DET = DET * (-1)
680 IF Q2$ = "Y" OR Q2$ = "y" THEN GOSUB 2000
690 IF NPIVCOL(K, 2) = K GOTO 770
700 IF Q2$ = "Y" OR Q2$ = "y" THEN PRINT "PIVOTING COLUMNS:"
710 IF Q2$ = "Y" OR Q2$ = "y" THEN PRINT "INTERCHANGE COLUMNS "; NPIVCOL(K,
2); " AND "; K
720 FOR I = 1 TO N
730 SWAP A(I, NPIVCOL(K, 2)), A(I, K)
740 NEXT I
750 DET = DET * (-1)
760 IF Q2$ = "Y" OR Q2$ = "y" THEN GOSUB 2000
770 IF K = N THEN GOTO 880
780 IF Q2$ = "Y" OR Q2$ = "y" THEN PRINT "PERFORM ELIMINATION:"
790 FOR I = K + 1 TO N
800 IF Q2$ = "Y" OR Q2$ = "y" THEN PRINT "DIVIDE ROW "; K; " BY "; A(K, K)
810 IF Q2$ = "Y" OR Q2$ = "y" THEN PRINT "MULTIPLY ROW "; K; " BY "; A(I, K); "AND
SUBTRACT FROM ROW "; I
820 MULT = -A(I, K) / A(K, K)
830 FOR J = NC TO K STEP -1
840 A(I, J) = A(I, J) + MULT * A(K, J)
850 NEXT J
860 IF Q2$ = "Y" OR Q2$ = "y" THEN GOSUB 2000
870 NEXT I
880 NEXT K
900 'Apply the back-substitution formulas
910 RANK = K - 1: PRINT "RANK ="; RANK: NMR = N - RANK
920 IF RANK = N THEN X(N) = A(N, N + 1) / A(N, N): NCOUNT = N - 1: GOTO 970
930 PRINT "THE PROGRAM SETS "; NMR; " UNKNOWN(S) TO UNITY,"
940 PRINT "AND REDUCES THE PROBLEM TO FINDING OTHER "; RANK; "
UNKNOWN(S).";
950 FOR JJ = 1 TO NMR: X(N + 1 - JJ) = 1: NEXT JJ
960 NCOUNT = RANK
970 FOR I = NCOUNT TO 1 STEP -1
980 SUM = 0
990 FOR J = I + 1 TO N
1000 SUM = SUM + A(I, J) * X(J)
```

```

1010 NEXT J
1020 X(I) = (A(I, N + 1) - SUM) / A(I, I)
1030 NEXT I
1050 'Interchange the order of the unknowns to correct for the column pivoting
1060 FOR K = N TO 1 STEP -1
1070 SWAP X(NPIVCOL(K, 2)), X(NPIVCOL(K, 1))
1080 NEXT K
1100 'Evaluate the determinant of the matrix
1110 FOR I = 1 TO N
1120 DET = DET * A(I, I)
1130 NEXT I
1140 PRINT
*****

1150 PRINT : PRINT "RESULTS BY BACK SUBSTITUTION:": PRINT
1160 FOR J = 1 TO N
1170 PRINT "X("; J; ") ="; X(J)
1180 NEXT J
1190 PRINT : PRINT "VALUE OF DETERMINANT="; DET: PRINT
1200 PRINT
*****

1210 PRINT
*****

1220 PRINT : PRINT "DO YOU WANT TO REPEAT THE CALCULATIONS": PRINT
"WITH MINOR CHANGES TO THE COEFFICIENTS(Y/N)": : INPUT V$
1230 IF V$ = "Y" OR V$ = "y" THEN 1240 ELSE 1250
1240 CLS : GOTO 270
1250 PRINT : INPUT "DO YOU WANT TO RESET ALL THE COEFFICIENTS(Y/N)": W$
1260 IF W$ = "Y" OR W$ = "y" THEN 1270 ELSE 1300
1270 PRINT : INPUT "IS THE NEW SET OF THE SAME ORDER AS THE PREVIOUS SET";
WW$
1280 IF WW$ = "N" OR WW$ = "n" THEN PRINT CHR$(12): RUN 100
1290 CLS : GOTO 160
1300 PRINT : PRINT
1310 PRINT "***** END OF PROGRAM
*****

```

```
1320 END
2000 '***** Subroutine 1: Print the matrix *****'
2010 '
2020 FOR KA = 1 TO N
2030 PRINT
2040 FOR J = 1 TO NC
2050 PRINT A(KA, J),
2060 NEXT J: PRINT : NEXT KA: PRINT
2070 PRINT
'*****'
2080 FOR IPAUSE = 1 TO 3000: NEXT
2090 RETURN
```

CLS

```

*****
!* THIS PROGRAM TAKES THE EXPERIMENTAL HEAT TRANSFER COEFFICIENT *
!* AS AN INPUT DATA, THEN CALCULATES FORCED CONVECTION HEAT TRA- *
!* NSFER COEFFICIENT BY DIFFERENT CORRELATIONS AT ANY OPEARATING- *
!* CONDITION. FINALLY IT CALCULATES PERCENTAGE OF ERROR BY COMP- *
!* ARING THE EXPERIMENTAL DATA WITH THE CALCULATED DATA. *
!* *
*****

```

```

DIM a(5), b(5), C(5), d(5), e(5)

```

```

LOCATE 6, 26

```

```

COLOR 13

```

```

INPUT " NUMBER OF DATA POINTS ="; N

```

```

LOCATE 14, 27: COLOR 30: PRINT "1- "; : COLOR 10: PRINT "GNIELINSKI
CORRELATION"

```

```

LOCATE 16, 27: COLOR 30: PRINT "2- "; : COLOR 10: PRINT "DITTUS AND BOELTER
CORRELATION"

```

```

LOCATE 18, 27: COLOR 30: PRINT "3- "; : COLOR 10: PRINT "SIDER AND TATE
CORRELATION"

```

```

LOCATE 20, 27: COLOR 30: PRINT "4- "; : COLOR 10: PRINT "PETUKHOV
CORRELATION"

```

```

COLOR 13: LOCATE 10, 20: INPUT " WHICH CORRELATION DO YOU WANT TO USE=";
s

```

```

DIM u(N), Tb(N), Ts(N), alpha(N), er(N)

```

```

DIM rho(N), rhos(N), mu(N), mus(N), mur(N), cp(N), cps(N)

```

```

DIM k(N), ks(N), pr(N), prw(N), Re(N), f(N), Nu(N), h(N)

```

```

ers = 0

```

```

m = 0

```

```

'VELOCITY DATA ;(m/s)

```

```

*****

```

```

FOR i = 1 TO N

```

```
READ u(i)
NEXT i
DATA .4867,.6686,.8097,.9961,1.1294,1.3084,1.5020,1.6687,1.8626,2.0598,2.2059
```

'BULK TEMPERATURE DATA

```
FOR i = 1 TO N
READ Tb(i)
NEXT i
DATA 41.45,41.10,41.54,41.87,41.72,41.27,41.59,41.82,41.78,41.71,41.77
```

'SURFACE TEMPERATURE DATA

```
FOR i = 1 TO N
READ Ts(i)
NEXT i
DATA 60.69,60.39,60.43,60.59,60.20,60.39,60.37,60.13,60.22,60.41,60.09
```

'HEAT TRANSFER COEFFICIENT DATA

```
FOR i = 1 TO N
READ alpha(i)
NEXT i
DATA 3359,4280,4948,5904,6538,7769,9157,10343,12097,14244,16458
```

'DENSITY

```
FOR i = 1 TO 5
READ a(i)
NEXT i
DATA 999.77646,.0098659931,9.9440839,-1.459856e-5,-.023065188
```

'VISCOSITY

```
FOR i = 1 TO 5
READ b(i)
NEXT i
DATA .042331327,.015376373,-8.1041623e-5,-6.0199321e-5,-1.7109247e-7
```

'HEAT CAPACITY

```
FOR i = 1 TO 4
READ C(i)
NEXT i
DATA 4.21767,.000639862,-.0103793,3.69219e-8
```

'THERMAL CONDUCTIVITY

```
FOR i = 1 TO 5
READ d(i)
NEXT i
DATA .31585599,.0010962597,.0027556261,-2.6684057e-6,-9.458429e-6
```

'PRANDTL NUMBER

```
FOR i = 1 TO 5
READ e(i)
NEXT i
DATA 3.666841,.018093368,-.0056055632,-4.1235142e-5,7.0159279e-6
```

CLS

PRINT : PRINT

IF s = 0 OR s > 4 THEN 30

IF s = 1 THEN PRINT TAB(25); "GNIELINSKI CORRELATION": PRINT TAB(31); "
(x=0.2986)" ELSE

IF s = 2 THEN PRINT TAB(25); "DITTUS AND BOELTER CORRELATION" ELSE

IF s = 3 THEN PRINT TAB(25); "SIDER AND TATE CORRELATION" ELSE


```
IF s = 4 THEN PRINT TAB(25); "PETUKHOV CORRELATION"
```

```
PRINT
```

```
PRINT TAB(8); CHR$(201);
```

```
PRINT CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
CHR$(205); CHR$(205);
```

```
PRINT CHR$(205);
```

```
PRINT CHR$(203); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
CHR$(205); CHR$(205); CHR$(205);
```

```
PRINT CHR$(203); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
PRINT CHR$(203); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
PRINT CHR$(203); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
PRINT CHR$(203); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
CHR$(205); CHR$(205); CHR$(205); CHR$(205);
```

```
PRINT CHR$(205);
```

```
PRINT CHR$(187);
```

```
PRINT TAB(8); CHR$(186);
```

```
IF s = 1 THEN PRINT TAB(10); " u(m/s)"; TAB(18); CHR$(186); TAB(21); "Tb(C)"; TAB(27);
```

```
CHR$(186); TAB(30); "Ts(C)"; TAB(37); CHR$(186); TAB(39); "h(Exp.)"; TAB(47);
```

```
CHR$(186); TAB(50); "h(Gnie)"; TAB(58); CHR$(186); TAB(61); "ERROR%"; TAB(69);
```

```
CHR$(186); TAB(8); ELSE
```

```
IF s = 2 THEN PRINT TAB(10); " u(m/s)"; TAB(18); CHR$(186); TAB(21); "Tb(C)"; TAB(27);
```

```
CHR$(186); TAB(30); "Ts(C)"; TAB(37); CHR$(186); TAB(39); "h(Exp.)"; TAB(47);
```

```
CHR$(186); TAB(50); "h(D&B)"; TAB(58); CHR$(186); TAB(61); "ERROR%"; TAB(69);
```

```
CHR$(186); TAB(8); ELSE
```

```
IF s = 3 THEN PRINT TAB(10); " u(m/s)"; TAB(18); CHR$(186); TAB(21); "Tb(C)"; TAB(27);
```

```
CHR$(186); TAB(30); "Ts(C)"; TAB(37); CHR$(186); TAB(39); "h(Exp.)"; TAB(47);
```

```
CHR$(186); TAB(50); "h(S&T)"; TAB(58); CHR$(186); TAB(61); "ERROR%"; TAB(69);
```

```
CHR$(186); TAB(8); ELSE
```

```
IF s = 4 THEN PRINT TAB(10); " u(m/s)"; TAB(18); CHR$(186); TAB(21); "Tb(C)"; TAB(27);
```

```
CHR$(186); TAB(30); "Ts(C)"; TAB(37); CHR$(186); TAB(39); "h(Exp.)"; TAB(47);
```

```
CHR$(186); TAB(50); "h(Pet)"; TAB(58); CHR$(186); TAB(61); "ERROR%"; TAB(69);
```

```
CHR$(186); TAB(8);
```

```

PRINT CHR$(204); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
CHR$(205); CHR$(205); CHR$(205); CHR$(205);
PRINT CHR$(206); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
CHR$(205); CHR$(205); CHR$(205);
PRINT CHR$(206); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
CHR$(205); CHR$(205); CHR$(205); CHR$(205);
PRINT CHR$(206); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
CHR$(205); CHR$(205); CHR$(205); CHR$(205);
PRINT CHR$(206); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205); ;
PRINT CHR$(206); CHR$(205); CHR$(205); CHR$(205); CHR$(205); CHR$(205);
CHR$(205); ; CHR$(205); CHR$(205); CHR$(205); CHR$(205);
PRINT CHR$(185)

```

```

FOR j = 1 TO N STEP 1

```

```

rho(j) = ((a(1) + a(3) * Tb(j) + a(5) * Tb(j) ^ 2) / (1 + a(2) * Tb(j) + a(4) * Tb(j) ^ 2))

```

```

rhos(j) = ((a(1) + a(3) * Ts(j) + a(5) * Ts(j) ^ 2) / (1 + a(2) * Ts(j) + a(4) * Ts(j) ^ 2))

```

```

mu(j) = ((b(1) + b(3) * Tb(j) + b(5) * Tb(j) ^ 2) / (1 + b(2) * Tb(j) + b(4) * Tb(j) ^ 2)) ^ 2

```

```

mus(j) = ((b(1) + b(3) * Ts(j) + b(5) * Ts(j) ^ 2) / (1 + b(2) * Ts(j) + b(4) * Ts(j) ^ 2)) ^ 2

```

```

cp(j) = (C(1) + C(2) * Tb(j) + C(3) * Tb(j) ^ .5 + C(4) * Tb(j) ^ 3)

```

```

cps(j) = (C(1) + C(2) * Ts(j) + C(3) * Ts(j) ^ .5 + C(4) * Ts(j) ^ 3)

```

```

k(j) = ((d(1) + d(3) * Tb(j) + d(5) * Tb(j) ^ 2) / (1 + d(2) * Tb(j) + d(4) * Tb(j) ^ 2)) ^ .5

```

```

ks(j) = ((d(1) + d(3) * Ts(j) + d(5) * Ts(j) ^ 2) / (1 + d(2) * Ts(j) + d(4) * Ts(j) ^ 2)) ^ .5

```

```

pr(j) = ((e(1) + e(3) * Tb(j) + e(5) * Tb(j) ^ 2) / (1 + e(2) * Tb(j) + e(4) * Tb(j) ^ 2)) ^ 2

```

```

prw(j) = ((e(1) + e(3) * Ts(j) + e(5) * Ts(j) ^ 2) / (1 + e(2) * Ts(j) + e(4) * Ts(j) ^ 2)) ^ 2

```

```

COLOR 1

```

```

' CALCULATION OF HEAT TRANSFER COEFFICIENT

```

```

!*****

```

```

IF s = 1 THEN 1 ELSE

```

```

IF s = 2 THEN 2 ELSE

```

IF s = 3 THEN 3 ELSE

IF s = 4 THEN 4

'GNIELINSKI CORRELATION

1

$Re(j) = \rho(j) * u(j) * .01473 / \mu(j)$

$f(j) = (1.82 * \text{LOG}(Re(j)) / 2.302585 - 1.64) ^ (-2)$

IF $Re(j) < 2300$ OR $Re(j) > 1000000$ THEN GOTO 10 ELSE

IF $pr(j) < .6$ OR $pr(j) > 2000$ THEN GOTO 20 ELSE

$Nu(j) = (f(j) / 8) * (Re(j) - 1000) * pr(j) / (1 + 12.7 * (f(j) / 8) ^ .5 * (pr(j) ^ (2 / 3) - 1))$

$Nu(j) = Nu(j) * (1 + 1 / 3 * (.01473 / .2986) ^ (2 / 3))$

$Nu(j) = Nu(j) * (pr(j) / prw(j)) ^ .11$

$Nu(j) = Nu(j) * .86 * (1.067 / 2.54) ^ -.16$

$h(j) = Nu(j) * k(j) / .01473$

$er(j) = (h(j) - \alpha(j)) / h(j) * 100$

COLOR 2

PRINT TAB(8); CHR\$(179); : PRINT USING "##.####"; TAB(10); u(j);

PRINT TAB(18); CHR\$(179); : PRINT USING "###.##"; TAB(20); Tb(j);

PRINT TAB(27); CHR\$(179); : PRINT USING "###.##"; TAB(29); Ts(j);

PRINT TAB(37); CHR\$(179); : PRINT USING "#####"; TAB(40); alpha(j);

PRINT TAB(47); CHR\$(179); : PRINT USING "#####"; TAB(51); h(j);

PRINT TAB(58); CHR\$(179); : PRINT USING "##.#"; TAB(61); ABS(er(j));

PRINT TAB(69); CHR\$(179);

GOTO 5

'DITTUS AND BOELTER CORRELATION

2

$Re(j) = \rho(j) * u(j) * .01473 / \mu(j)$

$Nu(j) = .023 * Re(j) ^ (.8) * pr(j) ^ (.4)$

$h(j) = Nu(j) * k(j) / .01473$

$er(j) = (h(j) - \alpha(j)) / h(j) * 100$

COLOR 2

PRINT TAB(8); CHR\$(179); : PRINT USING "##.####"; TAB(10); u(j);

```

PRINT TAB(18); CHR$(179); : PRINT USING "###.##"; TAB(20); Tb(j);
PRINT TAB(27); CHR$(179); : PRINT USING "###.##"; TAB(29); Ts(j);
PRINT TAB(37); CHR$(179); : PRINT USING "#####"; TAB(40); alpha(j);
PRINT TAB(47); CHR$(179); : PRINT USING "#####"; TAB(51); h(j);
PRINT TAB(58); CHR$(179); : PRINT USING "##.#"; TAB(61); ABS(er(j));
PRINT TAB(69); CHR$(179);
GOTO 5

```

'SIDER AND TATE CORRELATION

```

3
Re(j) = rho(j) * u(j) * .01473 / mu(j)
Nu(j) = .027 * Re(j) ^ (.8) * pr(j) ^ (1 / 3) * (mu(j) / mus(j)) ^ (.14)
h(j) = Nu(j) * k(j) / .01473
er(j) = (h(j) - alpha(j)) / h(j) * 100
COLOR 2
PRINT TAB(8); CHR$(179); : PRINT USING "##.#####"; TAB(10); u(j);
PRINT TAB(18); CHR$(179); : PRINT USING "###.##"; TAB(20); Tb(j);
PRINT TAB(27); CHR$(179); : PRINT USING "###.##"; TAB(29); Ts(j);
PRINT TAB(37); CHR$(179); : PRINT USING "#####"; TAB(40); alpha(j);
PRINT TAB(47); CHR$(179); : PRINT USING "#####"; TAB(51); h(j);
PRINT TAB(58); CHR$(179); : PRINT USING "##.#"; TAB(61); ABS(er(j));
PRINT TAB(69); CHR$(179);
GOTO 5

```

'PETUKHOV CORRELATION

```

4
Re(j) = rho(j) * u(j) * .01473 / mu(j)
f(j) = (1.82 * LOG(Re(j)) / 2.302585 - 1.64) ^ (-2)
IF Re(j) < 10000 OR Re(j) > 5000000 THEN GOTO 10 ELSE
IF pr(j) < .5 OR pr(j) > 2000 THEN GOTO 20 ELSE
mur(j) = mu(j) / mus(j)
IF mur(j) < .08 OR mur(j) > 40 THEN GOTO 25 ELSE
Nu(j) = (f(j) / 8) * Re(j) * pr(j) / (1.07 + 12.7 * (f(j) / 8) ^ (.5) * (pr(j) ^ (2 / 3) - 1)) * (mu(j) /
mus(j)) ^ (.11)

```

```
h(j) = Nu(j) * k(j) / .01473
```

```
er(j) = (h(j) - alpha(j)) / h(j) * 100
```

```
COLOR 2
```

```
PRINT TAB(8); CHR$(179); : PRINT USING "##.####"; TAB(10); u(j);
```

```
PRINT TAB(18); CHR$(179); : PRINT USING "###.##"; TAB(20); Tb(j);
```

```
PRINT TAB(27); CHR$(179); : PRINT USING "###.##"; TAB(29); Ts(j);
```

```
PRINT TAB(37); CHR$(179); : PRINT USING "#####"; TAB(40); alpha(j);
```

```
PRINT TAB(47); CHR$(179); : PRINT USING "#####"; TAB(51); h(j);
```

```
PRINT TAB(58); CHR$(179); : PRINT USING "##.##"; TAB(61); ABS(er(j));
```

```
PRINT TAB(69); CHR$(179);
```

```
5
```

```
m = m + 1
```

```
ers = ers + ABS(er(j))
```

```
NEXT j
```

```
PRINT TAB(8); CHR$(192);
```

```
PRINT CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
CHR$(196); CHR$(196); CHR$(196);
```

```
PRINT CHR$(193); CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
CHR$(196); CHR$(196); CHR$(196);
```

```
PRINT CHR$(193); CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
PRINT CHR$(193); CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
PRINT CHR$(193); CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
PRINT CHR$(193); CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
CHR$(196); CHR$(196); CHR$(196); CHR$(196); CHR$(196);
```

```
PRINT CHR$(217);
```

```
aver = ers / m
```

```
COLOR 4: PRINT : PRINT : PRINT ; TAB(17); "ABSOLUT MEAN AVERAGE ERROR =";
```

```
aver
```

```
END
```

```
10 : PRINT : PRINT : COLOR 20
PRINT TAB(30); " WARNING!!"
PRINT TAB(20); " REYNOLDS NUMBER IS OUT OF RANGE": END
```

```
20 : PRINT : PRINT : COLOR 20
PRINT TAB(30); " WARNING!!"
PRINT TAB(20); " PRANDTL NUMBER IS OUT OF RANGE": END
```

```
25 : PRINT : PRINT : COLOR 20
PRINT TAB(30); " WARNING!!"
PRINT TAB(20); " VISCOSITIES RATIO IS OUT OF RANGE": END
30 COLOR 20: PRINT TAB(25); "WARNING!! YOU DON'T HAVE THIS CHOISE": END
```

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