PART VI

FOULING STUDIES IN PERSPECTIVE

PART VI - FOULING STUDIES IN PERSPECTIVE

1. INTRODUCTION

Twenty years ago it was observed by Kern and Seaton[1] that heat exchanger fouling tends to increase asymptotically with time. While subsequent studies[2-6] have confirmed this overall behaviour, there appears to be a lack of agreement on how velocity, for example, affects the deposition and fouling process. Most of the fouling systems studied have shown a unique relationship between the various fouling variables. This seems to indicate the complex nature of heat transfer fouling and questions if the subject can ever be treated in terms of fundamental principles.

The present studies of deposition and fouling are concerned with three systems; paraffin wax-kerosene solutions, silica in geothermal waters and particulate magnetite in demineralised water. These studies cover a spectrum of phenomena and provide information on the various processes governing the growth of deposits in fouling. So far in the Thesis these studies have been dealt with separately only. It is of importance to consider them together and in relation to other previous studies of relevance.

2. MECHANISMS

The main types of fouling identified in Part I (solubility, particulate, reaction, biological and corrosion) are classified according to the process that gives rise to the deposition, but not necessarily the controlling mechanism. For example, calcium carbonate fouling at heated surfaces is caused by decreasing solubility while the rate of fouling in one study was controlled by the transport of material towards the wall[7]. The crystallisation of calcium carbonate may also influence the overall fouling process. In most fouling situations the deposit build-up depends on a number of variables and it may not always be possible to identify a controlling mechanism.

In Part II it was shown that paraffin wax deposition and fouling depends on such variables as flowrate, concentration and temperature. The experimental data showed that deposition decreased with flowrate but increased with concentration and temperature difference. It was suggested that the deposition process is mainly controlled by the shear stress at the wall. This means that the deposit strength and therefore the wax crystallisation are important in the deposition mechanism. The cohesive properties of the wax deposit will determine

its strength. Therefore, the deposition resulted from reduced solubility at the wall while the amount depositing was controlled by the shear stress.

It is interesting to compare the paraffin wax and particulate magnetite deposition results. In Part V it was shown that the deposition of magnetite particles depends on flowrate and bulk temperature. The experimental data showed that the rate of deposition decreased with flowrate as in the paraffin wax situation. Apparently, the deposit build-up depends on the shear stresses at the wall rather than particle transport (mass transfer) toward the wall. However, there are indications that at low concentrations the rate of mass transfer becomes important. It was suggested in Part V that the bulk temperature affects the deposition process through some reaction mechanism. It is considered likely that this reaction involves the bonding between particles (adhesion/cohesion) in the deposit. The deposit strength increases with temperature just as the strength of paraffin wax deposits increases with decreasing temperature. Because the deposit strength is most important in both paraffin wax and magnetite deposition their velocity dependence is similar.

It is recognised that paraffin wax deposition involves a crystallisation process at the cold surface. Because the experimental work was conducted at similar cold wall temperatures there are no data available to show the effect of this temperature on the wax formation process.

Colloidal particles of magnetite in water develop a surface electrical charge by surface hydration followed by the dissociation of surface hydroxyls[8]. At neutral and alkaline conditions (pH > 6.5 at 25°C) the particles will be negatively charged from the acidic dissociation:

$$[M(OH)]_s + H_2O \rightleftharpoons [MO^-]_s + H_3O^+ \qquad \cdots \quad (1)$$

where M represents the bulk of magnetite. A particle of magnetite approaching a deposit layer at the wall with a similar surface charge, will therefore have to overcome a potential (repulsive) barrier before depositing. On deposition the surface charge will presumably redistribute rapidly. The bonding of the particle to the surface will involve an acid-base reaction that may depend on temperature. It is possible that a reaction of this type is responsible for the effect of temperature on the deposition of particulate magnetite at the present experimental conditions.

In conventional boilers and water cooled reactors the situation is probably not

all that different and the deposition of particulate magnetite may involve a surface reaction. Although the colloidal behaviour of particles at high temperatures are unclear, surface hydroxyls may play an important role in deposition. Ferrous hydroxide in solution at temperatures > 200°C is promptly converted to magnetite[9] according to the reaction[10]:

$$3Fe(OH)_2 \rightleftharpoons Fe_3O_4 + 2H_2O + H_2 \qquad \qquad \dots (2)$$

This is how magnetite in boilers is formed, either in bulk or at a surface. The material depositing may therefore be particulate and/or soluable. It is clear that ferrous hydroxide formed at a corroding surface may deposit directly as magnetite. In that case the deposition process depends on the dehydration reaction shown above. At temperatures where the dehydration reaction occurs spontaneously the deposition process is unlikely to show a temperature dependence. However, at lower temperatures (< 200°C) the deposition may depend on temperature. In situations where particulate and soluable products are depositing at the same time, the latter may provide a cementing action for the former, thus creating an adherent deposit.

A comparison of the deposition of ferrous hydroxide from solutions at high temperatures to that of dissolved silica in geothermal waters may be made. In Part III it was postulated that the deposition of geothermal silica could be controlled by the dehydration of silicic acid H_4SiO_4 according to the expression:

$$Si(OH)_4 \rightleftharpoons SiO_2 + 2H_2O \qquad \qquad \dots (3)$$

Clearly, the dehydration of silica and iron are analogus. The difference between the systems appears to be of degree rather than nature. Part IV on Rippled Deposits showed how silica and magnetite may deposit out to form rippled and highly adherent deposits in heat exchanger and boiler tubes and thereby underlining their similarity.

3. DEPOSITION - RELEASE MODEL

The asymptotic behaviour of fouling is described by the empirical expression[1]:

$$R_f = R_f^* [1 - \exp(-\beta t)] \qquad \qquad \dots (4)$$

where R_f and R_f^* are the fouling resistance during build-up and at asymptotic

conditions, respectively. The β is a reciprocal time constant and t the time. In recent deposition and fouling studies[2-6,11] a great emphasis has been placed on finding experimental relationships for R_f^* and β because R_f can then be calculated with time. However, the asymptotic fouling resistance R_f^* is probably of greatest interest to designers of heat transfer equipment[4].

Flowrate appears to be the most important variable in describing deposition and fouling processes. In Table 1 the experimental relationships obtained in the various studies are given. The mechanism stated as controlling the deposition is also shown. These will be considered in relation to the deposition-release model proposed in Part II on paraffin wax deposition and Part V on the deposition of particulate magnetite.

Most recent attempts to formulate deposition and fouling processes have been based on the mass balance expression:

$$\frac{dX}{dt} = \phi_d - \phi_r \qquad \qquad \cdots \cdots (5)$$

Where X is the dependent variable (usually R_f, w or x the fouling resistance and the amount of deposit and its thickness) and ϕ_d and ϕ_r the deposition and release functions, respectively. This basic approach has met with some success in predicting the growth of deposits with time[1-6,11,13]. The model proposed in the present work is a deposition-release model, and was developed to predict the experimental results of the paraffin-wax and magnetite system, both of which are considered to be mainly cohesion controlled. The model should also predict the adhesion controlled gas oil fouling given in Table 1. The proposed model is as follows:

$$\frac{dX}{dt} = k_1 sN - k_2 \frac{X}{u^*} \tau_w \qquad \qquad \cdots \cdots (6)$$

where
- s = Stickability
- N = Mass flux
- u^* = Friction velocity
- τ_w = Shear stress
- k_1 = Deposition coefficient
- k_2 = Release coefficient

In Parts II and V the velocity dependence of the stickability and mass flux are

TABLE 1

Experimental Relationships in Deposition and Fouling

System	$(\frac{dX}{dt})_{t=0}$	X*	β	Control	Reference
Gas Oil	W^{-1}	W^{-2}	W	Adhesion	2
Sand water	$W^{0.92}$	$W^{-1.2}$	$W^{1.9}$	Mass transfer	3
Calcium carbonate	$Re^{0.68}$	-	-	Mass transfer	7
Magnetite	$Re^{1.074}$	-	-	Roughness	12
Hematite	$W^{0.3}$	$W^{-0.9}$	-	Corrosion	6
Calcium carbonate	-	$u^{-1.33}$	-	-	5
Hematite	Re^{0}	$Re^{-1.75}$	$Re^{1.75}$	Attachment	11
Paraffin wax	-	Re^{-2}	-	Cohesion	Part II
Magnetite	W^{-1}	-	-	Cohesion	Part V

TABLE 2

Relationships Derived from the Deposition-Release Model

Model type	$(\frac{dX}{dt})_{t=0}$	X*	β
Adhesion-Cohesion	$(u^*)^{-1}$	$(u^*)^{-2}$	u^*
Mass Transfer	u^*	$(u^*)^{-1}$	$(u^*)^2$

suggested as $s \propto \tau_w^{-1}$ and $N \propto u^*$.

The resultant model relationships are given in Table 2. It is seen that at fully turbulent conditions ($u^* \propto u$) the model predicts the paraffin wax, magnetite and gas oil experimental data.

As already stated, the present model was developed for adhesion/cohesion controlled deposition. A feature of the model is the inclusion of a deposit strength term, achieved by dividing the release function by the friction velocity. In Part II on Paraffin Wax Deposition and Fouling it was shown that deposit strength was proportional to flowrate. However, if the fouling process is controlled by mass transfer (and not the strength of deposit) there is no reason to include the strength of deposit term in the model and the release function becomes $\phi_r \propto X \tau_w$ as in most other models[1,2,3,5,11]. At the same time, the deposition function becomes dependent on mass flux only and $\phi_d \propto N$ since $s \sim 1$. Most particles that reach the wall adhere. The resultant model relationships are given in Table 2. At turbulent conditions the model is the same as originally proposed by Kern and Seaton[1] and Watkinson and Epstein[3]. The sand-water[3] and one of the calcium carbonate[7] systems appear to be mass transfer controlled. The experimental relationships for the other systems are apparently controlled by more complex mechanisms than adhesion/cohesion or mass transfer only. Nevertheless, it is encouraging that three different systems (paraffin wax, magnetite and gas oil) show similar deposition-release relationships.

4. DEVELOPMENTS

Most of the subjects discussed in the Thesis are concerned with the specific systems (paraffin wax, geothermal silica, rippled surfaces, particulate magnetite) being considered. There are therefore subjects of general relevance to deposition and fouling that have not been discussed; particularly new developments. It is of value to mention a few of these because they may become important in future deposition and fouling studies.

Cleaver and Yates[14] have recently studied in great detail the deposition and release of suspended particles in turbulent flow. Their studies are based on descriptions of the fine structure of the laminar sublayer in turbulent flows. The analysis assumes that particles are convected into the sublayer by a coherent downsweep and are then either deposited at the wall or transported back into the flow by an outward burst. Cleaver and Yates show that wall shear stress τ_w is a controlling parameter in particle release from a deposit surface. A critical

shear stress is postulated and compared to experimental data. Below the critical shear stress the rate of deposition increases with velocity but decreases above the critical value. It should be pofitable to compare this with the results of Watkinson and Epstein[3] (see Part I Section 3.2) where the initial rate of deposition decreased dramatically above a certain flowrate[10]. The downsweep-burst model of Cleaver and Yates predicts that the deposition of initially clean surfaces increases asymptotically with time as in the deposition-release model. For very large particles (impaction regime[15]) the model shows the same velocity dependence as the mass transfer controlled model above. Gutman[16] has successfully applied the downsweep-burst model to the fouling of reverse osmosis membranes.

An important parameter in the deposition-release model is the stickability s. In situations where all particles at the wall deposit s $\sim$ 1 and the surface may be described as ideal. In most particle deposition studies ideal surfaces have been used. But real surfaces in deposition and fouling are not ideal and s < 1. This creates a problem when calculating the foulant mass flux towards the wall N in the deposition-release model where the concentration at the wall is assumed zero (see Part VI Section 4). Boundary conditions of this type are not true when s < 1 because there will be a finite foulant or particle concentration at the wall. Reeks and Skyrme[17] have shown that a formalism common in neutron transport theory may be applied to particle deposition where the stickability is less than unity. It is possible that the approach of Reeks and Skyrme may provide a framework for future studies involving variable stickability.

The analogy between heat, mass and momentum transfer is well established and has played an important role in the development of the subjects. There appears to be an analogy between annular two-phase flow and particulate fouling that may assume some importance as more is known about the two phenomena. In annular two-phase flow the film flowrate depends on such processes as droplet deposition and liquid entrainment[18]. The mass flux of droplets toward the wall is usually given by conventional expressions involving a mass transfer coefficient and droplet concentration. This is analogous to the mass flux of foulant toward the wall. It has been suggested[19] that liquid entrainment from annular films may be related to a function of the form (τ_i m/σ) where τ_i is the interfacial shear stress, m the film thickness, and σ the surface tension. This may be compared to the release of foulant from the wall given by (τ_w x/u*) in the present deposition-release model. As surface tension σ increases liquid entrainment becomes more difficult, just as increased fluid velocity increases

the (bond) strength of deposits. It is notable that in annular two-phase flow the pressure drop can be correlated to m/d, where d is the tube diameter, just as the pressure drop in rough tubes can be related to e/d where e is the height of roughness element[18,20].

Reverse osmosis may also provide an analogy with deposition and fouling processes. As water from the feedstream is withdrawn through the membrane, salt tends to build up at the surface of the membrane[11,16]. Various relationships have been derived for the mass flux of water through the membrane and the build-up of salts[21,22]. It is possible that similar relationships can be used to describe deposition and fouling.

5. CONCLUDING REMARKS

The three fouling and deposition systems studied in the present work have shown considerable similarity in mechanisms and overall behaviour. The paraffin wax and magnetite systems are apparently influenced greatly by the adhesion/cohesion properties of the deposits while the magnetite and silica systems involve a dehydration reaction mechanism. The fact that gas oil fouling exhibits the same velocity dependence as the paraffin wax and magnetite systems, suggests that there are certain basic mechanisms in fouling that apply to a variety of situations.

The basic mass balance approach of the deposition-release model has been shown to work well for a number of fouling systems, particularly where the fouling resistance increases asymptotically with time. In silica fouling the deposition increases linearily with time. However, when the deposit is rippled the fouling resistance curve is spoon-like in shape. Silica deposits are possibly so adherent that the release function is negligible in comparison to the deposition function. This is probably a special case of the deposition-release model where the deposition function is expressed in terms of a concentration driving force and a temperature dependent reaction rate constant.

NOMENCLATURE

d	:	Tube diameter (m)
e	:	Roughness height (m)
f	:	Friction factor $(= \tau_w / \frac{1}{2}\rho u^2)$
k_1	:	Deposition coefficient
k_2	:	Release coefficient
m	:	Film thickness (m)
N	:	Mass flux toward the wall (kg/m^{2}s)
R_f	:	Fouling resistance (kW/m^2°C)$^{-1}$
R_f^*	:	Asymptotic fouling resistance (kW/m^2°C)$^{-1}$
Re	:	Reynolds number $(= ud/\nu)$
s	:	Stickability
t	:	Time (s)
u	:	Bulk velocity (m/s)
u^*	:	Friction velocity (m/s)
w	:	Amount of deposit (mg/cm^2)
W	:	Mass flowrate (kg/s)
x	:	Deposit thickness (m)
X	:	Fouling dependent variable
β	:	Reciprocal time constant (s^{-1})
ρ	:	Fluid density (kg/m^3)
σ	:	Surface tension (N/m)
ν	:	Kinematic viscosity (m^2/s)
τ_i	:	Interfacial shear stress (N/m^2)
τ_w	:	Wall shear stress (N/m^2)
ϕ_d	:	Deposition function
ϕ_r	:	Release function

REFERENCES

1. Kern, D Q, Seaton, R E, "A Theoretical Analysis of Thermal Surface Fouling", Brit Chem Eng, 4 (5), 258, (1959), and "Surface Fouling, How to Calculate Limits", Chem Eng Prog, 55 (6), 71, (1959).

2. Watkinson, A P, Epstein, N, "Gas Oil Fouling in a Sensible Heat Exchanger", Chem Eng Prog Symp Ser, 65 (92), 84-90, (1969).

3. Watkinson, A P, Epstein, N, "Particulate Fouling of Sensible Heat Exchangers", 4th Int Heat Transfer Conf, Versailles, (1970).

4. Taborek, J, Aoki, T, Ritter, R B, Palen, J W, Knudsen, J G, "Fouling : The Major Unresolved Problem in Heat Transfer", Chem Eng Prog, 68 (2), 59-67, (1972), and "Predictive Methods for Fouling Behaviour", Chem Eng Prog, 68 (7), 69-78, (1972).

5. Watkinson, A P, Martinez, O, "Scaling of Heat Exchanger Tubes by Calcium Carbonate", J Heat Transfer, 97 (4), 504-508, (1975).

6. Hopkins, R M, Epstein, N, "Fouling of Heated Stainless Steel Tubes by a Flowing Suspension of Ferric Oxide in Water", 5th Int Heat Transfer Conf, 2, 180-184, Tokyo, (1974).

7. Hasson, D, Avriel, M, Resnick, W, Rosenman, T, Windreich, S, "Mechanism of Calcium Carbonate Scale Deposition on Heat-Transfer Surfaces", Ind Eng Chem Fundamentals, 7 (1), 59-65, (1968).

8. Parks, G A, "The Isoelectric Points of Solid Oxides, Solid Hydroxides and Aqueous Hydroxo Complex Systems", Chemical Reviews, 65, 177-197, (1965).

9. Kabanov, L, "Heat and Mass Transfer as Related to Corrosion Product Deposition", Energia Nucleare, 18 (5), 285-294, (1971).

10. Gudmundsson, J S, "A Review of Rippled Deposits in Supercritical Once-Through Boilers", AERE-R 8738, (1977).

11. Carter, J W, Hoyland, G, "The Build up of Rust Fouling Layers on Membranes in Reverse Osmosis Flow Systems and its Calculation", 5th Int Symp Fresh Water Sea, 4, 21-29, Alghero, (1976).

12. Thomas, D, Grigull, U, "Experimental Investigation of the Deposition of Suspended Magnetite from the Fluid Flow in Steam Generating Boiler Tubes", Brennst-Wärme-Kraft, 26 (3), 109-115, (1974), AERE Translation LB/G/407/21, (1974).

13. Charlesworth, D H, "The Deposition of Corrosion Products in Boiling Water Systems", Chem Eng Prog Symp Ser, 66 (104), 21-30, (1970).

14. Cleaver, J W, Yates, B, "The Effect of Re-Entrainment on Particle Deposition", Chem Eng Sci, 31, 147-151, (1976).

15. Gudmundsson, J S, Bott, T R, to be published in J Aerosol Sci, (1977).

16. Gutman, R G, "The Design of Membrane Separation Plant : Part I - Design of Reverse Osmosis Modules ; Part 2 - Fouling of RO Membranes", Chem Engr No 322, 510-513, 521-523, (1977).

17. Reeks, M W, Skyrme, G, "The Dependence of Particle Deposition Velocity on Particle Inertia in Turbulent Pipe Flow", J Aerosol Sci, 7 (6), 485-495, (1976).

18. Hewitt, G F, "Vertical Annual Flow", in "Two-Phase Flow and Heat Transfer", edited by D Butterworth and G F Hewitt, Oxford University Press, (1977).

19. Hutchinson, P, Whalley, P B, "A Possible Characterisation of Entrainment in Annular Flow", Chem Eng Sci, 28, 274-275, (1973).

20. Schlichting, H, "Boundary-Layer Theory", McGraw Hill, (1968).

21. Srinivasan, S, Tien, C, Gill, W N, "Simultaneous Development of Velocity and Concentration Profiles in Reverse Osmosis Systems", Chem Eng Sci, 22, 417-433, (1967).

22. Derzansky, L J, Gill, W N, "Mechanisms of Brine-Side Mass Transfer in a Horizontal Reverse Osmosis Tubular Membrane", AIChEJ 20 (4), 751-761, (1974).