SURFACE INTERACTIONS AND DEPOSIT GROWTH IN FOULING OF HEAT EXCHANGERS

R. Oliveira, L. Melo, M. Pinheiro, M.J. Vieira

University of Minho, CQPA/INIC, 4700 BRAGA - Portugal

CONTENTS

Page

ABSTRACT

Fouling of heat exchangers is a costly problem in industry. There is a need for a better understanding of the phenomena involved in the build up of deposits on surfaces.

The paper reviews the basic mechanisms of fouling, emphasizing their rôle in determining the overall fouling rate. Mass transfer, adhesion, chemical or biological reactions can be the rate limiting processes depending on the design and operating conditions of the heat exchanger. Reference is made to the most common types of fouling, particularly in water systems, and to their interaction with corrosion of metallic surfaces.

Special attention is devoted to adhesion, since the formation of fouling layers is primarily a surface process. The main forces of adhesion and the methods for predicting adhesion tendencies are reviewed.

The paper presents and discusses data obtained in laboratory studies on fouling caused by inorganic particles, by microorganisms, and also by both of these types of foulants acting simultaneously. Synergistic phenomena (positive and negative) seem to occur when two or more types of foulants are present in the fluid, but the final result is still unpredictable. Data on the effects of fluid velocity, temperature and surface material are also presented and discussed.

1.   INTRODUCTION

Fouling is the undesirable accumulation of solid substances on surfaces that are in contact with liquid or gases. It occurs very often in sensible heat exchangers, boilers, nuclear reactors, automobile radiators, separation membranes, cooling towers, etc. and is due to a great variety of phenomena such as: polymerization of hydrocarbons (chemical reaction fouling), precipitation of calcium or magnesium salts (crystallisation fouling), adhesion and growth of microorganisms (biological fouling), deposition of suspended particles (particulate fouling) and in-situ corrosion of metallic surfaces (corrosion fouling). The last four examples are common situations in cooling water systems.

It is worth noting that corrosion phenomena are involved in two different types of fouling: the immediate deposit formation as the electrochemical reactions on the mettalic surface are occuring (in-situ corrosion fouling) and the deposition of particles released from oxide layers formed upstream (particulate fouling)[38]. Frequently, in-situ corrosion develops together with other forms of fouling (see section 2).

The costs associated to fouling are usually high, mainly when heat exchange equipment is concerned. They may include: the cost due to the need of providing extra heat transfer area to allow for the increase in the overall thermal resistance; the cost of antifouling equipment (water pre-treatment systems, for instance); the increased energy consumption due to higher pressure drops and/or lower heat transfer efficiencies; the cost of production losses caused by unwanted plant shut-downs; the costs of maintenance and cleaning. Surveys published 10-15 years ago indicated that the overall fouling costs may amount to 0.2 - 0.3% of the gross national product of countries such as the United Kingdom and the United States of America[66,67].

2.   FOULING MECHANISMS

The build-up of fouling layers, as Kern and Seaton saw it [35], is the result of a competition between two distinct processes: deposition and removal. This concept may be applied to all types of fouling, if it is understood that:

i)   "deposition" involves:

.   the transport of substances (molecules, ions, inert particles, microorganisms) towards the solid surface

.   adhesion of the foulant to the surface

.   changes within the deposit (biological growth of microorganisms, chemical reactions, dehydration, etc)

ii) "removal" represents the release of portions of the deposit caused by the action of the fluid (shear stress, turbulent bursts, solubilisation), followed by the reintegration of the removed particles/molecules back into the fluid.

Identification of the mechanisms that govern the build-up of deposits is a key factor in the understanding and control of fouling. It can be said that the mechanisms involved in the deposition process are, in most cases, consecutive, that is, they act in series: e.g., the adhesion of particles occurs after they have been transported to the surface. In such situations the slower phenomenon is the limiting step of the deposition rate. On the other hand, when comparing the contributions of deposition and removal — which are parallel (simultaneous) processes — the faster one will prevail in determining the overall fouling rate and, thus, the amount of deposit that is obtained.

A number of laboratory studies — some of which are reported below — were undertaken to evaluate the role of the individual mechanisms in different situations.

In the case of particulate fouling caused by aqueous suspensions, Watkinson and Epstein[74] and Melo and Pinheiro[42], amongst others, found that mass transfer of sand or kaolin

particles to the surface seemed to control the deposition rate when the fluid velocities were low (< 0.5 m/s): in fact, deposition (not overall fouling!) increased with flow rate, following the usual trend of mass transfer phenomena. In this circumstance, the number of particles that reach the surface per unit time is small, and their adhesion is facilitated by the low shear stress at the wall region. For higher velocities, such as those usually encountered in heat exchangers, the picture is altogether different: adhesion appears to be the limiting step in the deposition process and its rate decreases when the flow rate is increased; at the same time, the higher the fluid velocity, the higher is the removal rate, and the final result is often a significant reduction in the amount of deposit formed.

In corrosion fouling, deposition includes oxygen transfer and electrochemical reaction at the surface. Together with removal, these are the most important mechanisms involved. Since the electrochemical reaction is rather fast, oxygen mass transfer is frequently the limiting step in deposition. Furthermore, as the deposit grows, diffusion of oxygen through the fouling layer to the metallic surface becomes more difficult and, finally, the build-up of the oxide layer stops[63]. Fluid velocity has in this case contradictory effects, since it increases both deposition (by enhancing oxygen transport) and removal.

In the case of biofouling, several phenomena may be considered in the deposition process: the transport of microorganisms and of nutrients to the surface; the adhesion of microorganisms; the consumption of nutrients in the biological deposit. It is difficult to detect the controlling mechanisms in such a case. For instance, although higher velocities will favour the transport of microorganisms and nutrients to the deposit, increasing its growth rate, they will, at the same time, reduce cell adhesion. Often, the deposition rate was found to decrease with increasing fluid velocities[33,55], but an opposite behaviour was detected when low nutrient concentration and low velocities were used[21]. However, there is a significant increase in the removal rate with fluid velocity, and this effect seems to prevail usually in the overall fouling process.

Studies have also been carried out to assess the effects of temperature, since, as in the case of fluid velocity, temperature is usually a rather easy parameter to control in laboratory experiments. In general, fouling rates were found to increase with the temperature level, since it has a positive effect on chemical reaction rates and on adhesion tendencies. However, in the case

of biofouling, the growth rate of microorganisms is reduced above an optimum temperature level. Also, when normal solubility salts exist in the fluid, higher temperatures tend to avoid their precipitation.

In order to draw a structured image of the controlling mechanisms within the deposition process, they may be classified into large categories:

. transport processes: transport mechanisms (molecular and turbulent diffusion, inertia);

. surface and reaction processes: adhesion, surface chemical reactions (e.g., catalysis), fluid chemical reactions (such as crystallisation), biological growth, dehydration, etc.

As a general rule, it can be said that low fluid velocities and higher temperatures favour the control of the deposition rate by the transport processes, while higher velocities and lower temperatures shift the control towards the surface and reaction processes[54].

The removal rate is usually enhanced by high fluid velocities, altough the latter also originate more compact deposits, which are more difficult to remove. The effects of temperature in the detachment of deposits are often associated to the increase/decrease of the solubility of the solids and to the development of thermal stresses producing cracks in the fouling layers.

Industrial cases are frequently more complex than the ones mentioned above, since two or more different types of foulants may act simultaneously: soluble species and suspended particles; microorganisms and corrosion products, etc. Obviously, the mechanisms involved in each type of fouling will interact giving rise to synergistic phenomena which are very difficult to predict. A few examples can be given:

. In general, adhesion is more easy where corrosion layers are formed, on account of their roughness (they present a great number of suitable places for the "anchorage" of particles and microorganisms).

. Suspended particles may favour the formation of crystallisation nucleii and, thus, enhance precipitation of inorganic salts dissolved in water[28].

. In most cases (neutral and basic pH), the electrical charges of particles in a deposit are negative. Further deposition of similar particles is reduced by the repulsion of like charges. However, if cations produced by the corrosion of fouled metallic surfaces

diffuse through the deposit, they may neutralise the charges at the surface and favour the adhesion of new particles[60].

. Taborek et al.[65] found that the formation of calcium carbonate deposits from cooling water streams was reduced if the water contained also suspended particles. This was due to the fact that the mixed deposit was less resistant to the hydrodynamic removal forces than a pure calcarium layer.

. Interactions between corrosion and biofouling have been reported frequently. Some of the bacteria detected in biological deposits produce sulfur compounds (sulfate reducing bacteria) or acids, which attack the surface in contact with the biofouling layer[34]. On the other hand, metallic ions from Zn, Al, Cu are believed to inhibit the reproduction of microorganisms or the activity of the adhesive biopolymers produced by some bacteria[62]. Oxide layers may however favour the adhesion of microorganisms, not only due to roughness effects, but also to the greater availability of oligoelements such as Fe.

3. PARTICULATE FOULING

3.1 General Model

When a fluid carrying suspended particles flows in contact with solid surfaces, the particles tend to be transported to the wall and, after adhering to it, to form a more or less stable deposit, subject to the fluid shear stress forces. Transport, adhesion and removal are, then, the basic phenomena in particulate fouling, the first two representing the deposition process.

According to Kern and Seaton, the deposition flux (ϕ_d - the amount of particles deposited per unit area and unit time) is constant with time, while the removal flux (ϕ_r - the amount of deposit detached per unit area and unit time) increases as the deposit grows, due to the growing presence of "zones of weakness". The overall fouling rate, expressed in terms of the thermal resistance of the deposit (R_f) can then be given by

$$\frac{dR_f}{dt} = \phi_d - \phi_r \qquad [1]$$

If ϕ_d = constant and $\phi_r = \beta.R_f$, where β is directly proportional to the fluid shear stress

at the surface, the integration of Equation 1 results in:

$$R_f = R_f^\infty [1 - \exp(-\beta.t)] \qquad [2]$$

where $R_f^\infty = \phi_d/\beta \qquad [3]$

is the asymptotic fouling resistance (for $t = \infty$).

3.2 Deposition

The first step in particulate deposition is the transport of particles from the bulk fluid to the solid-fluid interface.

Melo and Pinheiro[42], amongst other authors, assumed that the transport flux of particles to the surface (ϕ_t) could be expressed as:

$$\phi_t = \frac{k_t (C_b - C_s)}{\rho_f k_f} \qquad [4]$$

where k_t is the mass transfer coefficient, C_b is the bulk concentration of particles and C_s is their concentration at the interface solid/fluid. ρ_f and k_f are the density and thermal conductivity of the deposit; they are included in the equation in order to express the transport flux (ϕ_t) in terms of the increase in thermal resistance per unit time and unit area.

Often, the mass transfer coefficient is evaluated using well-known correlations for molecular and turbulent diffusion. However, if the particles are large or dense, inertia and impaction mechanism may have to be taken into account, but the models proposed for these situations are far from being accurate, as stated in several reviews on particle transport models published in the last years[22,44,53].

Melo and Pinheiro[42,44] obtained data on the deposition of kaolin particles from water suspensions flowing in the annular section of a concentric tube heat exchanger, at velocities between 0.26 and 1.3 m/s (Reynolds No. = 2300 to 11040). The exchanger, sketched in Figure 1, consisted of a 2 meter long external perspex tube (ID = 36 mm) and a removable inner copper tube (OD = 25 mm) electrically heated. Temperatures of the fluid and of the copper tube wall, as well as pressure drops and heat fluxes, were measured, allowing the evaluation of the local

thermal resistances of the kaolin deposits during the build-up process. All fouling tests were run at constant heat flux (3000 W/m^2), constant kaolin concentration (2.2 g/l), constant bulk water temperature (12 °C) and constant pH (7.5). The kaolin particles were studied with a laser flow granulometer and a scanning electron microscope and can be roughly described as thin discs with mean diameter = 16 µm and mean thickness = 1 µm, which corresponds to an "equivalent particle diameter" of 7 µm. By measuring the thickness, weight and thermal resistance of the deposits, the following values for their density and thermal conductivity were obtained: ρ_f = 420 kg/m^3, k_f = 0.17 W/m.K.
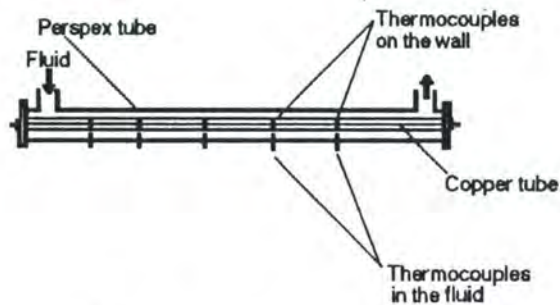

Figure 1 - Annular heat exchanger.

Fouling curves (R_f versus time), similar to the ones shown in Figure 2, were obtained at different Reynolds numbers.

By fitting equations 2 and 3 to the data, values for the deposition flux (ϕ_d) were evaluated at several points on the copper tube (Figure 3 shows only the results for the zone where the boundary layer was already fully developed). It seems that for low Reynolds numbers (less than 4000), mass transfer is the limiting step in the deposition process.

The transport flux in this range of low velocities was then evaluated using different mass transfer models[44]. An empirical expression similar to the classic mass transfer correlation of Linton and Sherwood[37] was found to describe the dependence of ϕ_t on the Reynolds number quite well:

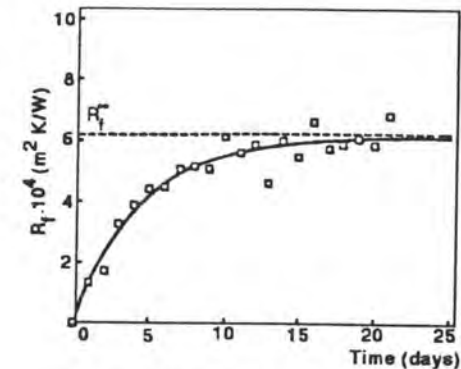$$Sh = 0.0465 \ Re^{0.74} \ Sc^{1/3} \qquad [5]$$

Figure 2 - Kaolin typical fouling curves.

The exponent on the Reynolds number is close to the usual turbulent diffusion dependence (0.8), indicating that this is the prevailing particle transport mechanism in the present case.

The "adhesion flux" (ϕ_a) - which is directly related to the number of particles adhering per unit time and unit area - is thought to be proportional to the concentration of particles near the surface[42]:

$$\phi_a = \frac{k_a \ C_s}{\rho_f \ k_f} \qquad [6]$$

where k_a is an adhesion rate coefficient.

A steady state is spontaneously attained between transport and adhesion, where:

$$\phi_t = \phi_a \equiv \phi_d \qquad [7]$$

In this case, after eliminating C_s in equations 4 and 6, the following expression is obtained:

$$\phi_d = \frac{C_b}{\rho_f \ k_f \ (1/k_t + 1/k_a)} \qquad [8]$$

k_t increases while k_a decreases with increasing fluid velocity. This means, for example, that when the velocity is high, adhesion will be the controlling mechanism:

$$k_t \gg k_a \quad \text{and} \quad \phi_d = \frac{k_a\, C_b}{\rho_f\, k_f} \tag{9}$$

The results shown in Figure 3 indicate that adhesion rates control deposition for Re > 4000 (fluid velocity > 0.4 m/s) since ϕ_d decreases with increasing Re. Liquid velocities in heat exchanger tubes are usually on the range of 1-3 m/s, meaning that adhesion is, as far as particulate fouling from Newtonian liquids is concerned, the most probable limiting step in the deposition process. Its study was undertaken in the case presented in Figure 3 (see section 3).
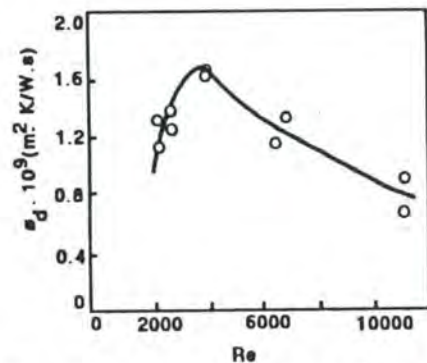

Figure 3 - Deposition flux versus Reynolds number.

It should be noted that equation 8 is similar, in its generic format, to the deposition model proposed by Beal[5], although this and other authors[74] used a different approach to define the deposition flux: they considered it to be the product of the transport flux by an "adhesion probability" ($0 \le S \le 1$), the latter being thought to be exponentially dependent on the absolute temperature (through an Arrhenius type expression) and inversely proportional to the shear stress exerted by the fluid at the solid/fluid interface. This confirms that adhesion is favoured by low fluid velocities and high temperatures.

Whichever model is used, there is always a great difficulty in predicting the parameters associated with the adhesion process (k_a, S). A necessary step is then to understand and to describe mathematically the adhesion forces, mainly particle/wall as well as particle/particle interactions. Due to its importance, a separate section of this paper (section 3.4) deals in more detail with relevant aspects of surface phenomena.

3.3   Removal

Removal rates are usually considered to increase with deposit thickness and with fluid shear stress at the surface, the latter depending on the square of the velocity. Nevertheless, since high velocities tend to originate greater cohesion within the fouling layer, the removal rates may be expected to depend on u^{2-a} rather than on u^2:

$$\phi_r = k_1\, f\, u^{2-a}\, R_f \tag{10}$$

where f is the friction factor. The problem here is how to evaluate parameters such as k_1, and a, which are related to the structure of the deposit. Once more, there is a need for a better quantitative description of the adhesion process, since a can be considered to be a measure of the cohesion of the fouling layer.

There is also a lack of knowledge as regards the effects of the hydrodynamic forces in deposit removal. Some studies on the structure of the boundary layer and on the mechanism of turbulent bursts brought some light to this problem, but reliable quantitative calculations are still not feasible[14,72,76].

Something may be said about the structure of the deposits.

Taborek et al[65] and Melo and Pinheiro[42] observed at least two distinct layers in the deposits: the inner one, near the wall, is hard and shows strong adherence, while the outer one, in contact with the fluid, is composed of loose particles which are more easily removed by the flowing fluid. In the case of the kaolin deposits, Melo and Pinheiro were able to quantify the mass percentage of each layer by performing tests where deposits obtained in the annular heat exchanger were subjected to increasing fluid velocities in a rotating cylinder apparatus[42]. The mass of deposit removed was evaluated at each rotating velocity. Values of the mass percentage of removed deposit were plotted against the rotating velocity (Figure 4), showing clearly the existence of a "loose non-adherent layer" in the outer part of the deposit (the one that was first removed in these experiments, using low rotating velocities). The inner zones were almost impossible to remove (the plateau zone in Figure 4), even when high shear stresses were applied. The fraction of "hard layer" seems to depend on the hydrodynamic conditions used in the formation of the deposit, ranging from 50% (for low Reynolds numbers) to 70% of the mass of the deposit.
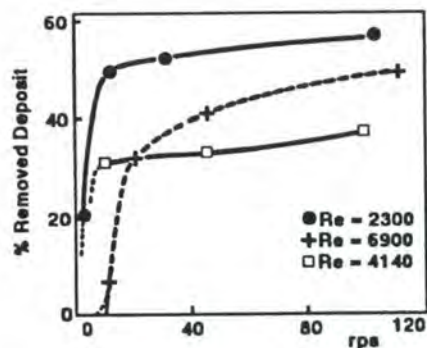
Figure 4 - Measurements of removal deposit for different rotating velocities.

3.4   Particle adhesion

Most of the fouling research has been devoted to the study of the transport mechanism of foulants towards the surface of deposition. However, not all the species that are able to reach the surface will stick to it, only some of them will give rise to the formation of deposits. This means that it is necessary a deeper knowledge on the conditions and forces responsible for adhesion in order to predict its occurance.

3.4.1   Free energy of adhesion

From a thermodynamic point of view adhesion is possible if the process leads to a negative change in the free energy of interaction. In other words, and neglecting electrical charge interactions, the adhesion of a particle (p) immersed in a liquid (l) to a surface (s) may be expected if[1]:

$$\Delta G^{ad} = \gamma_{sp} - \gamma_{sl} - \gamma_{pl} < 0 \qquad [11]$$

where ΔG^{ad} is the change in the free energy of adhesion and γ is the interfacial free energy between any two surfaces i and j, (γ_{ij}) expressed in terms of its dispersion and polar components by means of the geometric-mean equation[24,52]

$$\gamma_{ij} = \gamma_i + \gamma_j - 2 (\gamma_i^d \cdot \gamma_j^d)^{1/2} - 2 (\gamma_i^p \cdot \gamma_j^p)^{1/2} \qquad [12]$$

Usually, the dispersion and polar components of the liquids surface tension are obtained from the literature. For solids, those components are, commonly, determined by contact angle measurements, with series of liquids with known surface tensions, by a least square fitting of the data[15,65] according to

$$\text{Cos } \theta = -1 + \left\{ \left[2 (\gamma_s^d \cdot \gamma_l^d)^{1/2} \right] / \gamma_l \right\} + \left\{ \left[2 (\gamma_s^p \cdot \gamma_l^p)^{1/2} \right] / \gamma_l \right\} - (\pi_e / \gamma_l) \qquad [13]$$

θ denotes the contact angle and π_e stands for spreading-pressure, the latter being defined as the difference between the solid surface free energy in the air and the corresponding value measured in the presence of vapor molecules from the liquid used for contact angle measurements.

Using the approach of Busscher et al.[9,10] for the determination of the surface tensions of magnetite and copper, and the surface tension values obtained by Chibowski and Staszczuk for kaolinite[12], the values obtained for the free energies of adhesion of kaolin and magnetite particles in aqueous suspensions to copper surfaces are those presented in Table 1.

Table 1 - Free energies of adhesion $(mJ.m^{-2})$.

system	ΔG^{tot}	ΔG^d	ΔG^p
kaolin-copper-water	13	-11	24
magnetite-copper-water	-10	-6	-4

For the system kaolin-copper-water, having a $\Delta G^{tot} > 0$, no adhesion would be expected. However there is experimental evidence of its occurence, as was mentioned in the preceding sections.

Situations of energetically unfavourable adhesion occuring with microorganisms have also been reported in the literature[6,57]. However, in the case of living organisms, this violation of the basic principles of thermodynamics can be explained due to the presence of appendages, the excretion of exopolymers or the existence of localized hydrophobic groups, for instance.

In the present situation, the existence of a $\Delta G^d < 0$ can be a possible explanation, meaning that the adhesion of kaolin particles to copper is mainly due to dispersion interactions.

It must be stressed that the determination of the surface free energy of solids as well as the determination of spreading-pressures are still very controversial.

As far as spreading-pressures are concerned, the main controversy is about the experimental methodologies used[23].

However, in the case of surface free energies the problem goes even further, because there are distinct theoretical approaches considering different natures for the components and in the most extreme situation, that of the "equation of state", the surface tension may not be divided into components[11, 64,69]. The more recent works of van Oss and his collaborators[70] have improved the theory considering the existence of surface tension components.

The above mentioned thermodynamic criteria have been used quite sucessful to predict the possibility of adhesion[5,6,58]. But, despite being possible, adhesion may not occur, because there is a great number of factors that can influence the forces generated between the interacting bodies.

3.4.2 DLVO theory

The forces between interacting bodies are ruled by DLVO theory, named after Derjaguin and Landau[71] and Verwey and Overbeek[68]. Formerly derived to describe the stability of lyophobic colloids, it has been applied to deposition studies, since Marshall and Kitchener[40] established the parallelism between the two types of phenomena.

According to this theory, the potential energy of interaction (V) between two bodies immersed in a third medium is due to the combined effects of van der Waals forces of attraction and electrical double-layer forces, these having commonly a repulsive effect.

Thus,

$$V = V_W + V_{DL} \qquad [14]$$

where V_w is the potential energy associated to van der Waals interactions and V_{DL} is the potential energy due to the double-layer forces.

When the total potential energy of interaction is plotted against the distance between the interacting bodies the result is an energy profile characterized by an infinite primary minimum, corresponding to a maximum of stability. This profile may also display an energy barrier and a
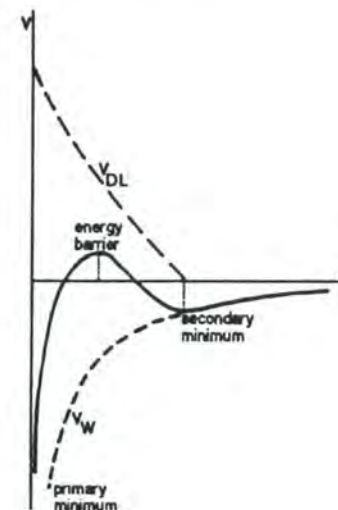
Figure 5 - Total potential energy of interaction (DLVO theory) versus distance.

secondary minimum (Figure 5), having respectively, a height and a depth that depend on the values of the parameters affecting both types of forces.

Van der Waals forces comprise the fluctuating dipole-induced dipole (dispersion or London) interactions, the randomly orienting dipole-induced dipole (induction or Debye) interactions and the randomly orienting dipole-dipole (orientation or Keesom) interactions.

For some reasons, only the dispersion interactions have been considered to be of preponderant importance between macroscopic bodies in condensed systems[25,51]. These forces are influenced by the geometries of the interacting bodies[72,73] and by their nature; this last feature is taken into account in a parameter named "Hamaker Constant".

Solid bodies immersed in aqueous media acquire electrical charge due to specific interactions with the ions in solution. This leads to a redistribution of charges (ions) near the solid surface, on account of coulombic attractions and repulsions, generating what is called the "electrical double-layer"[30]. So, double-layer forces are dependent on the concentration and

valency of ions and this is taken into consideration in the Debye-Hückel parameter (κ), given by

$$\kappa^2 = \frac{e^2}{\varepsilon\,KT} \sum_i z_i^2\, n_{io} \tag{15}$$

with

e - electrical charge of the electron

ε - electrical permittivity of the medium

K - Boltzmann constant

T - absolute temperature

z_i - valency of ion i

n_{io} - number of ions i per volume

Another point to be taken into account is the mode of interaction because either the surface potential or the charge can be kept constant while the ineracting bodies are approaching[59].

As mentioned before, these interactions are commonly repulsive, because most of the solid surfaces, in polar systems, especially in aqueous media, became negatively charged, and when approaching they repel each other.

In aqueous systems pH plays an important role, because it can affect the Debye-Hückel parameter and zeta-potential values and has the advantage of being an operating variable quite easy to control.

Several experiments were carried out to study the effect of pH in the formation of deposits of kaolin and magnetite particles on copper surfaces from flowing aqueous suspensions. pH values were in the range 7 - 10.5 and for every tested value two distinct types of runs were performed, in one case the pH value was kept constant by addition of NaOH and in the other case the controlling chemical was Na_2CO_3.

The test cell is a 2 metre long annular duct, placed horizontally, consisting of a copper tube having an outer diameter of 16 mm inserted in a perspex tube with an internal diameter of 32 mm, similar to the one that is schematically represented in Figure 1.

The copper tube is commercial drawn tubing. Before being used the tubes were cleaned with an acidic solution, left to flow for 2 hours and afterwards rinsed with water.

The aqueous suspensions flowing at a velocity of 0.415 m/s and having a bulk temperature of 20°C were of 1.5 g/l in the case of kaolin and 2.0 g/l for magnetite.

Every experiment had a duration of 20 days and the final thicknesses of the deposits, formed on the outer wall of the copper tubes, were measured by a micrometer coupled to an electrical circuit[41].

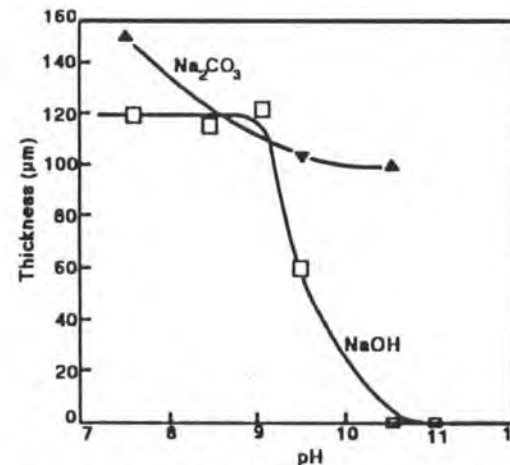The results obtained are those presented in Figures 6 and 7.

Figure 6 - Thickness of kaolin deposits as a function of pH.

From their observation two aspects are worth being pointed out:

i - The deposit thickness decreases with increasing pH. The only exception was obtained for magnetite at pH = 8.5. However, this result was masked, because magnetite contained quartz and chlorite and those minerals were prone to deposit at this pH value. This was confirmed by an EDS (Energy Dispersion Spectroscopy) analysis of the deposits.

ii - For each pH value the thickness of the deposits is higher in the presence of Na_2CO_3, having a steeper decrease with pH when the controlling chemical is NaOH.

Using the thermodynamic criterion, no explanation was found for these observations. The values of ΔG were not affected by pH. Several measurements of surface tensions were performed using solutions of NaOH and of Na_2CO_3 in the pH range 7.5 - 10.5 and no alterations were found, within 1 mJ.m^{-2}, relatively to the surface tension of pure water.
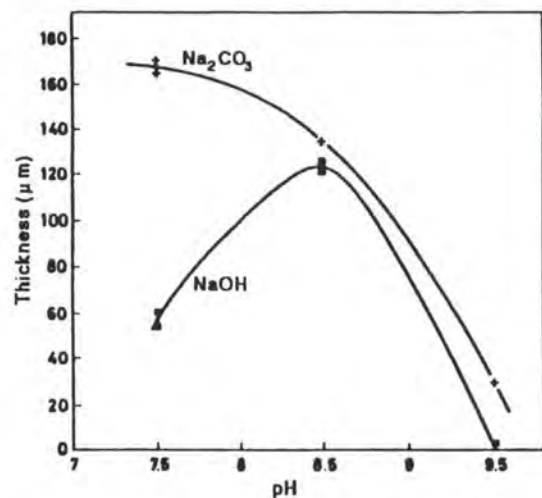
Figure 7 - Thickness of magnetite deposits as a function of pH.

Another possibility of explanation was tried through the zeta potential values of the solids involved.

Zeta potential values were obtained through Smoluchowski equation using electrophoretic mobility data obtained in a Zetameter apparatus. For each solid two types of suspensions were prepared. In one case NaOH was used to obtain the desired values of pH, and in the other the control was made by means of Na_2CO_3. For each of those chemicals several suspensions were prepared to cover the pH range 7 - 10.5. In order to avoid the existence of extraneous ions, no buffer solutions were used, but the microelectrophoresis experiments were performed in a N_2 atmosphere to account for alterations in the pH, due to the dissolution of atmospheric CO_2. The copper had to be ground to fine particles in order to be kept in suspension. The values obtained are presented in Figures 8, 9 and 10.

As can be seen, the zeta potential values are increasingly negative as the pH is raised by the addition of Na_2CO_3. This behaviour was expected, because Na_2CO_3 is a weaker basis than NaOH , meaning that it is necessary to add more electrolyte to obtain the same pH value.
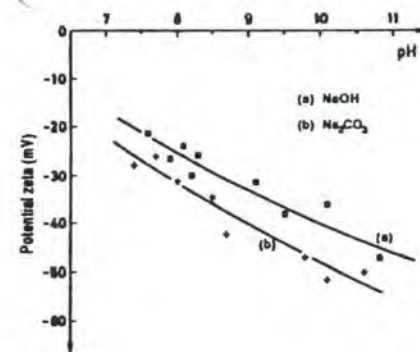

Figure 8 - Zeta potential of kaolin *vs* pH.

Consequently, there is an increase in the ionic strenght of the medium, giving rise to a greater compression of the electrical double-layer, yielding more negative zeta potential values.

The dependence of the zeta potential on the pH for copper, in the presence of NaOH, has a peculiar behaviour. The zeta potential values become less negative above pH = 8. Similar situations have been observed in other systems and explained considering that some ions can be specifically adsorbed[30]. However, if more than one type of ions is specifically adsorbed, this phenomenon does not occur, which can be the case when Na_2CO_3 is present in the solution.
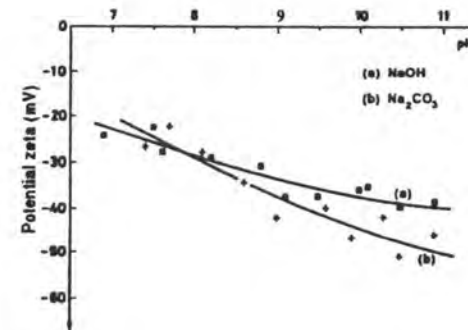

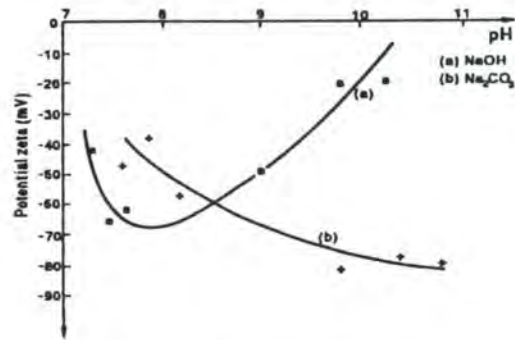Figure 9 - Zeta potential of magnetite *vs* pH.

Figure 10 - Zeta potential of kaolin *vs* pH.

When zeta potential values of both interacting bodies become more negative, the repulsion between them tends to increase, inhibitting the adhesion. This can be used to explain why the deposits thickness decreases with increasing pH, whenever this increase leads to more negative zeta potential values.

According to the above reasoning, it would be expected that the kaolin deposits on copper in NaOH solutions would be thicker for higher pH values.

By the same token, the deposits in the presence of Na_2CO_3 would be thinner, because for each pH value the zeta potential values are more negative in medium with Na_2CO_3 than with NaOH.

In the formation of deposits two steps can be considered. The first one is the adhesion of the particles to the surface until a monolayer is formed (heterocoagulation). The second one is the growing of the deposits, the interactions being then between particles (homocoagulation).

When comparing the deposits thickness of kaolin on copper at pH = 7.5 (120 μm) and at pH = 10.5 (≃ 0 μm) it can be thought that the controlling step is heterocoagulation. Some factors must be responsible for its inhibition as the pH increases.

In flowing systems the formation of deposits is the result of two competitive processes: deposition (which includes adhesion) and removal. The latter is due to the hydrodynamic forces acting on the deposited particles.

So, it can be considered that the removal process becomes more effective as the pH is raised.

However, according to the DLVO theory the particles stabilize in an infinite primary minimum and this would require an infinite energy to make them surmount the energy barrier in the opposite way.

As early as 1937, Hamaker[26] has suggested the existence of short range repulsive forces to explain the desorption of coagulated particles. Those short range repulsive forces are responsible for the creation of a finite primary minimum, and have been considered to be due to Born repulsions, arising when the interacting bodies come too close[61].

Kallay et al.[31] have explained the desorption of hematite particles deposited on steel beads, associating the Born repulsion to DLVO theory. But, they did not use an equation for the calculation of those forces. They made the following assumption:

$$V_{BR} = 0 \quad \text{at} \quad H > d_o$$
$$V_{BR} = \infty \quad \text{at} \quad H < d_o$$

where V_{BR} is the potential energy associated to the Born repulsion, H is the distance between the interacting bodies and d_o is the distance of closest approach or the distance of equilibrium.

In order to quantify the energy associated with those forces, the equations concerning the most common interacting geometries (plate/plate, sphere/sphere and sphere/plate) where derived[50], Table 2.

Table 2 - Potential energy of interaction due to Born repulsion for different geometries when $R \gg H$.

Geometry	Equation
plate/plate	$V_{BR} = \dfrac{A\, d_o^6}{48\, \pi\, H^8}$
sphere/sphere	$V_{BR} = \dfrac{A\, d_o^6\, R_1\, R_2}{168\, (R_1 + R_2)\, H^7}$
sphere/plate	$V_{BR} = \dfrac{A\, d_o^6\, R}{168\, H^7}$

R is the radius and A is the Hamaker constant.

The following expression is suggested for the calculation of d_o:

$$\Delta G^{ad} = \frac{A}{12\pi\, d_o^6} \qquad\qquad [16]$$

In order to apply the DLVO theory, it is necessary to know the geometries of the interacting bodies and the mode of interaction of their electrical double-layers.

An equivalent radius was determined for the kaolin particles, meaning that the geometry was assumed to be of the sphere/plate type.

For the mode of interaction of the double-layers the following assumptions were made:

1 - interaction at constant potential-equation of Hogg, Healy and Fuerstenau[29];

2 - interaction at constant-charge equation of Wiese and Healy [75];

3 - mixed case - equation of Kar, Chander and Mika[32];

4 - mixed case - considering the average between cases 1 and 2.

The best agreement with the experimental results is obtained considering the interaction at constant potential because it yields a shallower primary minimum and a lower energy barrier (Figure 11) with increasing pH, making the re-entrainment of particles more likely to occur.
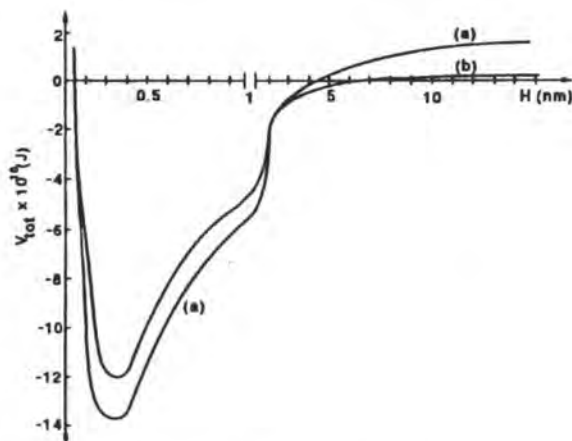

Figure 11 - Total potential energy of interaction vs distance, between copper and kaolin at constant potential: (a) pH = 7.5 (NaOH); (b) pH = 10.5 (NaOH).

It must be stressed that, although most of the clay minerals are of the constant charge type[65], there are arguments in favour of the constant potential behaviour. Kaolinite has a point of zero charge (p.z.c.) between pH 3 and 4[16]. This charge reversal means that there is no constancy of the bulk surface charge. Moreover, the zeta potential becomes more negative as the pH increases which can be due to the adsorption of OH^-, creating a situation that is typical of a constant potential type.

The association of Born repulsion with DLVO theory was applied succesfully to explain the influence of pH in the formation of the deposits, even in the case of magnetite. But, it cannot explain the difference in thickness observed between the deposits obtained with NaOH and Na_2CO_3.

A possible explanation for this fact can be given taking into account that DLVO theory was derived for symmetrical electrolytes, which is not the case.

Another point that must have an important contribution was observed during the experiments. It was easier to keep the particles in suspension when the medium was controlled with Na_2CO_3. If the particles are in suspension this means that there is a reduced formation of flocs. Flocs are dense and tend to deposit by gravity, mainly in the mixing tank, decreasing the concentration of particles in the suspension. The above mentioned behaviour in the presence of Na_2CO_3 is in accordance with the observations of Michaels and Bolger[44] that polianionic electrolytes are effective in promoting deflocculation.

4.   BIOFOULING

Biological films are in general composed of several species of microorganisms depending on the capacity of surviving of each one. In fact, the number and species of organisms vary with the ambiental conditions especially as regards nutrient concentration, fluid temperature, pH or dissolved oxygen.

Generally, biofilms contain bacteria as the dominant population since they can compete with other microorganisms due to their higher specific growth rate and facility to adapt to different conditions[2].

Pseudomonas fluorescens is recognized[36] as one of the dominant bacteria existing in contaminated waters utilized in several industrial processes. There are in fact some experimental works[19,27,46] in which this microorganism was used to study the problem of biofouling. However, industrial fluids, namely those circulating in cooling water systems contain different types of foulants. For this reason the films formed are in general constituted by a complex matrix of living matter and other suspended particles.

4.1   Biofilm formation

The mechanism of biofilm formation includes not only the physico-chemical considerations discussed for the inorganic fouling but also those related with the biological characterization of living particles.

In fact, it is thought that in the initial phase of biofilm formation the solid surfaces become covered by a thin organic film composed of glycoproteins and polysacharides that exist dissolved in the fluids. This process depends naturally on the characteristics of the solid surfaces, specially on the surface tension[3]. Measurements of the contact angle between fluids and solid surfaces allow the determination of surface free energies of different materials[4] and constitute an important tool for predicting the accumulation of the first layers of biofilms. In fact, a decrease in the free energy of adhesion may act as the driving force for initiation of the fouling process (see section 3).

It is interesting to note that for the particular case of biological fluids, Dexter[18] refers the existence of an interval of critical surface tensions for which the adhesion of microorganisms is less favourable. Materials like FEP (Fluorinated Ethylene Polypropylene), PVF (Polivinylidinefluoride) or PTFE (Politetrafluorethylene) are included in this interval, whereas most engineering coatings have higher surface tensions than those.

Results obtained by Mott and Bott[47] could probably be explained on the basis of the surface tension differences between the materials utilised. In this work antifouling surface qualities were registered for FEP when compared with stainless steel surfaces.

The attachment of microorganisms to solid surfaces depends on the forces that are present when the cells approach the surfaces. Those forces include the electrical forces and the van

der Waals forces, among others. As   concerns electrical forces, the existence of opposite charges of particles and surfaces may represent an important factor for the mutual attraction.

As the surface electrical charges depend on the pH, some experimental work has been done in order to justify different behaviours for the attachement of microorganisms. For instance, the electrokinetic potentials were determined for the case of the microorganism *Pseudomonas fluorescens* and for different metals[56]. The results are presented in Figure 12 as a function of pH.
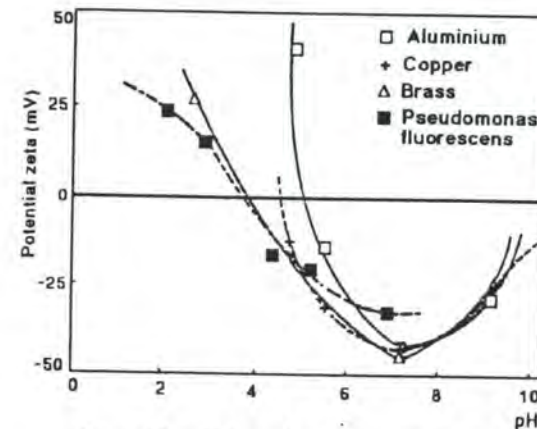

Figure 12 - Values of zeta potentials *vs* pH.

It can be noted from this figure that only for very low pH values, bacteria and metals have opposite charges which could potentiate the period of colonization. Since this bacterium does not grow at these pH values, biofouling data were obtained for higher values (7 and 9) and they do not show significant differences as regards the values of thickness or weight for the first layers when utilizing surfaces like copper, aluminium or brass[56].

The repulsion exerted by the electrical forces can be overcome if microorganisms that are retained near the surfaces (by van der Waals forces) are able to produce biopolymers that act as a cement and fill the space between the cells and the solid surfaces. However, this process becomes more difficult for high velocities. Neverthless, higher velocities favour the growth and reproduction of microorganisms that are able to attach to the surfaces, on account of the higher rate

of diffusion of nutrients and oxygen to the cells. For instance, it can be seen from the results
presented in Table 3 that the films formed when using water contaminated with *Pseudomonas
fluorescens* show a higher density when the fluid velocity is 0.43 m/s, utilizing different metal
deposition surfaces. Under these conditions it is thought that the production of biopolymers by the
cells is also increased due to the greater availability of nutrients. These biopolymers contribute
strongly to the total biomass as well as to the higher cohesion of the deposits.

Table 3 - Biofilm density (Kg/m^3) for different fluid velocities.

	Fluid velocity	
	0.43 m/s	0.13m/s
copper	57.9	22.0
aluminium	61.0	26.1
brass	66.4	18.9

Temperature and pH constitute also important factors in the process of deposit build-up,
as they influence the growth and reproduction of microorganisms. Figure 13 shows the effect of
temperatures, when using *Escherichia coli* as the dominant bacteria in the fluid. Note that the
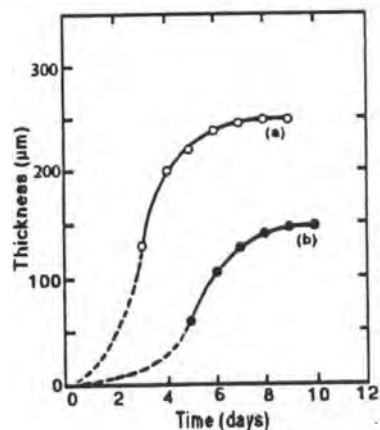optimum temperature for growth of these bacteria is 37°C.

Figure 13 - Effect of temperature on the biofilm formation: (a) 35°C; (b) 30°C.

The results obtained for the biofilm density at two different pH (Table 4) for the case of
Pseudomonas fluorescens reveal the influence of this factor, taking into account that the specific
growth rate for this microorganism is about 53% higher for pH = 7 than for pH = 9.

Table 4 - Biofilm density (Kg/m^3) dependence on fluid pH.

	pH = 7	pH = 9
copper	57.9	44.3
aluminium	61.0	41.8
brass	66.4	35.8

The results shown in Table 3, Table 4 and Figure 13 were obtained utilizing water
contaminated with the mentioned bacteria, circulating in a closed circuit containing the test duct
(Figure 14). The test plates inserted in this duct were easily removed in order to observe the
deposits.
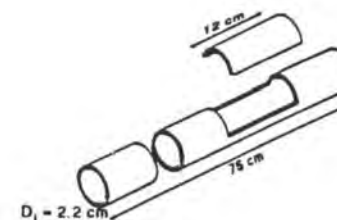
Figure 14 - The test duct and the removing plate.

4.2   The interpretation of biofouling curves

The overall process of biofouling, as the other types of fouling, is generally described by
an asymptotic curve to which the basic model of Kern and Seaton can be fitted.

The influence of fluid velocity on the formation of the biofouling was studied by several
authors[7,20,27,56] utilizing different methods of evaluation. The results represented in Figure 15
show the variation of heat transfer resistance with time for several fluid velocities[56].

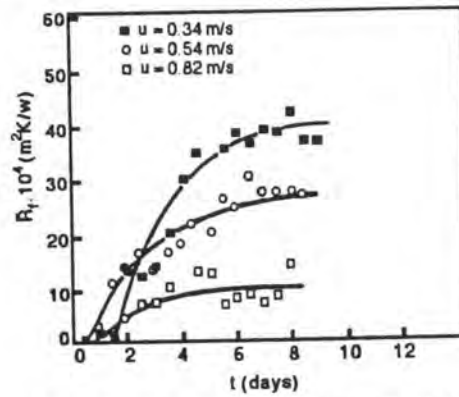Figure 15 - Fouling curves for different velocities.

It can be noted that the asymptotic values of R_f decrease with the increase in velocity, suggesting that the increase in the rate of removal due to shear stress is higher than the possible increase in the deposition rate associated with the higher velocities.

By fitting the Kern and Seaton model to each curve represented in Figure 15 it is possible to determine the values for the deposition flux ϕ_d (equation 2). The continuous decrease of this flux with the increase of Reynolds number shown in Figure 16 indicates that the transport mechanism is not the controlling step.
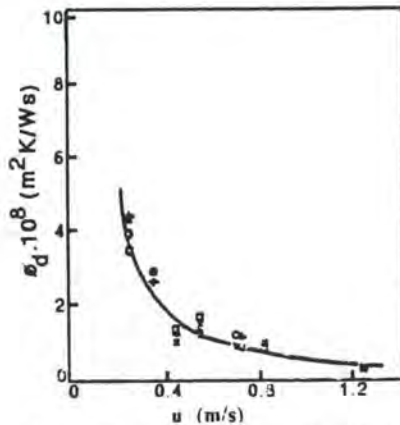

Figure 16 - Deposition flux versus fluid velocity.

It is important to mention that the deposition flux ϕ_d in the specific case of biofouling involves two contributions, which can be considered separately:

. fluid and interface processes, ϕ_{d_1}, related with the transport and adhesion of microorganisms to the deposition surface, and

. fluid and biofilm processes, ϕ_{d_2}, including the transport of nutrients to the deposit followed by biological growth and reproduction, and by exopolymers production.

As the two groups of processes occur simultaneously, the deposition flux can be defined as:

$$\phi_d = \phi_{d_1} + \phi_{d_2} \tag{17}$$

In order to investigate the individual contribution of the terms ϕ_{d_1} and ϕ_{d_2}, some experiments were conducted where the nutrients were removed from the flowing fluid after the asymptotic resistance was reached. Under these conditions the growth of microorganisms becomes negligible and the curve tends to a new asymptotic value as it can be seen from Figure 18. Note that a similar behaviour was observed by Bott and Miller (8) when using fluid velocities of 0.5 m/s.

The experimental results were obtained utilizing a glass tank continuosly fed with water at 27°C and contaminated with a pure culture of *Pseudomonas fluorescens* grown in a fermenter. The glucose concentration was kept at 0.03 g/l by a constant flow of nutrients (glucose 5%, peptone 2.5% and yeast extract 1.25%) and the bacterial concentration at 6×10^7 cells/ml.

The fouling fluid circulated in a semicircular perspex duct. Biofilm accumulated on an aluminium plate and was monitored by heat transfer measurements, in four different positions (A, B, C and D) along the plate, this one being heated by water at 60°C.
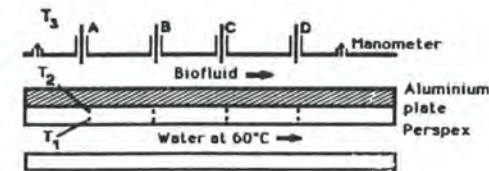

Figure 17 - Bifouling test section.

Figure 18 represents typical biofouling curves - one for low and the other for high velocity - with nutrient removal at $t = t_o$.
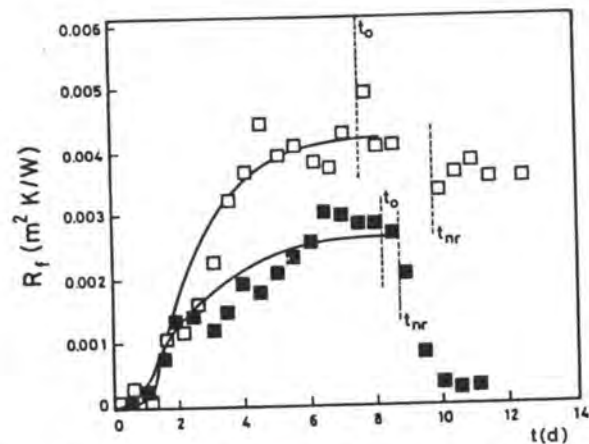

Figure 18 - Fouling curves with suppression of nutrients, □ u = 0.34 m/s and ■ u = 0.71 m/s.

Considering Δt as the interval between the removal of nutrients (t_o) and the time when the curve begins to decrease (t_{nr}), a higher value is obtained for the lower velocity (Table 5).

Table 5 - Values of Δt for the higher and the lower velocities.

Velocity m/s	Δt (days)
0.34	2.0
0.71	1.0

The compactness of the biofilm increases with velocity[7], decreasing the water and nutrient content of the biofilm. These nutrients held by the matrix can be used by microorganisms after nutrient suppression from the flowing fluid. As a higher content of nutrients is observed for the lower velocity, the biofilm can be maintained for a longer period of time, before stopping the growth.

5.   INTERACTION BETWEEN DIFFERENT FOULING AGENTS

Up to now, few laboratory studies have been carried out on the effects caused by the simultaneous presence of two (or more) foulants. Some of them are reported below, for the case of cooling water fouling. Two industrially common situations were artificially created for this purpose: the interaction between different types of inorganic particles (clay and iron oxides) and the interaction between microorganisms and inert particles.

5.1   Kaolin-magnetite systems

Table 6 compares the thickness of the deposits obtained from pure kaolin suspensions[42] and from kaolin-magnetite suspensions[48]. The experiments were carried out in the same apparatus, (Figure 1), using similar operating conditions, except for the composition of the suspension (pH = 7.5, duration of the tests ≈ 30 days). The values refer to the zones in the annular section where the flow was already fully developed.

Table 6 - Average deposit thickness (µm) obtained from different particulate suspensions as a function of the Reynolds number (Re).

Re	kaolin (2.2 g/l)	kaolin (2.2 g/l) magnetite (0.4 g/l)	kaolin (1.5 g/l) magnetite (0.7 g/l)
4 150	92	73	73
6 230	–	61	60
6 900	87	–	–
8 300	–	43	42
10 400	–	42	39
11 040	42	–	–

In every case, the thickness of the deposit decreases as the Reynolds number increases. This could be expected, since the higher shear stresses make adhesion difficult and, at the same time intensify the hydrodynamic removal forces acting on the deposit.

Surprisingly, however, the mixed suspension originated smaller amounts of deposit than the kaolin suspension, even when the total particle concentration was greater than that of the latter. It was shown before[42] that, in the range of Reynolds numbers indicated in Table 6, the

deposition rate was limited by the adhesion process. Therefore, it can be concluded that the surface interactions between the two types of particles tend to inhibit deposit growth.

At pH = 7.5, the electrokinetic potentials of kaolin, magnetite and copper (the deposition surface) are all in the same range (- 30 mV to - 50 mV), causing repulsive identical forces between the different materials[48]. On the other hand, the potential energy of attraction is quite different: the Hamaker constant for the interaction kaolin-magnetite is more than 20 times greater than the value for the interaction kaolin-kaolin[43]. If the potential energy curve for each interaction is examined, it is found that the energy barrier is much lower in the case of the kaolin-magnetite layer, whereas the primary minimum is deeper and the secondary minimum is shallower. That is, the particles that tend to stand in the secondary minimum, in the first phase of adhesion, are easily removed by the liquid flow. However, those that manage to reach the deep primary minimum will be able to resist the hydrodynamic forces much better and form stable layers. That is why the mixed deposits are not only thinner but also more hard than the pure kaolin ones[43].

Obviously , there are other important factors that were not taken into account in this discussion, such as the shapes of the two types of particles. The kaolin particles are flat disks, whereas the magnetite particles are similar to rhomboidal solids. This may play a significant rôle in the adhesion process. For instance, a flat disk usually adheres more easily to a smooth surface than a more or less isometric solid. Also, it is not known if kaolin and magnetite start to agglomerate in the suspension, or if their interaction occurs mainly in the deposit. The mass transfer and attachment processes will certainly be much affected by such mechanisms.

5.2   Bacteria-kaolin systems

The effect of suspended inorganic particles in biofouling formation is not yet well known. The few studies that have been published on this subject were carried out with mixed suspensions of microorganisms (*Pseudomonas fluorescens*) and clay (kaolin) particles[39,55,49]. The results obtained so far are not fully conclusive. They seem to indicate that the presence of particles may lead to a higher biofilm development rate. However, the extended lag or induction phase detected by Lowe et al.[39] in the initial period of biofilm formation was not always confirmed in the experiments made by the other authors.

Oliveira et al.[49] carried out several runs with mixed kaolin-bacteria suspensions (6×10^7 bacteria/ml and 150 mg of kaolin/l). The experimental procedure was similar to the one mentioned in section **4.2**, except for the fact that there was one more fouling agent. The thermal resistance of the mixed biofilm increased with time until an asymptotic value was reached, as it happened in the case of pure bacteria suspensions. In general, a greater amount of biofilm was obtained, as shown in Table 7. This effect seems to be more pronounced for higher velocities.

Table 7 - Asymptotic thermal resistances of biofilms.

Fouling agent	Fluid velocity (m/s)	$R_f^{\infty} \cdot 10^4$ (m² . K/W)
Bacteria	0.34	42
Bacteria	0.54	31
Bacteria	0.82	10
Bacteria	1.24	3.6
Bacteria + kaolin	0.28	41
Bacteria + kaolin	0.59	35
Bacteria + kaolin	0.87	20
Bacteria + kaolin	1.24	7.4

Values of ϕ_d calculated from the fouling curves showed a decrease of the deposition flux with velocity in both types of deposits. Slightly higher values of ϕ_d were found for the mixed deposits.

Several hypothesis can be stated to explain this behaviour. Since the kaolin particles have lower thermal condutivities than the pure biofilm, higher thermal resistances would be expected when the particles are present in the fouling layer. Nevertheless, it should be stressed that Lowe et al.[39] observed that the weight of bacteria-kaolin deposits was greater than the weight of pure biological films formed in the same hydrodynamic conditions.

Other effects may play a rôle in this process. The metabolic rates of bacteria may be enhanced by the presence of the inorganic particles, since the mixed biofilms tend to be more porous, increasing the diffusion rates of nutrients to the inner layers of the biofilm, and —— at the same time —— of toxic metabolites in the opposite direction. It is also thought that water and nutrients may be adsorbed on the kaolin surfaces providing new sources of nutrients for the growth of the biofilm when those particles are within the deposit. Inhibitory effects may be reduced by adsorption of metabolites on the particle surfaces.

To test these arguments, some experiments were carried out where nutrients were removed from the fluid after the bacteria-kaolin deposit reached the asymptotic plateau. The amount of deposit started to decrease some time after the supression of nutrients, but the mixed deposit maintained its structure for a longer time than the pure bacterial film. In Table 8, Δt represents the time interval from the moment the nutrients were supressed to the moment the biofilm started to collapse.

Table 8 - Effect of nutrient supression on biofilms.

Fouling agent	Fluid velocity (m/s)	Δt (days)
Bacteria	0.34	2
Bacteria	0.52	1
Bacteria	0.71	1
Bacteria + kaolin	0.36	2.5
Bacteria + kaolin	0.59	2.5
Bacteria + kaolin	0.72	2.0
Bacteria + kaolin	0.93	2.5

These results indicate that the structure and/or biological activity on the biofilm in the presence of kaolin particles is really different. In fact, they suggest that the mixed deposit may contain a greater amount of nutrients (due to higher diffusion rates or to the fact that the kaolin particles may act as reservoirs of nutrient within the biofilm) and/or that the deposit has a more stable structure that enables it to resist for a longer time to the hydrodynamic forces of the fluid after the nutrient source is supressed. Probably, this explains why the effect of fluid velocity on Δt is not clearly detected in the bacteria-kaolin biofilms.

Once more, the differences between the two types of biofilms can be more clearly detected in the range of higher velocities. In this range, the diffusion rate of nutrients and kaolin is higher and that may as well contribute to a higher availability of nutrients in the inner layers of the biofilm.

6.   CONCLUSIONS

Fouling of heat exchangers still remains a major problem to be solved. In each of the so-called fouling categories (each one including only one type of foulant), special attention should

be devoted to the understanding and modelling of phenomena such as adhesion, changes within the deposit and dettachment (removal) of the deposit. In particular, a much deeper knowledge of the adhesion/cohesion forces involved in deposit formation is needed in order to be able to predict not only the adhesion tendency but also the rate at which adhesion and removal occur.

An even greater task has to be performed as regards the prediction and control of the interactions between different types of foulants. The effect of surface corrosion, for instance, is often very important since it usually increases the fouling rate and, at the same time, it may be induced or facilitated by the formation of a deposit on the metallic surface.

In every case, the identification of the mechanisms governing the fouling rate is a key factor. In situations such as the deposition of suspended inorganic particles, it is usually observed that adhesion is the rate-limiting step in the range of fluid velocities occuring in heat exchanger tubes. Surface interactions are also responsible for the unexpected decrease in the fouling rate when different particles — kaolin and magnetite — were mixed in the same aqueous suspension. Changes in the conditions for biological reproduction and growth seem to explain the apparent increase in fouling rates when clay particles were added to a bacterial suspension — the understanding of the biological mechanisms and of the structure (compactness, composition) of the deposit are here at stake.

Studies on the nature (composition, roughness, etc.) of the surfaces involved in adhesion (particles, microorganisms, solid substrata) are obviously of prime importance in order to establish the type of material or coating capable of delaying the most the initial adhesion of the fouling layer. If this is accomplished, the heat exchanger can remain in operation for a longer time before it is cleaned, the energy and production losses are greatly reduced and, on the whole, the capital and operating costs of heat exchange equipment are optimized.

NOMENCLATURE

A - Hamaker constant

a - empirical parameter

C_b - bulk concentration of particles (kg/m^3)

C_s - concentration at the interface solid/fluid (kg/m^3)

d_o - distance of equilibrium (m)

e - electrical charge of electron (C)

f - friction factor

ΔG^{ad} - variation of free energy of adhesion (J/m^2)

ΔG^d - dispersion component of the free energy (J/m^2)

ΔG^p - polar component of the free energy (J/m^2)

ΔG^{tot} - total free energy (J/m^2)

H - distance between interacting bodies (m)

K - Boltzmann constant (J/K)

k_a - adhesion rate coefficient (/m/s)

k_1 - parameter related with the structure of deposit

k_f - thermal conductivity of deposit (W/m.K)

k_t - mass transfer coefficient (m/s)

n_{io} - number of ions i per volume

Re - Reynolds number

R_f - thermal resistance of biofilm ($m^2.K/W$)

R_f^∞ - asymptotic thermal resistance of biofilm ($m^2.K/W$)

R_i - radius of particle i (m)

S - adhesion probability

Sc - Schmidt number

Sh - Sherwood number

t - time (s)

Δt - time interval between removal of nutrients and the decrease in R_f (s)

t_{nr} - time when R_f starts to decrease after supression of nutrients (s)

T - absolute temperature (K)

u - fluid velocity (m/s)

V - potential energy of interaction (J)

V_{BR} - potential energy associated with the Born repulsion (J)

V_W - potential energy associated to van der Waals interactions (J)

V_{DL} - potential energy due to the double-layer forces (J)

Z_i - valency of ion i

β - parameter related to the strenght of deposit (s^{-1})

γ_{ij} - interfacial free energy between bodies i an j (J/m^2)

γ_{pl} - interfacial free energy between a particle and a liquid (J/m^2)

γ_{sp} - interfacial free energy between a surface and a particle (J/m^2)

γ_{sl} - interfacial free energy between a surface and a liquid (J/m^2)

ε - electrical permittivity (F/m)

$\emptyset_a$ - adhesion flux (m^2 K/W.s)

$\emptyset_d$ - deposition flux (m^2 K/W.s)

$\emptyset_{d_1}$ - deposition flux due to transport and adhesion of microorganisms (m^2 K/W.s)

$\emptyset_{d_2}$ - deposition flux due to transport of nutrients and biological processes in the deposit (m^2 K/W.s)

$\emptyset_r$ - removal flux (m^2 K/W.s)

$\emptyset_t$ - transport flux (m^2 K/W.s)

π_e - spreading pressure (J/m^2)

ρ_f - film density (kg/m^3)

θ - contact angle (degree)

REFERENCES

1 - D.R. Absolom, F.V. Lamberti, Z. Policova, W. Zingg, C.J. van Oss and A.W. Neumann; App. Env. Microbiology **46** 90 1983.

2 - S. Aiba, A.E. Humphrey, N.F. Millis; Biochemical Engineering, Univ. Tokio Press 1973.

3 - J.D. Andrade; "Surface and Surface Analysis of Polymer - Polymer Surface Dynamics" in Fouling & Cleaning in Food Processing Eds. Lund, Plett, Sandu, Madison. Wisconsin, 79 1985.

4 - R.E. Baier; Acad. Med. **48** (2) 257 1972.

5 - S.K Beal.; Nucl. Sci. & Engin. **40** 1 1970.

6 - M.N.Bellon-Fontaine, N. Mozes, H.C. van der Mei, J. Sjollema, O. Cerf., P.G. Rouxhet and H.J. Busscher; Cell Biophysics, **17** 93 1990.

7 - T.R. Bott, M.M.V.P.S. Pinheiro; Can. J. Chem. Eng. **55** 1977.

8 - T.R. Bott, P.C. Miller; J. Chem. Techn. Biotechnol. **33B** 1983.

9 - H.J. Busscher, Ph. D. Thesis, University of Groningen 1985.

10 - H.J. Busscher, G.A.M. Kip, A. van Silfhout and J. Arends; J. Coll Int. Sci. **114** 307 1986.

11 - H.J. Busscher and A.W.J. van Pelt; J. Material Sci. Letters **6** 815 1987.

12 - E. Chibowski and P. Staszczuk; Clays and Clay Minerals **36** 455 1988.

13 - J.D. Cleaver, B. Yates; J. Coll and Int. Sci., **44** (3) 464 1973.

14 - J.D. Cleaver, B. Yates; Chem. Eng. Sci. **31** 147 1976.

15 - J.R. Dann; J. Colloid Interface Sci. **32** 321 1970.

16 - A. Delgado, F. Gonzállez-Caballero, J.M. Bruque; J. Coll. Int. Sci. **113** 203 1986.

17 - B.V. Derjaguin, L.D. Landau; Acta Phys. Chim. USSR **14** 633 1941.

18 - S.C. Dexter; J. Coll. Int. Sci. **70** 2 1979.

19 - J.E. Duddrige, C.A. Kent, J.F. Law "Bacterial Adhesion to Metallic Surfaces" in Prevention of Fouling, Nottingham University, April 1981.

20 - J.E. Duddrige, C.A. Kent, J.F Law.; Biotech. & Bioeng. 24 153 1982.

21 - J.E. et al. Duddrige; "Effects of Flow on Biofilm Development", in Bryers and Cole (Eds.) , "Fouling of Heat Exchangers Surfaces", 717, United Engineering Trustees, Inc., USA, 1983.

22 - N. Epstein; "Particulate Fouling of Heat Transfer Surfaces: Mechanisms and Models", in Melo, Bott and Bernardo (Eds.) "Fouling Science and Technology", 143-164, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.

23 - H.Y. Erbil; J. of Adhesion Science and Technology, **3** (1) 29 1989.

24 - F.M. Fowkes; Ind. Eng. Chem. **12** 40 1964.

25 - F.M. Fowkes; "Physicochemical Aspects of Polymer Surfaces"; K.L. Mittal, Ed.; Plenum: New York, **2** 583 1983.

26 - H.C. Hamaker; Rec. Trav. Chim. **56** 3 1937.

27 - D.W.S. Harty; Ph. D. Thesis, University of Birmingham, 1980.

28 - D. Hasson; "Precipitation Fouling", in Somerscales & Knudsen (Eds.), Fouling of Heat Transfer Equipment, 527-568, Hemisphere Publ. Corp., New York, 1981.

29 - R. Hogg, T.W. Healy and D.W. Fuerstenau; Trans. Faraday Soc. **62** 1638 1966.

30 - R.J. Hunter; "Zeta Potential in Colloid Science" Academic Press 1988.

31 - R.J. Kallay, B. Biskup, M. Tomic, E. Matijevic; J. Coll. Int. Sci **114** 357 1986.

32 - G. Kar, S. Chander and T.S. Mika; J. Coll. Int. Sci. **44** 347 1973.

33 - C.A. Kent, et al.; "The Effects of Shear Stress on Biofouling Deposit Formation and Removal", Proceedings of the 7th Intern. Heat Transfer Conf., **6** 387-390, Hemisphere Publ. Corp., N.Y., 1982.

34 - C.A. Kent.; "Biological Fouling: Basic Science and Models", in Melo, Bott & Bernardo (Eds.). Fouling Science and Technology, 207-221, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.

35 - D. Kern, R. Seaton; Brit. Chem. Eng. **4** (5), 258, 1959.

36 - L. Knovak; "Control of the Rhine Water Fouling" in Fouling of Heat Transfer Equipment, Eds: Somerscales e Knudsen, Hemisph. Publ. Corp. 397, 1981.

37 - W.H. Linton, T.K. Sherwood; Chem. Eng. Progr., **46**, 258, 1950.

38 - D.H. Lister; "Corrosion Products in Power Generating Systems", in Somerscales & Knudsen (Eds.), Fouling of Heat Transfer Equipment, 135-200, Hemisphere Publ. Corp. New York, 1981.

39 - M.J. Lowe, J.E. Duddridge, A.M. Pritchard, T.R. Bott; Symp. Series, **86** 1984.

40 - J.K. Marshall, J.A. Kitchener; J. Coll. Int. Sci. **22** 342 1966.

41 - L.F. Melo and J.D. Pinheiro; "Fouling Tests: Equipment and Methods", in Fouling in Heat Exchanger vol. 35, pp. 43-49, Ed. Suitor & Pritchard, Amer. Soc. Mech. Eng. - HTD 1984.

42 - L. Melo, J.D. Pinheiro; "Particulate Fouling: Controlling Processes and Deposit Structure", in Tien. Carey & Ferrel (Eds.), "Heat Transfer 1986", Vol. 6, 2781-2786, Hemisphere Publ. Corp., New York, USA, 1986.

43 - L. Melo and J.D. Pinheiro; "Fouling by Aqueous Suspensions of Kaolin and Magnetite: Hydrodynamic and Surface Phenomena Effects", in Melo, Bott and Bernardo (Eds.) "Fouling Science and Technology", 173-189, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.

44 - L. Melo and J.D. Pinheiro; "Particle Transport in Fouling caused by Kaolin-water Suspensions on Copper Tubes"; Can. J. Chem. Eng., **66**, 36 1988.

45 - A.S. Michaels, J.C. Bolger; I & EC Fundamentals **14** 3 1964.

46 - P.C. Miller; Ph. D. Thesis, University of Birmingham, 1982.

47 - I.E.C. Mott, T.R. Bott; "The adhesion of biofilms to selected materials of construction for heat exchangers" Proc. of the International Heat Transfer Conference, Jerusalem 1990, Vol. 5, 21-26, Hemisphere Publishing Corporation.

48 - D.R. Oliveira, L. Melo and J.D. Pinheiro; "Fouling by aqueous suspensions of kaolin and magnetite", 2nd UK National Conference on Heat Transfer, vol. 1, 187-197, Glasgow, 1988.

49 - D.R. Oliveira, M.J. Vieira, L.F. Melo and M.M. Pinheiro; "Interaction Between Different Fouling Agents in Water Systems", Proc. of the International Heat Transfer Conference, Jerusalem 1990, vol. 5, 103-108, Hemisphere Publishing Corporation.

50 - D.R. Oliveira; Ph. D. Thesis, Universidade do Minho 1991.

51 - J.Th.G. Overbeek; Colloid Science; Kruyt, H.R., Ed.; Elsevier: Amesterdam vol I, 245 1952.

52 - D.K. Owens and R.C. Wendt; J.; App. Polymer Sci. **13** 1741 1969.

53 - P.G. Papavergos, A.B. Hedley; Chem. Eng. Res. Des., **62**, 275 1984.

54 - J.D. Pinheiro; "Fouling of Heat Transfer Surfaces", in Kakaç, Bergles & Mayinger (Eds). Heat Exchangers: Thermal-Hydraulic Fundamentals and Design, 1013-1035, McGraw-Hill, 1981.

55 - M.M. Pinheiro et al.; "Effect of Design and Operating Variables on Biofouling", in Melo, Bott and Bernardo (Eds.) "Fouling Science and Technology", 223-232, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.

56 - M.M. Pinheiro, L.F. Melo, T.R. Bott, J.D. Pinheiro and L. Leitão; Canadian J. of Chem. Eng., **66**, 63, 1988.

57 - I.H. Pratt-Terpstra, A.H. Weerkamp and H.J. Busscher; Current Microbiology **16** 311 1988.

58 - I.H. Pratt-Terpstra, A.H. Weerkamp and H.J. Busscher; J. of Dental Research **68** 463 1989.

59 - R. Rajagopalan, J.S. Kim; J. of Colloid Int. Sci., **83** 428 1981.

60 - R.S. Rodliffe; "Chemiphoresis as the particulate corrosion product deposition - an explanation for autoretardation", C.E.G.B. Report nº RD/B/N4374, U.K., 1978.

61 - E. Ruckenstein, D.C. Prieve; A.I. Ch.E. Journal **22** 276 1976.

62 - M. Sjadzali; "Studies in Biological Fouling: Adhesion of Microorganisms to a Selection of Surfaces", MSc. Thesis, University of Birmingham, U.K., 1980.

63 - E.F.C. Somerscales, M. Kasemi; "Fouling due to In-Situ Corrosion Products", in Suitor & Pritchard (Eds.) "Fouling in Heat Exchange Equipment", 1- 9, Americ. Soc. Mech. Eng., New York, USA,. 1984.

64 - J.K. Spelt and A.W. Newmann; Langmuir **3** 588 1987.

65 - J. Taborek et al.; Chem. Eng. Progr., **68** (2), 59, 1972.

66 - P. Thackery; "The Cost of Fouling in Heat Exchange Plant", Proc. of Conf. "Fouling-Art or Science?", 1-9, Univ. Surrey, UK, 1979.

67 - W.L. Van Nostrand, S.H. Leach and J.L. Haluska; "Economic Penalties Associated with Fouling of Refinery Heat Transfer Equipment" 619-643, Hemisphere Publ. Corp., New York, 1981.

68 - H. Van Olphen; An Introduction to Clay Colloid Chemistry, Wiley & Sons, New York, 1963.

69 - C.J. Van Oss, R.J. Good and M.K. Chaudhury; Langmuir **4**, 884, 1988.

70 - C.J. Van Oss, M.K. Chaudhury and R.J. Good; Chem. Rev. **88**, 927, 1988.

71 - E.J.W. Verwey, J.Th.G. Overbeek; "Theory of Stability of Lyophobic Colloids" Ed. Elsevier Amesterdam, 1948.

72 - J. Visser; Ph. D. Thesis, Council for National Academic Awards, London, 1973.

73 - M.J. Vold; J. Coll. Sci. **9** 451 1954.

74 - A.P. Watkinson, N. Epstein; "Particulate Fouling of Sensible Heat Exchangers", 4th International Heat Transfer Conf., Vol. 1, paper HE 1.6., Versailles. France, 1970.

75 - G.R. Wiese and T.W. Healy; Trans. Faraday Soc. **66** 490 1970.

76 - B.P.K. Yung; Ph. D.Thesis, University of Birmingham, U.K., 1986.