



# Understanding Adhesion: A Means for Preventing Fouling

R. Oliveira

Engenharia Biológica,  
Universidade do Minho,  
Braga, Portugal

■ Adhesion of particulate materials is an important step in the formation of fouling. Because the size of such materials is generally less than  $1\ \mu\text{m}$ , the phenomenon can be described in terms of colloid chemistry. Accordingly, the net force of interaction between foulants and the surface has been described in terms of DLVO theory (van der Waals attraction and electrostatic double-layer repulsion). However, those forces are sometimes not sufficient to describe the formation of fouling. Recent works have made it possible to calculate the effect of hydrophobic interactions and steric forces, which can also be taken into account. In aqueous media, the various types of interactions can be strongly affected by the pH, the ionic strength, the type of ions, and the presence of polymeric molecules. The objective of this work is to give a general overview of the basic physicochemical factors playing a role in fouling and to outline some practical aspects related to the theoretical reasoning to help prevent or at least mitigate fouling.

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**Keywords:** *adhesion, DLVO theory, surface free energy, hydrophobic interactions, steric forces, ionic strength, ion bridging*

## INTRODUCTION

The accumulation of inorganic particles, microorganisms, macromolecules, and corrosion products on heat exchanger surfaces gives rise to the so-called fouling phenomenon. The development of fouling is perceived as a multistage process, of which adhesion of the fouling agents to surfaces is an essential step.

Fouling occurs when gravitational forces are negligible; this means that only particulate materials of colloidal size (with dimensions  $\leq 1\ \mu\text{m}$ ) will adsorb onto solid surfaces immersed in flowing fluids. Larger particles are not able to adhere, because gravitational and hydrodynamic forces are strong enough to remove them.

The principal attractive forces between colloidal particles are due to *van der Waals* interactions. However, when the particles are immersed in liquid medium, as it is very often the case in heat exchangers, electrostatic double-layer forces can develop; these forces are generally repulsive. Consequently, the adhesion step in a fouling process has been described in the literature in terms of the theory used to explain the stability of lyophobic colloids—the DLVO theory, named after *B. V. Derjaguin, L. D. Landau, E. J. W. Verwey, and J. Th. G. Overbeek* [1, 2].

In addition to DLVO forces (van der Waals and electrostatic), other types of interactions—such as hydrophobic interactions in polar media, ion bridging, and steric interactions in the presence of polymers—can play impor-

tant roles. In bifouling, the adhesion of microorganisms can be strongly dependent on their external appendages.

The net effect is a balance between all possible interactions. A knowledge of the roles of the main variables affecting the interactions outlined above is of great importance, because their correct manipulation can help to prevent or at least mitigate fouling.

## DLVO FORCES

### *Van der Waals Forces*

*Van der Waals* forces are dependent on the geometry and on the physical and chemical properties of the interacting bodies. The most common interacting geometries can be very often approximated to a sphere-plate type or to a plate-plate type (two parallel semi-infinite plates), although other geometries also can be considered [3]. It is customary to calculate energies rather than forces, which are easily interconverted, taking into account that force is the derivative of energy with respect to distance. The correspondent energy is given, for sphere-plate and two-plate geometries, respectively, by

$$V_{\text{wsp}} = -\frac{AR}{6H}, \quad (1)$$

$$V_{\text{wpp}} = -\frac{A}{12\pi H^2}, \quad (2)$$

Address correspondence to Dr. R. Oliveira, Engenharia Biológica, Universidade do Minho, 4709 Braga Codex, Portugal.

where  $R$  is the radius of the spherical particle,  $H$  is the distance of separation, and  $A$  is the *Hamaker* constant. This constant, which accounts for the molecular nature of the interacting entities, is named after *H. C. Hamaker* [4], who extended *F. London's* theory [5] to the interaction between solid bodies, assuming the additivity of molecular interactions. The *Hamaker* constant for the interaction in vacuum of two solid bodies of the same material (i) can be calculated from the molecular properties of the material by the relation

$$A_{ii} = 3/4\pi^2 N_i^2 \alpha^2 h \nu_0, \quad (3)$$

where  $N_i$  is the number of atoms per unit volume,  $\alpha$  is the static polarizability of the atom  $i$ ,  $h$  is Planck's constant, and  $\nu_0$  is the frequency of the electron in the ground state [6]. For the interaction of two different bodies (1 and 2) in vacuum, the resulting *Hamaker* constant is the geometric mean of the individual constants. If the two different materials 1 and 2 are immersed in a medium 3, the overall *Hamaker* constant is given by

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}). \quad (4)$$

The additivity principle is not strictly valid for condensed media interactions. In 1972, Visser [6] presented an excellent review of all the available methods for the calculation of *Hamaker* constants. Thenceforward, it is worth noting the work of *Israelachvili* [7], assuming some simplifications to calculate the *Hamaker* constants from optical data in the ultraviolet region, and the approach proposed by *van Oss* and collaborators [8], based on surface free energy calculations.

According to the approach based on the surface free energy, the *Hamaker* constant is calculated by

$$A_{ii} = \gamma_i^{\text{LW}} 0.24\pi H_0^2, \quad (5)$$

where  $\gamma^{\text{LW}}$  is the *Lifshitz-van der Waals* (apolar) component of the surface free energy and  $H_0$  is the equilibrium separation between the interacting bodies (see the section on hydrophobic interactions), determined by the balance between *Born* repulsion and *van der Waals* attractive forces. The approach of *van Oss* et al. [8] is a very simple method, when compared with the tiresome calculations based on the optical properties proposed by *Israelachvili* [7]. Moreover, despite the improvements in the obtention of electromagnetic data, it is still very difficult to have enough data for a great number of materials.

### Electrostatic Double-Layer Forces

When solid bodies are immersed in a liquid medium, especially in water, they show a generalized tendency to acquire an electrical surface charge, owing to preferential adsorption of ions, by dissociation of surface groups or by isomorphous substitutions in the lattice (e.g., clay minerals). At neutral pH, most of the solid bodies, including microorganisms, possess a net negative charge.

The charge acquisition by a surface immersed in an aqueous medium promotes a redistribution of the ions in solution. The ions of opposite charge (counter-ions) will be attracted to the surface, whereas the ions of same sign (co-ions) will be repelled. This effect creates an electrical double layer at the proximity of the surface. When two charged solid bodies of like sign approach each other, the interpenetration of the two double layers will lead to repulsion.

The potential energy arising from the interpenetration of electrical double layers depends on the geometry of the interacting bodies and on the electrical behavior during the interaction. Generally, it is assumed that the interactions may occur either at constant surface potential or at constant surface charge.

An estimate of the energy of interaction for the sphere-plate type geometry is given by Eq. (6) when the interaction takes place at constant surface potential [9] and by Eq. (7) when the surface charge is kept constant [10].

$$V_{\text{DL-sp}}^{\psi} = \varepsilon\pi R \left\{ (\psi_{01} + \psi_{02})^2 \ln[1 + \exp(-\kappa H)] + (\psi_{01} - \psi_{02})^2 \ln[1 - \exp(-\kappa H)] \right\}, \quad (6)$$

$$V_{\text{DL-sp}}^{\sigma} = -\varepsilon\pi R \left\{ (\psi_{01} - \psi_{02})^2 \ln[1 + \exp(-\kappa H)] + (\psi_{01} + \psi_{02})^2 \ln[1 - \exp(-\kappa H)] \right\}, \quad (7)$$

where  $V_{\text{DL}}^{\psi}$  and  $V_{\text{DL}}^{\sigma}$  are the potential energies of interaction at constant potential and at constant charge, respectively;  $\psi_{01}$  and  $\psi_{02}$  are the electrical surface potentials of the flat surface and spherical particle at infinite separation;  $R$  is the sphere radius;  $\varepsilon$  is the electrical permittivity of the medium; and  $\kappa$  is the reciprocal double-layer thickness, or *Debye-Hückel* parameter, given in SI units by

$$\kappa^2 = \frac{1000e^2 N_A}{\varepsilon K_B T} \sum z_i^2 M_i, \quad (8)$$

where  $e$  is the electron charge,  $N_A$  is *Avogadro's* number,  $K_B$  is Boltzmann's constant,  $T$  is the absolute temperature,  $z_i$  is the counter-ion valence, and  $M_i$  is the counter-ion molarity.  $1/\kappa$  has the dimensions of length, and this is why it is called the double-layer thickness, being always related to the ionic strength of the medium. This relation arises from the definition of ionic strength ( $I$ ), which for a symmetric electrolyte is given by

$$I = \frac{1}{2} \sum z_i^2 M_i. \quad (9)$$

Equations (6) and (7) are valid only for surface potentials  $< 25$  mV, although they can be used without significant errors for potentials of as much as 60 mV, when  $\kappa H > 10$  [11].

The condition of constant surface potential is considered to exist if the surface charge is determined by the adsorption of ions, whereas the situation of constant surface charge is generally assumed when isomorphous substitutions take place [11]. The most common case in biological systems is an intermediate situation where the surface charge is acquired by ionization or dissociation of surface groups. Several models are found in the literature [12–15] to deal with such complex situations.

There is still a practical impossibility in determining the surface potentials; thus, in all the calculations, they are replaced by zeta potential values [16]. Zeta potential values of small particles are easily obtained by microelectrophoresis. The same technique can be used for surfaces of macroscopic bodies after grinding; otherwise streaming-potential measurements can be utilized for such bodies.

## DLVO Theory

As outlined before, according to DLVO theory, adhesion is determined by the balance between the attractive *van der Waals* forces and the commonly repulsive forces due to electrical double-layer interactions. By convention, attractive forces are negative and repulsive forces are positive. When the latter are predominant, the total potential energy of interaction as a function of the distance between two bodies can assume the profile illustrated in Fig. 1. this convention makes it possible to speak of the “height” of the energy barrier and the “depth” of the minima. According to DLVO theory, the primary minimum is of infinite depth. This means that the interacting bodies will attain maximal stability in the primary minimum of energy.

The existence of a secondary minimum permits an explanation for the reversibility of adhesion [17]. Interacting bodies stabilized in the secondary minimum of energy are still capable of Brownian motion and can be easily removed, for instance, by washing.

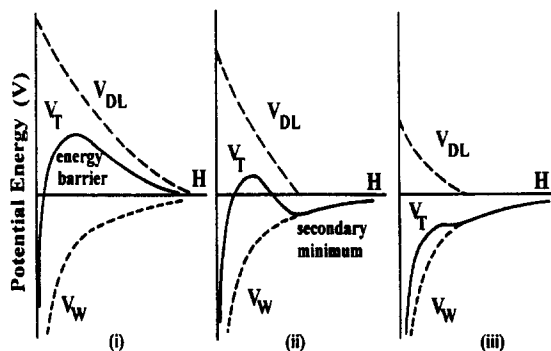
The energy profile is affected by all the parameters mentioned before; ionic strength is very important in the determination of the height of the energy barrier. As can be seen from Fig. 1, an increase in ionic strength lowers the energy barrier and hence favors adhesion. Ruckenstein and Kalthod [18] presented an interesting simulation of the effect of all the parameters affecting the energy profile.

## OTHER FORCES

The experimental evidence for forces other than DLVO forces is well established in a great number of cases; but owing to their complexity, these other forces are not easily translated in mathematical terms, and so they have been mentioned only to explain deviations from the theoretical previsions.

## Hydrophobic Interactions

Hydrophobic interactions are considered to be attractive; if they have a repulsive effect, they are referred to as “hydration pressure.” According to *van Oss* and collaborators [8], those forces, based on electron donor–electron acceptor (*Lewis* acid–base) interactions in polar media



**Figure 1.** DLVO potential energy of interaction between two bodies having the same sign charge: (i) low ionic strength; (ii) intermediate ionic strength; (iii) high ionic strength.

(e.g., water), are responsible for all the anomalies found in the theoretical interpretation of interfacial interactions in such media, because they can surpass the DLVO forces by as much as two decimal orders of magnitude. These authors consider that the surface tension ( $\gamma$ ) of a given substance comprises two components: one arising from nonpolar interactions of the *Lifshitz–van der Waals* type ( $\gamma^{LW}$ ) and the other due to polar interactions of the electron donor–electron acceptor type ( $\gamma^{AB}$ ), similar to *Lewis* acid–base interactions (including the special case of hydrogen donor–hydrogen acceptor interactions). The surface tension is then expressed by

$$\gamma = \gamma^{LW} + \gamma^{AB}, \quad (10)$$

with

$$\gamma^{AB} = 2(\gamma^+ \cdot \gamma^-)^{1/2}, \quad (11)$$

where  $\gamma^+$  and  $\gamma^-$  are the electron acceptor and the electron donor parameters of the acid–base component of the surface tension, respectively.  $\gamma^{LW}$ ,  $\gamma^+$ , and  $\gamma^-$  can be determined from contact angle measurements with at least three different liquids of well-known surface tensions. For the calculation of the apolar component, liquids such as  $\alpha$ -bromonaphthalene, diiodomethane, or decane are used; whereas, for the determination of the polar component, the liquids normally used are water, formamide, and glycerol.

On the basis of previous works of other authors, *van Oss* et al. [8] proposed the following equation for the calculation of the decay with distance of the free energy ( $\Delta F^{AB}$ ) for the polar interaction between two flat plates:

$$\Delta F_{pp}^{AB} = \Delta F^{AB}(H_0) \exp[(H_0 - H)/\lambda]. \quad (12)$$

Using the approach of *Derjaguin* [9], Eq. (12) can be modified to obtain the equation for the sphere–plate type conformation, which is

$$\Delta F_{sp}^{AB} = 2\pi R \lambda \Delta F^{AB}(H_0) \exp[(H_0 - H)/\lambda], \quad (13)$$

where  $\lambda$  is the correlation length pertaining to water molecules,  $H_0$  is the equilibrium distance,  $H$  is the distance, and  $\Delta F^{AB}(H_0)$  is the free energy at the distance of equilibrium. This equation is valid if  $H > \lambda$ . For pure water, the value of  $\lambda$  is about 0.2 nm. At higher ionic strengths, the values of  $\lambda$  are related to the dimensions of the hydrated ions and can be as high as 1.2 nm [8]. The average value found for the minimum distance of equilibrium ( $H_0$ ) is 0.157 nm, with a standard deviation of 0.007 nm [8].

Free energy  $\Delta F^{AB}(H_0)$  is a function of the electron donor ( $\gamma^-$ ) and electron acceptor ( $\gamma^+$ ) parameters of the polar component ( $\gamma^{AB}$ ) of the surface tension (surface free energy) of the interacting bodies [8].

If a material 1 interacts with a material 2 when immersed in a medium 3, the polar component of the free energy of interaction is expressed by

$$\begin{aligned} \Delta F_{132}^{AB}(H_0) &= 2 \left\{ (\gamma_3^+)^{1/2} \left[ (\gamma_1^-)^{1/2} + (\gamma_2^-)^{1/2} - (\gamma_3^-)^{1/2} \right] \right. \\ &\quad + (\gamma_3^-)^{1/2} \left[ (\gamma_1^+)^{1/2} + (\gamma_2^+)^{1/2} - (\gamma_3^+)^{1/2} \right] \\ &\quad \left. - (\gamma_1^+ \cdot \gamma_2^-)^{1/2} - (\gamma_1^- \cdot \gamma_2^+)^{1/2} \right\}. \quad (14) \end{aligned}$$

The free energy of polar interactions, as expressed by Eqs. (12) and (13), has the dimensions of energy (joule). The DLVO theory can be extended by also integrating the hydrophobic interactions; this can be done by adding the free energy of polar interactions ( $\Delta F^{AB}$ ) to the two parameters constituting this theory—namely,  $V_w$  and  $V_{DL}$ .

### Short-Range Repulsive Forces

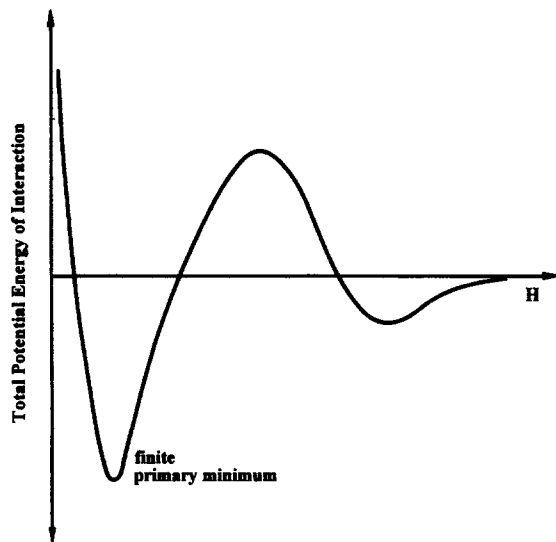
The effects of hydrodynamic forces on the removal of deposited materials can be explained only if the primary minimum of energy attained by the interacting bodies is of finite value [17–20]. Otherwise, an infinite value of energy would be necessary to promote the detachment of deposited particles. A similar explanation was suggested by Hamaker [4] when studying the reepitization (defloculation) of colloidal particles.

A finite primary minimum is obtained by considering the effect of a short-range repulsive force, which determines the minimum distance that interacting bodies can approach without repulsion of their atomic orbitals. This is a *Born* repulsion type of force expressed for sphere-plate and plate-plate conformation by, respectively,

$$V_{BR_{sp}} = \frac{AH_0^6 R}{168H^7}, \quad (15)$$

$$V_{BR_{pp}} = \frac{AH_0^6}{48\pi H^8}. \quad (16)$$

If DLVO theory is extended to account for the effect of those short-range repulsive forces, we obtain a possible profile for the total potential energy of interaction as presented in Fig. 2. *Frens* and *Overbeek* [14] claimed that *Born* repulsions do not arise between coagulated particles, although they have considered that Brownian collisions cannot bring two particles close than twice the distance between the particle surface and the outer *Helmothz* plane of the electrical double layer.



**Figure 2.** Total potential energy of interaction, taking into account short-range repulsive forces (*Brown* repulsion).

### Steric Interactions

Steric interactions may arise between polymer-coated surfaces and can be very important, especially in biological systems, where macromolecules are always present either free or attached to the cell surface (polysaccharides, proteins, glycoproteins, lipopolysaccharides, teichoic acids, etc.). The adsorption of such soluble macromolecules may occur before any appreciable microbial adhesion takes place, giving rise to the so-called conditioning of the surface.

The potential energy of interaction between two uncharged polymer-coated surfaces is complex. The few existing mathematical models include some parameters that are difficult to obtain. Therefore the values assumed have not always matched experimental evidence.

Essentially, these models consider the additive contribution of three terms [21–23]:

1. a mixing term related to the polymer segment concentration in the interacting zone;
2. an elastic term related to the loss of configurational entropy of the polymer; and
3. an adsorption, or bridging, term (important at low coverage).

The complexity increases when the surface layers are electrically charged or if the polymers are polyelectrolytes.

### Ion Bridging

Positively charged ions can act as bridging agents between two negatively charged surfaces. Bivalent cations, such as  $Ca^{2+}$  and  $Mg^{2+}$ , are considered the most effective ion binders. They are especially important in the adhesion of microorganisms [24, 25]. Different mechanisms have been proposed to explain the role of the bivalent ions in the process of adhesion of microbial cells, including the formation of a cation bridge between the cell and the substratum [24] and the precipitation of polymers, mediated by the cation, between the cell and the substratum [26]. *Van Oss* et al. [27] proposed that  $Ca^{2+}$  can depress the monopolar electron donor parameter of the surface tension of the interacting bodies, depressing their mutual repulsion and their degree of hydration and resulting in a decrease of hydration pressure.

The effect of other cations is not predictable, mainly when microbial adhesion is concerned. A study on the adhesion of *Pseudomonas fluorescens* to copper, brass, and aluminum surfaces showed that the formation of deposits is delayed in the presence of  $Cu^{2+}$  and  $Zn^{2+}$  ions because these ions have a pronounced inhibitory effect on the growth of this microorganism [28].

## PRACTICAL ASPECTS

To give a better understanding of the theoretical reasoning that has been presented so far, a few practical aspects related to the controlling and mastering of fouling are outlined in this section.

### Type of Surface

Care should be taken in surface finishing; otherwise, particles can be trapped in crevices and cracks, and nonspherical particles may move along the surface to find a position

of larger intimate contact. On the other hand, if the surface presents a microroughness, the minimal number of contact points may reduce the possibility of adhesion [29]. Interference with the *van der Waals* variables, so as to reduce fouling, is rather difficult, because in the majority of situations it is not possible to modify the shape and the nature of the interacting bodies.

Precoating the surface with polymers is advisable when colloidal suspensions are to be stabilized by the addition of polymers. The same polymer must be used to prevent the formation of polymer bridging that would be easily established with the bare surface. Proteins are known to establish hydrophobic interactions; so, when processing biological fluids with high protein content (e.g., milk), one should try to minimize protein adsorption. This can be achieved by promoting the formation of hydration layers onto hydrophobic surfaces.

Bacteria adhere more readily to hydrophobic surfaces than to hydrophilic ones [30]. Adsorption of dissolved substances (e.g., fatty acids and hydrocarbons) onto hydrophilic surfaces (e.g., glass and metals) may increase bacterial attachment. The presence of such substances in solution is to be avoided if microbial attachment is undesirable.

### pH, Ionic Strength, and Type of Ion

Ionic strength and pH are two important variables that can be related: a change in pH is accompanied by a change in ionic strength (the reverse may not always be true). In a study of the deposition of kaolin particles onto copper surfaces as a function of pH, it was found that the deposit was much thicker when the pH was kept constant by the addition of  $\text{Na}_2\text{CO}_3$  than by the addition of NaOH (Fig. 3) [20].  $\text{Na}_2\text{CO}_3$  is a weaker base than NaOH, which means that, to attain the same pH value, it is necessary to add larger amounts of this electrolyte. Although the zeta potential values of the kaolin particles were slightly more negative in the presence of  $\text{Na}_2\text{CO}_3$ , the significant increase in ionic strength, promoting a decrease in the height of the energy barrier, can be considered responsible for the greater thickness of the deposit. When NaOH was used, the measured zeta potential values also became more negative with the increase of pH. However, the small amount of this strong electrolyte required to increase the pH was not enough to promote considerable

changes in ionic strength, to counterbalance the other effect. As the pH was raised, a significant decrease in the thickness of the deposits was obtained; at pH = 10.5, the amount of deposit was not measurable, which can be attributed to the increase in electrostatic repulsion between the more negative particles and the negatively charged surface of deposition. It must be noted that the experiments with  $\text{Na}_2\text{CO}_3$  also showed a decrease in deposit thickness with increasing pH values; however, this decrease was less marked. Figure 3 shows that similar results were obtained with the use of magnetite particles instead of kaolin.

Adjustment of pH is also very important when proteins are potential foulants. Those macromolecules are very sensitive to pH changes, and a small shift in pH can markedly alter their surface charge and conformation, reversing their ability for adhesion.

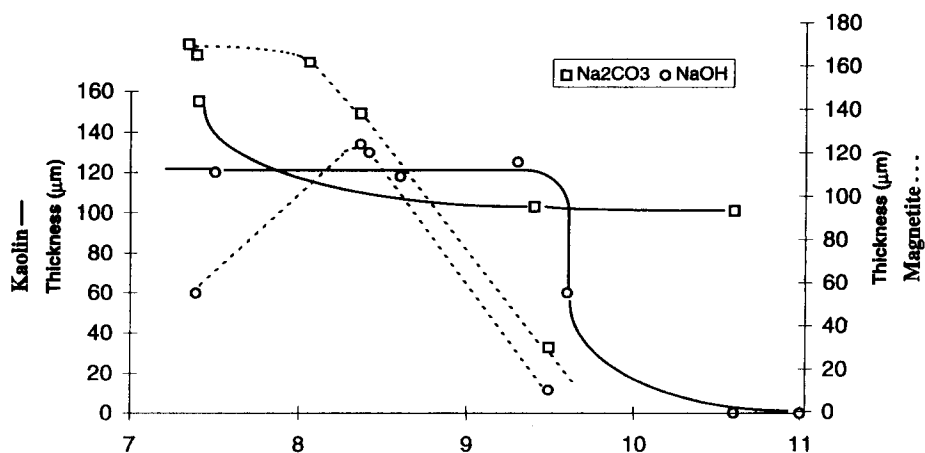
As mentioned before, divalent cations, such as  $\text{Ca}^{2+}$ , can have a strong binding effect; this effect can be minimized by the addition of calcium binders, such as polyphosphates or EDTA.

### Electrical Charge of Particles

The presence of hematite particles ( $\text{Fe}_2\text{O}_3$ ) or hydrous alumina [ $\text{Al}(\text{OH})_3$ ] should be avoided, because, at neutral pH values, those particles carry a positive charge and are promptly attracted to surfaces, forming a positively charged coating ready to attract negative particles. Removal of such deposits is rather difficult because they are strongly bound by electrostatic interactions.

An electrochemical treatment to prevent fouling, based on the alteration of particle charge, is now available, having the trade name of Zeta Rod [31]. The installation of an insulated and sealed electrode into a metal pipe or vessel forms a capacitor within which the surface charge is elevated on wetted surfaces of the containment as well as any particles in suspension. The alteration in surface charge is readable as an elevation in zeta potential. The generated field strength across the water is a function of charge voltage, system dimensions, and the dielectric constant of the water.

The polarity of the charge imposed upon the conductor within the electrode determines the polarity to be imposed upon the suspended particles. The inner-layer ions of the double layer may thus be manipulated to be anions



**Figure 3.** Thickness of kaolin and magnetite deposits as a function of pH and type of chemical ( $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ ) used to control the pH of the medium.

or cations to control the effect of electrostatic double-layer forces, according to the isoelectric properties of the species. However, at high ionic strengths, the efficiency of the system is reduced; this effect can be offset by elevating the voltage level with which the capacitor system is charged. Field studies have shown that an increase from 10,000 V DC to 30,000 V DC could restore the antifouling effect in waters having high concentrations of polyvalent ions [31].

### CONCLUSION

Understanding the fundamentals of adhesion can guide us to create conditions that will reduce the attractive forces and enhance the repulsive interactions so that fouling will be prevented. In addition, in flowing systems, it is also important to avoid dead spaces or stagnant zones; high fluid velocities will create high drag forces that will promote the detachment of foulants.

### NOMENCLATURE

$A$	Hamaker constant, J
$e$	electrical charge of electron, C
$\Delta F^{AB}(H_0)$	change of free energy due to polar interactions at the distance of equilibrium, J
$\Delta F_{pp}^{AB}$	change of free energy due to polar interactions between two flat plates, J
$\Delta F_{sp}^{AB}$	change of free energy due to polar interactions between a sphere and a flat plate, J
$h$	Planck's constant, J/s
$H$	distance between interacting bodies, m
$H_0$	distance of equilibrium between interacting bodies, m
$I$	ionic strength of the medium, mol/dm <sup>3</sup>
$K_B$	Boltzmann's constant, J/K
$M_i$	counter-ion molarity, mol/dm <sup>3</sup>
$N_A$	Avogadro's number
$N_i$	number of atoms of material $i$ per unit volume
$R$	radius of particle, m
$T$	absolute temperature, K
$V_{BR}$	potential energy associated with Born repulsion, J
$V_{DL}$	potential energy due to double-layer forces, J
$V_{DL}^{\psi}$	potential energy due to double-layer forces interacting at constant surface potential, J
$V_{DL}^{\sigma}$	potential energy due to double-layer forces interacting at constant surface charge, J
$V_w$	potential energy due to van der Waals forces, J
$z_i$	valence of counterion $i$
<b>Greek Symbols</b>	
$\alpha$	polarizability, C <sup>2</sup> J <sup>-1</sup> m
$\gamma^{AB}$	acid-base (polar) component of the surface tension, J/m <sup>2</sup>
$\gamma^+$	electron acceptor parameter of the polar component of surface tension, J/m <sup>2</sup>

$\gamma^-$	electron donor parameter of the polar component of surface tension, J/m <sup>2</sup>
$\epsilon$	electrical permittivity, F/m
$\kappa$	reciprocal of double-layer thickness, m <sup>-1</sup>
$\lambda$	correlation length of water molecules, m
$\psi_{0i}$	electrical potential of surface $i$ , V

### REFERENCES

- Derjaguin, B. V., Theory of the heterocoagulation, interaction and adhesion of dissimilar particles in solutions of electrolytes. *Discuss. Faraday Soc.* **18**, 85, 1955.
- Verwey, E. J. W., Overbeek, J. Th. G. *Theory of Stability of Lyophobic Colloids*. Elsevier, Amsterdam, 1948.
- Hiemenz, P. C., *Principles of Colloid and Surface Chemistry*. Marcel Dekker, New York, 1985.
- Hamaker, H. C., A General Theory of Lyophobic Colloids. *Physica*, **4**, 1058, 1937.
- Visser, J., The adhesion of colloidal particles to a planar surface in aqueous solutions, Ph.D. Thesis, Council of National Academic Awards, London, 1973.
- Visser, J., On Hamaker Constants: A Comparison Between Hamaker Constants and Lifshitz-van der Waals Constants. *Adv. Colloid Sci.* **3**, 331-363, 1972.
- Israelachvili, J. N., Measurement of Forces Between Surfaces Immersed in Electrolyte Solutions. *Faraday Disc. Chem. Soc.* **65**, 20-24, 1978.
- van Oss, C. J., *Interfacial Forces in Aqueous Media*. Marcel Dekker, New York, 1994.
- Hogg, R., Healy, T. W., and Fuerstenau, D. W., Mutual Coagulation of Colloidal Dispersions. *Trans. Faraday Soc.* **62**, 1638-1651, 1966.
- Wiese, G. R. and Healy, T. W., Effect of particle size on colloid stability. *Trans. Faraday Soc.* **66**, 490, 1970.
- Rajagopalan, R., and Kim, J. S., Adsorption of Brownian Particles in the Presence of Potential Barriers: Effects of Different Modes of Double Layer Interaction. *J. Colloid Interface Sci.* **83**, 428-448, 1981.
- Gregory, J., Interaction of Unequal Double Layers at Constant Charge. *J. Colloid Interface Sci.* **51**, 44-51, 1975.
- Kar, G., Chander, S., and Mika, T. S., The Potential Energy of Interaction Between Dissimilar Electrical Double Layers. *J. Colloid Interface Sci.* **44**, 347-355, 1973.
- Frens, G., and Overbeek, J. Th. G., Repeptization and the Theory of Electrostatic Colloids. *J. Colloid Interface Sci.* **38**, 376-387, 1972.
- Lyklema, J., Colloid Stability as a Dynamic Phenomenon. *Pure Appl. Chem.* **52**, 1221-1227, 1980.
- Hunter, R. J., *Zeta Potential in Colloid Science*. Academic Press, London, 1988.
- Ruckenstein, E., Reversible Rate of Adsorption or Coagulation of Brownian Particles: Effect of the Shape of Interaction Potential. *J. Colloid Interface Sci.* **66**, 531-543, 1978.
- Ruckenstein, E., and Kalthod, D. G., Role of Hydrodynamics and Physical Interactions in the Adsorption and Desorption of Hydrophobic or Globular Proteins. In *Fundamentals and Applications of Surface Phenomena Associated with Fouling and Cleaning in Food Processing*, B. Hallstrom, D. B. Lund, Ch. Trägårdh, Eds., pp. 115-167, Tylosand, Sweden, 1981.
- Kallay, N., Biskup, B., Tomic, M. and Matijevic, E., Particle adhesion and removal in model systems. *J. Colloid Interface Sci.* **114**, 357-362, 1986.
- Oliveira, R., Melo, L., Pinheiro, M., and Vieira, M. J., Surface Interactions and Deposit Growth in Fouling of Heat Exchangers. *Corrosion Rev.* **11** (1-2), 55-95, 1993.

21. Vrij, A., Polymers at Interfaces and the Interactions in Colloidal Dispersions. *Pure Appl. Chem.* **48**, 471–483, 1976.
22. Napper, D. H., Steric Stabilization. *J. Colloid Interface Sci.* **58**, 390–407, 1977.
23. Scheutjens, J. M. H. N., and Fleer, G. J., Effect of Polymer Adsorption and Depletion on the Interaction Between Two Parallel Surfaces. *Adv. Colloid Interface Sci.* **16**, 361–380, 1982.
24. Marshall, K. C., Stout, R., and Mitchell, R., Mechanism of the Initial Events in the Sorption of Marine Bacteria to Surfaces, *J. Gen. Microbiol.* **68**, 337–348, 1971.
25. Fletcher, M., and Floodgate, G. D., An Electron Microscopic Demonstration of an Acidic Polysaccharide Involved in the Adhesion of a Marine Bacterium to Solid Surfaces. *J. Gen. Microbiol.* **74**, 325–334, 1973.
26. Rutter, P. R., The physical chemistry of the adhesion of bacteria and other cells, in *Cell Adhesion and Motility*, A. S. G. Curtis and J. D. Pitts, Eds., pp. 103–135, Cambridge University Press, London, 1980.
27. van Oss, C. J., Chaudhury, M. K., and Good, R. J., Monopolar Surfaces. *Adv. Colloid Interface Sci.* **28**, 35–64, 1987.
28. Vieira, M. J., Oliveira, R., Melo, L., Pinheiro, M. M., and Martins, V., Effect of Metallic Ions on the Adhesion of Biofilms Formed by *Pseudomonas fluorescens*. *Colloids Surf. B Biointerfaces* **1**, 119–124, 1993.
29. Visser, J., Adhesion and removal of particles, I, in *Fouling Science and Technology*, L. F. Melo, T. R. Bott and C. A. Bernardo, Eds., pp. 87–104, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.
30. Fletcher, M., Bright, J. J., and Pringle, J. H., Attachment of Aquatic Bacteria to Solid Surfaces. In *Fouling of Heat Exchanger Surfaces*, R. W. Bryers, S. S. Cole, Eds., pp. 33–49, Engineering Foundation, New York, 1983.
31. Pitts, M. M., Jr., Fouling Mitigation in Aqueous Systems Using Electrochemical Water Treatment. Proc. of the Engineering Foundation Conf. on Fouling Mitigation of Industrial Heat Exchangers, Shell Beach, California, June 18–23, 1995.

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Received April 17, 1996; revised September 13, 1996