FOULING BY AQUEOUS SUSPENSIONS OF MAGNETITE PARTICLES - THE EFFECT OF pH AND IONIC STRENGTH

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ABSTRACT

Particles adhesion is one of the fundamental steps in heat exchanger fouling. Surface interactions are affected by a considerable number of factors related to the nature of the surfaces involved, and to the composition and dynamics of the fouling fluid.

Although quantitative predictions of the rate of adhesion are still not feasible in practical situations, the evaluation of the potential energy of interaction between two surfaces *"in each vicinity"* can be a valuable tool for the qualitative assessment of the fouling tendencies. For that purpose experimental determination of the parameters characterizing the physico-chemical properties of the interacting surfaces are required.

The present paper reports studies on particulate fouling caused by aqueous suspensions of magnetite on copper surfaces.

A series of experiments were carried out at different pH values in the range of 7.5 - 9.5. For each pH two distinct types of experiments were performed: in one case the pH was controlled with NaOH and in the other the pH controlling medium was Na_2CO_3. Each run lasted 20 days and at the end the thickness of the deposits was measured by means of a micrometer coupled to an electrical circuit.

The zeta potentials and surface tensions of the solids were measured and used in the interpretation of the results, which was carried out in terms of the DLVO Theory.

1. INTRODUCTION

Although it is generally accepted that particulate fouling of heat exchangers involves three sequential steps - transport, adhesion and removal - most of the studies reported until now have been focused on the mechanisms responsible for the transport of particles to the surfaces where the deposition takes place.

However, the fact that particles reach the surface does not mean that they will be attached to it. So, attachment is another prerequisite for the occurrence of fouling and is related to the flow conditions and to the physico - chemical properties of the surface, the particles and the suspending fluid, which give rise to interaction forces capable of keeping the two interacting solids together.

Among the large number of factors affecting the process of adhesion, both the pH and the ionic strength of the medium play an important role when aqueous suspensions are concerned.

As iron oxide particles are very often present in industrial waters, at least as a corrosion product, it was decided to study the influence of the pH and, in certain way, of the ionic strength on the deposition of magnetite particles on copper surfaces.

2. THEORETICAL

The stability of colloidal suspensions is described by the so called DLVO theory, named after *Derjaguin* and *Landau* [1] and *Verwey* and *Overbeek* [2]. This theory has also been applied to deposition studies, since *Marshall* and *Kitchener* [3], established the parallelism between the two types of phenomena.

DLVO theory considers the total energy of interaction between two bodies, immersed in a third medium, as the result of the *Van der Waals* (V_W) and double-layer (V_{DL}) interactions.

To account for removal, it has been suggested that the *Born* repulsion (V_B), arising at short distances, should be considered in order to modify the energy profile, its effect being the creation of a finite primary minimum [4,5]. Otherwise it would be impossible to remove particles stabilized in an infinite energy well.

Thus, the total potential energy of interaction (V_T) is expressed by:

$$V_T = V_W + V_{DL} + V_B \tag{1}$$

Considering the interaction between a sphere and a flat plate at constant surface potential, each of the partial energies is given by [6, 7, 8]:

$$V_W = -\frac{AR}{6H} \tag{2}$$

$$V_{DL} = +\varepsilon\pi R\left[(\psi_{01}+\psi_{02})^2 \ln\left(1+\exp(-\kappa H)\right) + (\psi_{01}-\psi_{02})^2 \ln\left(1-\exp(-\kappa H)\right)\right] \tag{3}$$

$$V_B = \frac{A\, d_0^{6}\, R}{168\, H^7} \tag{4}$$

where

A - *Hamaker* constant

Experimental Heat Transfer, Fluid Mechanics, and Thermodynamics 1991
J.F. Keffer, R.K. Shah, and E.N. Ganić, Editors

R - particle radius
H - distance between interacting bodies
ε - electric permittivity of the medium
ψ_{oi} - electric surface potential of body i
κ - *Debye-Hückel* parameter (reciprocal double-layer thickness)
d_0 - distance of closest approach

Those equations hold for $R >> H$.

It is worth noting a few points about some of the parameters mentioned above:

. the *Debye-Hückel* parameter (κ) can be evaluated by means of [7]

$$\kappa = \frac{e^2}{\varepsilon K_B T} \sum_i Z_i^2 \, n_{io} \qquad (5)$$

where

e - electron charge
K_B - Boltzmann constant
T - absolute temperature
Z_i - valency of ion i
n_{io} - bulk concentration of ion i;

. due to the practical impossibility of determining the values of ψ_{oi} it is common practice to replace them by the corresponding zeta potential values [9];

. the distance of closest approach (d_0) can be determined using the following equation [11]

$$\Delta G^d = \frac{A}{12\pi \, d_0{}^2} \qquad (6)$$

ΔG^d is the dispersion component of the free energy of adhesion.

ΔG^{ad} is the free energy of adhesion, related to the surface tensions (γ) of the interacting bodies by means of [12]

$$\Delta G^{ad} = \gamma_{sp} - \gamma_{sl} - \gamma_{pl} \qquad (7)$$

where s stands for solid surface, p for particles and l for liquid.

The interfacial energy between any two bodies i and j can be calculated by the geometric mean equation [13]

$$\gamma_{ij} = \gamma_i + \gamma_j - 2\left(\gamma_i^d \cdot \gamma_j^d\right)^{1/2} - 2\left(\gamma_i^p \cdot \gamma_j^p\right)^{1/2} \qquad (8)$$

with γ^d and γ^p denoting, respectively the dispersion and polar components. The surface free energies of solids can be determined by contact angle measurements, with liquids of known surface free energies, by a least square fitting of the data, according to [14]

$$\cos\theta = -1 + \{[2(\gamma_s^d \cdot \gamma_l^d)^{1/2}]/\gamma_l\} + \{[2(\gamma_s^p \cdot \gamma_l^p)^{1/2}]/\gamma_l\} - (\pi_e/\gamma_l) \qquad (9)$$

θ is the contact angle and π_e is the spreading-pressure, defined as the difference between γ_s - value in the air - and γ_{sv} - value in the presence of the liquid used for contact angle measurements.

3. EXPERIMENTAL METHODS

Particles

The magnetite particles (offered by Vicominas, a Mining Company in Vila Real - North of Portugal) used in this study had a broad range of sizes, as determined by laser granulometry, with an average size around 10 µm. An X - ray diffraction analysis showed that *chlorite*, *quartz* (silicious materials) and *hematite* were present as contaminants.

Fouling tests

These tests were performed with aqueous suspensions of 2 g/l of magnetite, at pH in the range 7.5 - 9.5, bulk water temperature 20°C, flowing at a velocity of 0.415 m/s (*Reynolds* number = 5800). The test section is an annular duct, 2m long, assembled horizontally, consisting of a commercial copper tube (OD = 16 mm) inserted in a perspex tube (ID = 32 mm).

For each pH value two distinct types of experiments were performed: in one case the pH was kept constant by addition of NaOH and in the other the controlling medium was Na_2CO_3.

The addition of the electrolytes was done automatically by means of a pH controller linked to an electronic valve.

Each run lasted 20 days and at the end the thickness of the deposits was measured by a micrometer coupled to an electrical circuit [15].

The copper tubes, one for each experiment, were cleaned with a dilute solution of acetic acid and rinsed with water.

Zeta potential determinations

Zeta potential calculations were performed by micro-electrophoresis using the *Smoluchowski* equation [19].

The electrophoretic mobility data were obtained in a *Zetameter* apparatus. For each of the solids - *magnetite* and *copper* - two types of suspensions were prepared: in one case the desired values of pH were obtained via addition of NaOH and in the other the electrolyte used was Na_2CO_3.

In order to avoid possible effects of extraneous ions no buffers were used. However, to account for alterations in pH due to the dissolution of CO_2, the suspensions were prepared in a N_2 atmosphere.

Copper had to be ground to small particles in order to be suspended.

Contact angle measurements and surface free energy calculations

The contact angle measurements were carried out employing the sessile drop technique and the approach of *Busscher et al.* [16], using as wetting agents, water, α-bromonaphthalene and mixtures of water n-propanol.

The pure liquids reference states are mentioned elsewhere [17].

The surface free energies were calculated by a least square fitting of the data, obtained from contact angle measurements, according to equation (9).

The copper surface was cleaned using the same procedure mentioned for the fouling tests.

4. RESULTS

The zeta potential values for copper and magnetite are presented, respectively, in Figures 1 and 2.

In the case of copper, for pH values above 8, in the presence of NaOH, the zeta potential tends to decrease in magnitude.

This particular trend has been observed in other systems and seems to be due to specific adsorptions of some ions [9]. However, when Na_2CO_3 was used, this effect may have been counterbalanced by an increase in the ionic strength which affected the extension of the double layer, shifting the zeta potentials towards more negative values.

The values of contact angles, surface free energies and π_e, for copper and magnetite are summarized in Table I.

Table I
Contact angles (degree), surface free energies and spreading pressures (mJ.m^{-2}) for copper and magnetite

Solid	θ_{wat}	$\theta_{\alpha\text{-br}}$	πe	γ_s	γ_s^d	γ_s^p
copper	80.4	29.2	23	49	39	10
magnetite	51.1	0.0	35.1	89.3	44.4	44.9

It must be stressed that those values report to the magnetite and copper used, both being quite impure, and cannot be used as reference values.

The free energy of adhesion between magnetite and copper when immersed in water is given by equation (7), the results being presented in Table II.

Table II
Free energy of adhesion (mJ.m^{-2})

System	ΔG^{ad}	ΔG^{d}	ΔG^{p}
magnetite/copper/water	- 10	- 6	- 4

The deposits obtained in the fouling tests, were dark grey and for pH values in the range 7.5 - 8.5 they covered all the copper surface, displaying a very homogeneous aspect. **Figure 3** shows the deposit thickness as a function of pH and type of chemicals used to control the medium.

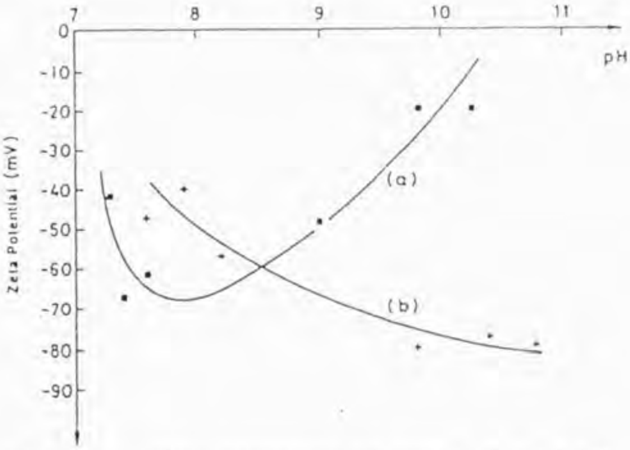

Figure 1 - Zeta potentials for copper versus pH: **(a)** pH controlled with NaOH; **(b)** pH controlled with Na_2CO_3.

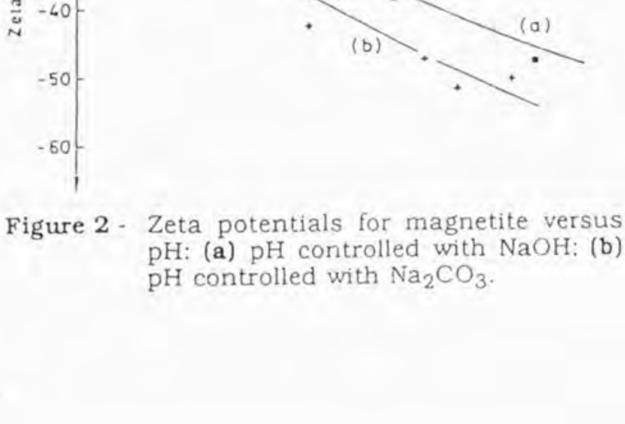

Figure 2 - Zeta potentials for magnetite versus pH: **(a)** pH controlled with NaOH; **(b)** pH controlled with Na_2CO_3.

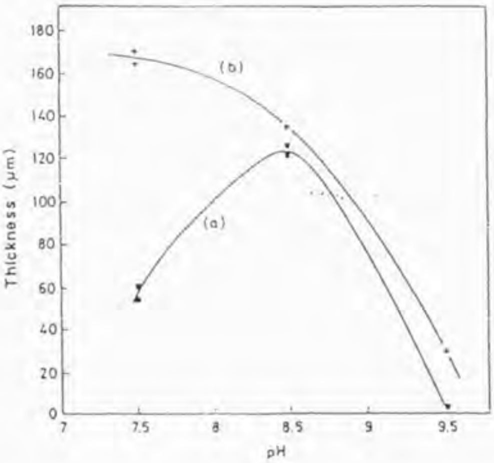

Figure 3 - Thickness of magnetite deposits versus pH: **(a)** pH controlled with NaOH; **(b)** pH controlled with Na_2CO_3.

As a general trend, it can be said that an increase in pH promotes a decrease in the deposit thickness, although at pH 8.5 in the presence of NaOH a different behaviour can be observed.

5. DISCUSSION

The formation of deposits includes two distinct types of interactions: the first one occurs between suspended particles and the clean surface of deposition until a monolayer is formed; during the second one, the interactions will be between the deposited particles and the ones still in suspension. It should be stressed that this study is mainly concerned with the interactions between the magnetite particles and the copper surface (heterocoagulation).

It is expected that the total potential energy curves, for the interaction magnetite/water//copper/, at pH = 7.5 have features different from the ones at pH = 9.5, in order to explain why there is no formation of deposits at pH ≥ 9.5, while at pH = 7.5 they are likely to occur.

In the present situation the most important factors affecting the shape of the curves are the ionic strength, related to the *Debye-Hückel* parameter, and the zeta potential values, since both depend on the pH value.

The values of the *Debye-Hückel* parameter, as a function of pH and type of chemicals are listed in Table III.

The corresponding values of the zeta potential can be read from Figure 1 and 2.

Table III
Debye-Hückel parameter (m^{-1})

pH	NaOH	Na_2CO_3
7.5	1.95×10^7	3.58×10^7
9.5	3.90×10^7	5.98×10^7

Although they are not directly affected by pH two other parameters are worthy of some coments - the radius of the particles and the *Hamaker* constant.

As was said before, magnetite particles had a wide range of sizes, but the deposits, when observed by scanning electron microscopy, showed that they were only composed by particles having sizes under 5 µm, with most of the particles under 1 µm. It must be stated that the observations were focused on the deposit formed on the lower part of the copper tube, where no gravitic sedimentation is likely to occur.

The *Hamaker* constant for the interaction magnetite (1)/water (3)/copper (2) was considered to be $A_{132} = 9.5 \times 10^{-20}$ J. This value was obtained from:

$$A_{132} = (A_{131} \times A_{232})^{1/2}$$

where $A_{232} = 3 \times 10^{-19}$ J, value determined for copper by *Lifshitz* theory [18] and $A_{131} = 3 \times 10^{-20}$ J, value considered for magnetite. This last value was determined by *Fowkes* [10] for hematite and accepted here for magnetite, because no references were found in literature about magnetite *Hamaker* constants.

No great error is expected in making this assumption, because both mineralogical species are iron oxides. In fact, since the differences detected between oxides in general are not of major importance [19, 20], by a greater reason it will not be expected to find distinct values between these two oxides in particular.

Moreover this value is comprised in the range for oxides as determined by the *Lifshitz* theory [21].

Figure 4 shows the total potential energy curves calculated for the case where NaOH is used as controlling medium.

As can be seen, the curve for pH = 7.5 has a deeper primary minimum (V_0) than the curve for pH = 9.5. This means that particles can attain a higher stability at pH = 7.5. At pH = 9.5, the energy barrier $V_{max} - V_0$ is less than for pH = 7.5 which suggests that it is not very difficult to remove particles deposited in the primary minimum.

The ease of removal can be responsible for the much smaller amount of deposit formed in this condition.

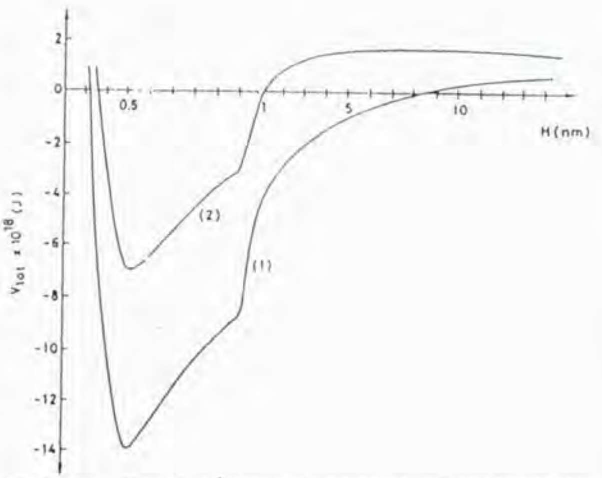

Figure 4 - Total potential energy of interaction between a magnetite particle and a copper surface at constant potential vs distance: **(1)** pH = 7.5 (NaOH); **(2)** pH = 9.5 (NaOH).

For the case where Na_2CO_3 is used the corresponding curves are those in **Figure 5**.

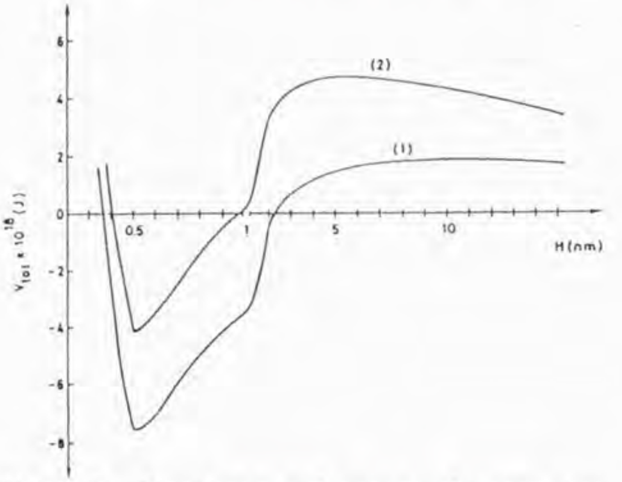

Figure 5 - Total potential energy of interaction between a magnetite particle and a copper surface at constant potential vs distance: **(1)** pH = 7.5 (Na_2CO_3); **(2)** pH = 9.5 (Na_2CO_3).

In this situation the curve for pH = 9.5 has a quite high energy barrier which is thougth to prevent adhesion. Neverthless, if the particles acquire enough kinetic energy, they can surmount the energy barrier and then it will be very difficult to remove them. This hypothesis is supported by a qualitative analysis of the deposits obtained by Energy Dispersion Spectroscopy. As can be observed from **Figure 6**, the deposit formed at pH = 9.5 in the presence of Na_2CO_3 is mainly formed by iron oxide, while in the others a great amount of silicates is present. This means that only iron oxide particles, because of their higher density, may acquire the kinetic energy that enables them to surpass the energy barrier.

Figure 6, may also justify the high thickness of deposits formed at pH = 8.5 with NaOH, which seems to be due to a great amount of silicious materials (the copper peaks are due to metalic surface under the deposit).

It was not expected to find similar curves for pH = 9.5 (NaOH) and pH = 7.5 (Na_2CO_3), because the amount of deposit formed in the latter situation was much higher. A few reasons can be given for this fact. First of all, the anions in solution are different and their effect is not known; moreover, Na_2CO_3 is not a symetrical electrolyte and this feature seems to affect theoretical predictions, as observed experimentally by *Israelachvili* and *Adams* [22], who reported that electrolytes of the type 2:1 can be responsible for a reduction in the double-layer repulsion.

Figure 6 - Qualitative analysis of the deposits of magnetite particles on copper tubes obtained by EDS.

Second, the deposition of silicates is much more efective at low pH values (**Figure 6**), which masks the real thickness of the deposits (in terms of pure magnetite).

Finally, it was more difficult to keep constant the bulk concentration of particles as the pH was raised, because they showed an increased tendency for sedimentation in the mixing tank. Temporary changes in concentration could have affected the rate of transport to the surface. It was also observed that particles with sizes above 5 µm did not appear in the deposit, which may confirm the existence of a sedimentation effect.

CONCLUSIONS

- Generally, an increase in pH to a value above 7 promotes a decrease in the deposition of magnetite particles on copper surfaces.
- A pH control with Na_2CO_3 enables the formation of thicker deposits than if NaOH is used.
- pH values in the range 7.5 - 8.5 favours the deposition of silicious materials (*quartz and chlorite*).
- The effect of pH in the formation of magnetite deposits can be satisfactory explained by taking into account the combined effects of DLVO interactions and *Born* repulsions. This means that the evaluation of the total potential energy of interaction can be a valuable tool for the qualitative assessment of the fouling tendencies.

NOMENCLATURE

A - Hamaker constant, J
d_0 - distance of closest approach, m
e - electron charge, C
ΔG^{ad} - free energy of adhesion, $J.m^{-2}$
ΔG^{d} - dispersion component of the free energy of adhesion, $J.m^{-2}$
H - distance between interacting bodies, m
K_B - Boltzmann constant, J/K
n_{io} - bulk concentration of ion i, ions/m^3
R - particle radius, m
T - absolute temperature, K
V_B - potential energy of interaction due to Born repulsion, J
V_{DL} - potential energy of interaction due to the electrical double layer, J
V_T - total potential energy of interaction, J
V_W - potential energy of interaction due to Van der Waals forces, J
Z_i - valence of ion i

Greek Symbols

γ - surface tension, $J.m^{-2}$
γ^d - dispersion component of surface tensio $J.m^{-2}$
γ^p - polar component of surface tensio $J.m^{-2}$
ε - electric permittivity of the medium $C^2/N\,m^2$
θ - contact angle, degrees
κ - Debye-Hückel parameter, m^{-1}
π_e - spreading pressure, $J.m^{-2}$
ψ_{oi} - electric surface potential of body i, V

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