Fouling by aqueous suspensions of kaolin and magnetite

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Experimental studies on particulate fouling were carried out in annular cross sections using aqueous kaolin and kaolin-magnetite suspensions. Tests with kaolin-water suspensions showed that the pH and the ions in solution have a significant effect on the amount of deposit. Increasing the pH above 7, the amount of deposit tends to decrease. However the extent to which the thickness decreases is very much dependent on the chemical substances used to control the pH. The presence of magnetite in kaolin suspensions at pH = 7.5 reduced the amount of deposit, although increasing its mechanical strength. This seems to be due to the magnitude of the adhesion forces between the particles, which is greater in the presence of iron oxide.

1 INTRODUCTION

After twenty years of more or less intense research, it is not surprising that fouling is still an unresolved problem in heat transfer equipment, since the number of variables that affect it is quite large and their mutual interactions are often complex.

The aim of the present work is to study the influence of a few of those variables related to the fluid properties in the build-up of deposits of kaolin and magnetite particles, from aqueous suspensions, onto a copper surface.

Particulate fouling is generally defined as the deposition of solid particles onto heat transfer sufaces. It is assumed, after Kern and Seaton [1] and a great number of other researchers, that there are three main processes governing the extent and rate of fouling:

- transport of particles to the surface;
- adhesion to the surface;
- re-entrainment of particles from the surface.

Thus fouling arises as a competion between a deposition flux, involving the first two processes and a removal flux, both being related with the fluid velocity.

The deposition process, as stated by Pinheiro [2] and other researchers, can be controlled either by the transport flux at low fluid velocities, when the mass transfer rate can be much slower than the adhesion rate, or by the

adhesion flux at higher velocities. The removal flux is also affected by the velocity because increasing the flow rate produces higher shear stresses which, at the same time, tend to create more compact deposits.

The particle transport process can be governed by different mechanims [3] such as diffusion ($t_p^+ \leq 0.1 - 0.2$) or inertia ($t_p^+ > 0.1 - 0.2$) where t_0^+, the dimensionless relaxation time, is expressed by:

$$t_p^+ = \frac{(u^*)^2 \, \rho_p \, D_p^2}{18 \, \mu \, \nu}$$

Larger particles and higher fluid velocities result in great values of t_p^+ and of the mass transfer flux.

Other factors, such as surface roughness, temperature gradients and lift forces have been also reported to affect particle transport.

Although transport mechanisms can explain the way a particle reaches a wall, they cannot predict if adhesion is going to occur and what degree of cohesion will be displayed by the deposit. To obtain this information it is necessary to concentrate efforts on the understanding of physico-chemical phenomena affecting the interaction between particles and surface.

Most particles involved in fouling phenomena are of colloidal dimension, because large particles are not likely to adhere on account of gravitational and fluid dynamic forces that are strong enough to remove them away from the wall.

In colloid chemistry [4] it is generally considered that the forces of attraction are dominated by London-Van der Waals forces. In aqueous media, other forces are also likely to occur, such as: hydrogen bonding, surface hydration and double-layer interactions (often with a repulsive effect). At the pH considered in this work (above 7), kaolin, magnetite and copper are electrophoretically negative [5, 6], indicating the presence of electrostatic repulsive forces. Nevertheless, the theory of double-layer interaction cannot be applied straightforwardly to explain all the properties of kaolin suspensions. Thiessen [7] has found that clay platelets adsorb negatively charged gold particles on their edges. According to Van Olphen [8] the basal surfaces of kaolin platelets, under acidic conditions, are negatively charged and the edges are positively charged, but increasing the pH a charge reversal of the edges occurs.

The force of adhesion between particles and substrate is then the overall result of many interactions and a great number of factors affect each contribution. Actually, the number of factors involved is so large that it is possible to sketch only a general picture. In this specific situation – an immersed system – the following factors can be listed as relevant to adhesion:

- pH and ionic strength;
- particle size and shape;
- surface type (nature and morphology);
- ion bonding;
- influence of ionic surfactants.

As the number of parameters involving both particles and substrate is very large, and different types of forces contribute to the adhesion process, it is very difficult to measure the absolute value of the adhesive force. However, data on relative values of these forces, in different environments, can be more easily obtained.

For this purppose different types of methods can be used [9], one being

the removal of deposits by means of a rotating cylinder apparatus.

The mechanism of detachment is not yet well known, but Visser [10] made some experiments that show a proportionality between the force of adhesion and a function of the wall shear stress and particle diameter.

2 EXPERIMENTAL

2.1 Types of tests

Three types of tests were performed:

i) "Kaolin fouling tests" – in this kind of tests attention was focussed on the effects that pH, ionic strength and type of ions may have in the deposition of kaolin particles. They were performed in an annular test section, with the chemicals and pH values shown in Table 1 below.

Table 1 Chemicals and pH values

NaOH	Na_2CO_3	$NaCH_3COO$
7.5	7.5	7.5
8.5	---	8.0
9.0	---	---
9.5	9.5	---
10.5	10.5	---
11.0	---	---

ii) "Kaolin-magnetite fouling tests", that were carried out to study the influence of fluid velocity in the formation of deposits by an aqueous suspension of kaolin and magnetite particles. These experiments were also performed in an annular test section.

iii) "Cohesion tests", that were carried out in a rotating outer-cylinder apparatus, with samples obtained from the above mentioned fouling tests.

2.2 Annular test sections

A 2 metre long horizontal annular test section was used in the "kaolin-magnetite fouling tests". This test section is composed of a copper tube 25 mm diameter placed inside a perspex tube of 36 mm diameter and is inserted in a closed loop circuit containing a stirred cooling tank of 250 liter and PVC tubes of 25 mm diameter.

Several tests were performed with the kaolin-magnetite suspension flowing at Reynolds numbers between 3000 and 10500 at pH = 7.5, bulk water temperature 10 °C, the concentrations of kaolin and magnetite being respectively 1.5 g/l and 0.7 g/l. A micrometer based device was used to measure the final deposit thickness.

The "kaolin fouling tests" were performed in a similar horizontal test section with the same length (2 m) but with different tube diameters (15 mm for copper tube and 32 mm for perspex tube). The kaolin concentration was 1.5 g/l, bulk water temperature 18 °C and the Reynolds number was always 6500. In

each run the pH was kept constant by means of a pH controller and only one chemical substance was used to maintain the pH at the desired value. In some runs the electrical conductivity of the suspension was monitored by a conductivity meter.

In most experiments the same pre-treatment was made on the surfaces: first of all, a solution containing acetic acid was left to flow for two hours, then the tubes were washed for the next two hours with a solution of sodium carbonate, and after that, the tank was filled with water and the pH set to the desired value.

2.3 Rotating cylinder apparatus

This test probe is composed by a rotating outer cylinder 8 cm long, made of perspex tube (36 mm or 32 mm according to the case), and a stationary inner copper tube, easily removable, that was obtained in each case from samples of the fouled copper tubes. The rotating cylinder is connected to an electrical motor with controlled input voltage and its rotating velocities were measured with a stroboscope.

The sample was dried in a stove, weighed and placed inside the apparatus leaving it to soak for about one hour in distilled water. Then the outer tube was rotated at low velocity for 3 minutes, the sample was dried and weighed and the procedure was repeated more times, each time increasing the rotating velocity.

2.4 Particles

The size distribution of the kaolin and magnetite particles was determined by means of a laser granulometer.

The kaolin particles have an average diameter of 12 μm and a density of 2600 Kg/m^3.

The magnetite particles are heavier with a density of 5200 Kg/m^3 and an average diameter of 20 μm.

3 RESULTS AND DISCUSSION

3.1 Tests with kaolin

Each fouling test performed with aqueous suspensions of pure kaolin at different pH had a duration of 20 days.

Fig. 1 presents the experimental results obtained when sodium carbonate (curve (a)) and sodium hydroxide (curve (b)) were used to control the pH level. The data refers to a region 1.2 m downstream from the inlet end of the annulus.

As a general conclusion, raising the pH above 7 results in a decrease of deposit thickness, and this effect occurs drastically in the presence of sodium hydroxide. A possible explanation can be given in terms of the kaolin zeta potential. Since this one becomes increasingly more negative with increasing pH (via addition of monovalent bases as NaOH) |5, 6, 11|, a stronger repulsive force is expected between the two negatively charged interacting bodies and consequently, a reduction in the amount of deposit.

When sodium carbonate was used, the reduction in thickness was not so pronounced and, for the same pH, a larger amount of deposit was obtained than in the presence of sodium hydroxide. In this specific case the main factors that can be responsible are the type of ions and the ionic strength.
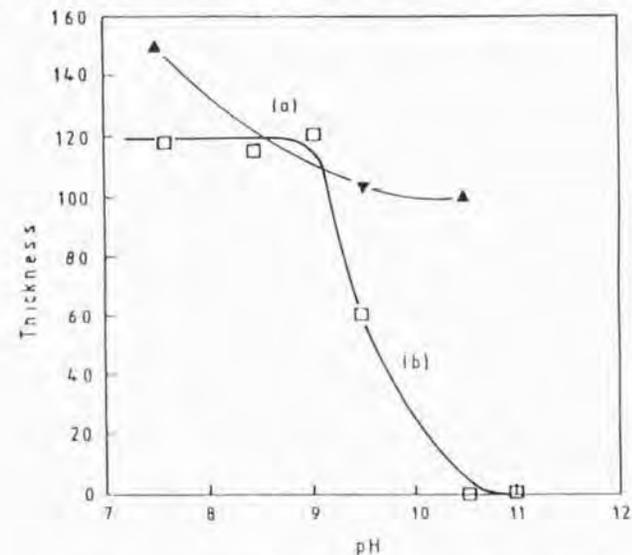
Fig. 1 - Deposit (kaolin) thickness vs pH. pH controlled with (a) Na$_2$CO$_3$; (b) NaOH.

Although many reports can be found in literature about the role played by different types of cations in particle adhesion |9|, there is a lack of information about the anions.

A possible explanation for the dissimilar features of deposits obtained with the two chemicals can be sought from the DLVO-theory |10|, which describes the balance between Van der Waals attraction and double-layer repulsion. This balance can be represented by a potencial energy of interaction versus distance diagram. Such a diagram is shown in fig. 2 for the case of two likely charged interacting surfaces.

The potential energy of interaction V and the force of adhesion F$_A$ are related by:

$$F_A = \frac{dV}{dH}$$

where H is the distance between the interacting species.

The distance at which the two bodies interact has an important effect on the intensity and stability of the adhesive force; particles depositing in a secondary minimum can be more easily removed than those stabilized in a primary minimum. The occurence of a secondary minimum depends on the ionic strength of the solution |12|. At low ionic strength, V shows a positive maximum and this one constitutes an energy barrier preventing the approach between the interacting bodies. If the ionic strength increases, the maximum in V is reduced and some particles may have enough thermal energy to overcome the barrier; at larger separations a secondary minimum occurs where particles can be captured without actually reaching the surface.
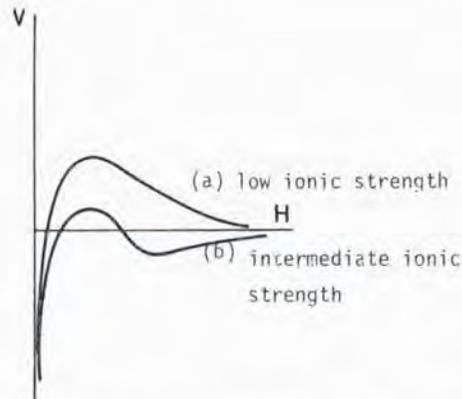
Fig. 2 - Potential energy of interaction between
two likely charged bodies vs distance.

For the same pH, a solution made with sodium carbonate has a higher ionic
strength than a solution of sodium hydroxide because the former is a weaker
base. So, the deposition of kaolin particles is facilitated in the presence
of sodium carbonate because a larger number of particles can reach the primary
minimum, due to the lowering of the energy barrier, and a great number of them
can be deposited in the secondary minimum giving rise to a thicker deposit.

According to theory, when deposition takes place in a secondary minimum
the adhesive force is not so strong. This can be confirmed by the removal
experiments, carried out in the rotating cell, as can be seen in fig. 3 and
fig. 4, for the results obtained at pH = 9.5. The deposit was much more easily
removed when the fouling test was done with carbonate.
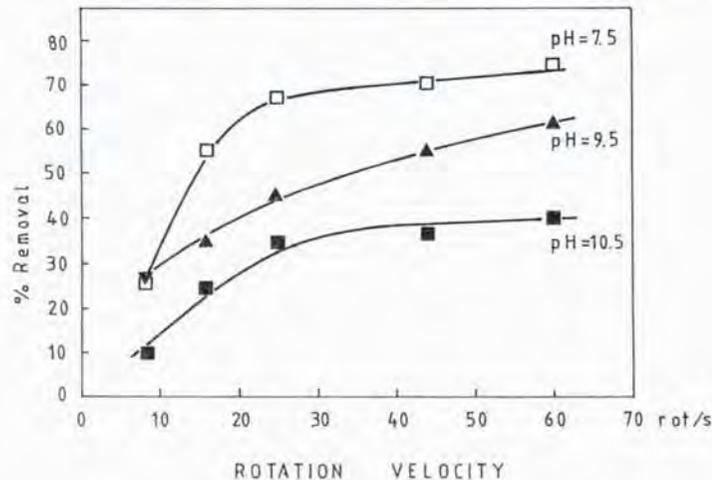
However, for each chemical (fig. 3 or fig. 4), increasing the pH
increases the difficulty of removal. This can be related to the deposit
structure, where (at least) two distinct layers have been observed [13, 14],
the outer one being more loosely packed and the inner one more compact. The
fraction of loose layer seems to be dependent on the deposit thickness: if the
deposit is very thin, this fraction tends to be very small and removal becomes
more difficult.

Other runs were performed using sodium acetate as the pH control medium.
The acetate ion has a lower alkaline character than the carbonate ion, giving
rise to solutions with very high ionic strengths even at lower pH.

Despite the increase in ionic strength the deposits built up with acetate
ion were much thinner than the ones formed with carbonate, at the same pH. The
deposit thickness decreased in the presence of the chemicals in the following
order:

$$Na_2CO_3 > NaOH > NaCH_3COO$$

Michael and Bolger [11] refer that some electrolytes, such as sodium
chloride, can cause deflocculation of a kaolin suspension due to a reduction
in the electrostatic edge-to-face attraction between platelets, arising from
the ability of these solutes to compress the electrical double-layer.
Moreover, according to swelling studies of clays [15], the hydration energy
of the interlayer cation can be related to the interlayer spacings, the effect
of the interlayer cation being the neutralization of the two interacting
negatively charged surfaces.

Fig. 3 - Mass % of removed deposit (kaolin) vs velocity of rotation.
Deposition with pH controlled using Na_2CO_3
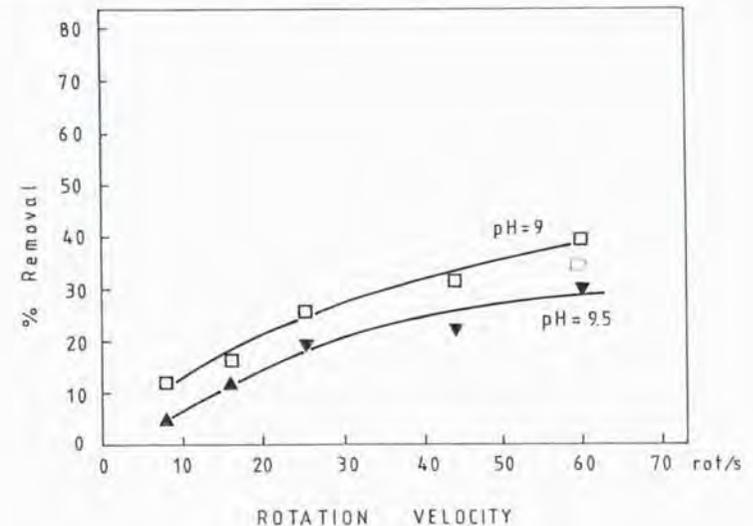
Fig. 4 - Mass % of removed deposit (kaolin) vs velocity of rotation.
Deposition with pH controlled using NaOH.

Although in the present study the cation used was the same, a possible justification for the differences observed in the deposit thickness can be given in term of its concentration. The sodium ion concentration increased in the following order:

$$NaOH < Na_2CO_3 < NaCH_3COO$$
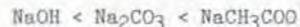
A small increase in the cation concentration promotes the neutralization of a larger number of negatively charged sites and helps adhesion to occur. Further increase in concentration can lead to repulsion phenomena and to a decrease in the degree of adhesion.

A point that seems interesting to emphasize is that before most of the runs with carbonate were started, it was observed that a great number of very small gaseous bubbles stuck to the surface underneath the copper tube and to the upper part of the perspex tube, which were actually the regions that became fouled. The small bubbles could be due to a release of carbon dioxide, in the presence of traces of acetic acid (used in surface conditioning).

In this case, the first interaction seems to be between kaolin particles and a liquid-gas interface in detriment of the interaction with the copper surface, the former being accomplished with less difficulty.

It is also worth noting that in one of the kaolin-magnetite tests a similar phenomenon took place. Those regions where small bubbles were detected (on the upper part of the perspex tube) were more readily fouled with magnetite particles. This suggests that gaseous bubbles act as particle "binders" and if they remain stuck to a substrate they will promote the adhesion of the first layer. This particularly strong interaction betweew particles and liquid-gas interfaces was observed by Visser |10|, in the removal of submicron particles adhering to a surface, when they were touched by an air bubble. Leenaars |16| recently demonstrated the same phenomenon both in theory and by experiment, taking into account the different forces present and the values of the contact angles.

This feature was confirmed in some of the removal experiments, namely in one made with a sample from a test with sodium carbonate at pH = 10.5. When the sample was immersed in distilled water many gaseous bubbles adhered to the surface and remained there even after the rotation was performed. However, when the sample was removed from the solution the bubbles detached, pulling away some deposit and the surface appeared as if it had been pierced by a needle.

3.2 Tests with kaolin-magnetite particles

The effect of fluid velocity on the thickness of the deposits obtained with a mixed suspension of kaolin and magnetite is represented in curve (a) fig. 5.

Curve (b) was obtained by Melo |13| in the same experimental rig working only with kaolin particles. In both cases the data refer to a point located 1.10 m downstream from the inlet end, the total concentration of particles was 2.2 g/l and the pH = 7.5. Comparing the two curves it can be seen that the kaolin-magnetite system gives rise to thinner deposits under similar conditions. In fact, the deposits are quite homogeneous and cover the surface as a thin film, although, for low fluid velocities some isolated spots of magnetite particles appear on the surface.

The two systems did not show the same trend in what concerns the relation between fluid velocity and deposit thickness, fig.5. For the mixed system, increasing the fluid velocity decreases the thickness, but in the case of pure kaolin the amount of deposit reaches a maximum about Re = 4000.
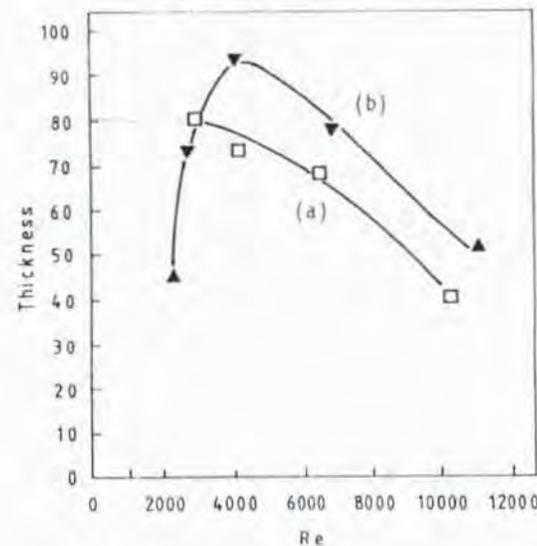
Fig. 5 - Deposit thickness vs Re (at pH=7.5)
(a) kaolin-magnetite; (b) kaolin.

Discussing his results, Melo |5| proposed that for 2300 < Re < 3850 mass transfer was the controlling mechanism. In this range of Reynolds numbers the dimensionless relaxation time ($t_p^+ < 0.015$) is much smaller than 0.1 and the transport mechanism is likely to be diffusion. However for Re > 4000 a change of control seemed to occur, adhesion being slower than mass transfer and therefore, the controlling step. His considerations were also based on calculations of fouling resistances and deposition fluxes.

In the mixed system, deposition seems to be controlled by the adhesion process in the range of Reynolds numbers studied. Although the deposition fluxes of the mixed suspension were not evaluated, greater amounts of deposit would be expected if mass transfer were the governing step of deposition. In fact, for Re = 5000 $t_p^+ << 0.1$ in the case of kaolin and $t_p^+ > 0,1$ in the case of magnetite, suggesting that a transition in the transport mechanism occurs for magnetite near this Reynolds number. Thus, for higher velocities magnetite mass transfer will probably be determined by an inertial mechanism which leads to a greater increase in the values of the transport flux with the Reynolds number. It would be then expected an increase in the amount of deposit with Re, if mass transfer were the controlling step. As this does not occur, it is assumed that deposition is governed by the adhesion process.

The kaolin-magnetite deposits have also a higher mechanical resistance as can be seen by comparing fig. 6 and fig. 7, where the results of removal tests are represented.

This is not totally true at low Reynolds numbers on account of the

presence of magnetite spots on the surface which were loosely held and therefore easily detached. Although they occur sparsely, as magnetite particles are very heavy, their contribution to the overall weight in the thin deposit was very high.
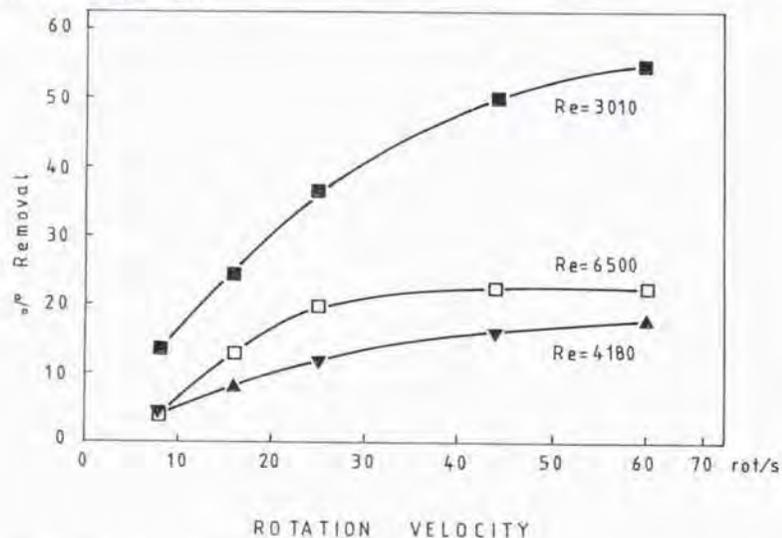
ROTATION   VELOCITY

Fig. 6 - Mass % of removed deposit (kaolin-magnetite) vs rotation velocity. Deposit at different Re.
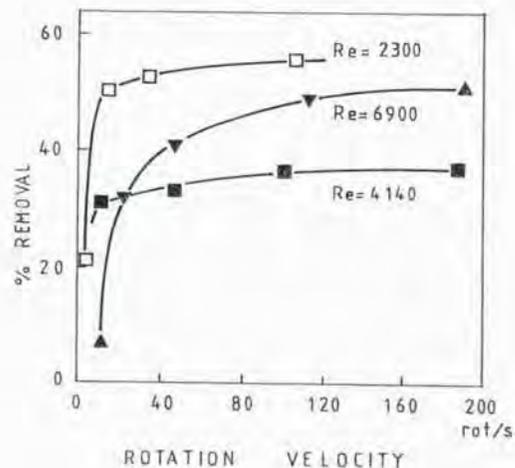
ROTATION   VELOCITY

Fig. 7 - Mass % of removed deposit (kaolin) vs rotation velocity. Deposition at different Re.

The higher mechanical resistance for the mixed deposit could be predicted in terms of Van der Waals forces. Melo (5) showed that the Hamaker constant for the interaction kaolin-magnetite is almost 25 times greater than the one for the interaction kaolin-kaolin.

The kaolin-magnetite deposits are thinner than the kaolin ones, although the former were obtained from tests that lasted for 30-35 days, as compared to 20 days for the pure kaolin runs. Thus it seems that the interaction between the two types of particles may lead to a lower fouling rate.

4 CONCLUSIONS

Fouling tests were carried out with kaolin-water suspensions (at different pH and ionic strengths and fixed flow rate) and with kaolin-magnetite suspensions (at different flow rates and fixed pH). The "mechanical strength" (or "cohesion") of the various deposits obtained from these tests was compared by performing removal experiments in a rotating cylinder apparatus.

The main conclusions are:

a)   For the kaolin-water suspensions:
   - Increasing the pH above 7 decreases the thickness of the deposit and increases its mechanical strength. However, the magnitude of this effect depends on the type of chemicals used in pH control.
   - For the same pH, higher thicknesses are obtained by increasing the ionic strength up to a certain limit. Further increases tend to reduce the amount of deposit.
   - The presence of liquid-gas interface (e.g., a gaseous bubble) seems to affect deposition, enhancing the adherence of the particles.

b)   For the kaolin-magnetite suspension:
   - Increasing the fluid velocity (for Re > 3000) decreases the thickness of the deposit and increases its cohesion.
   - The presence of magnetite reduces the amount of deposit (as compared to the pure kaolin deposits) and increases its mechanical strength.

LIST OF SYMBOLS

D_p -   equivalent particle diameter, m
F_A -   overall adhesion force, N
H -   separation (interaction) distance, m
Re -   Reynolds number
t_p^+ -   particle dimensionless relaxation time
u^* -   friction velocity, m/s
V -   overall potential energy of interaction, J
ρ_p -   particle density, Kg/m^3
μ -   dynamic viscosity, Ns/m^2
υ -   kinematic viscosity, m^2/s

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