Kinetics of Deposition of Colloidal Metal Oxide Particles on a Steel Surface[*],[1]

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The deposition of spherical α-Fe$_2$O$_3$ and rod-like β-FeOOH particles on steel from aqueous dispersions of different pH and ionic strength using a packed column technique has been studied. A procedure was developed by which the coagulation of the suspended particles was minimized even in the presence of high electrolyte concentrations during the duration of an experiment. In the absence of the potential barrier the results agree with the theoretical expectations based on the convective diffusion model. The same interpretation applies to the effects of the pH and of the indifferent electrolyte if the influence of electrostatic forces is taken into consideration.

A batch technique was used to investigate the equilibration phenomena in the same system at room temperature and at 210 ^{0}C.

INTRODUCTION

The adhesion of colloidal particles from liquid dispersions on solid substrates finds many applications such as in filtration, corrosion, detergency, coatings, etc. Phenomena involved depend on the forces between the particle and the surface and on the factors affecting the transport of dispersed solids to and from the substrate. The latter is determined by the characteristics of the liquid flow and by the Brownian motion of the particles.

This work examines the problems of deposition of uniform colloidal metal oxide colloids from aqueous dispersions on a stainless steel surface. Specifically, considerations are given to the kinetics of particle adhesion in the absence and in the presence of repulsive forces as affected by the change in the pH and by the addition of indifferent electrolytes as well as by the increase in the surface coverage of the substrate by deposited particles.

DEPOSITION IN THE ABSENCE OF THE REPULSION BARRIER

A. Experimental Technique

The rate of particle deposition was examined by a packed column technique modified to allow investigations at high ionic strength or near the isoelectric point of the dispersed solids.[1] Normally, the latter conditions lead to rapid coagulation which makes the interpretation of data difficult, if not impossible. In the experiments reported in this work the effects of the destabilization of dispersions in course of the adhesion process were avoided by a convenient design for mixing the stable sol with the electrolyte (or with a pH adjusting) solution (illustrated in Figure 1). The two reacting liquids were introduced by
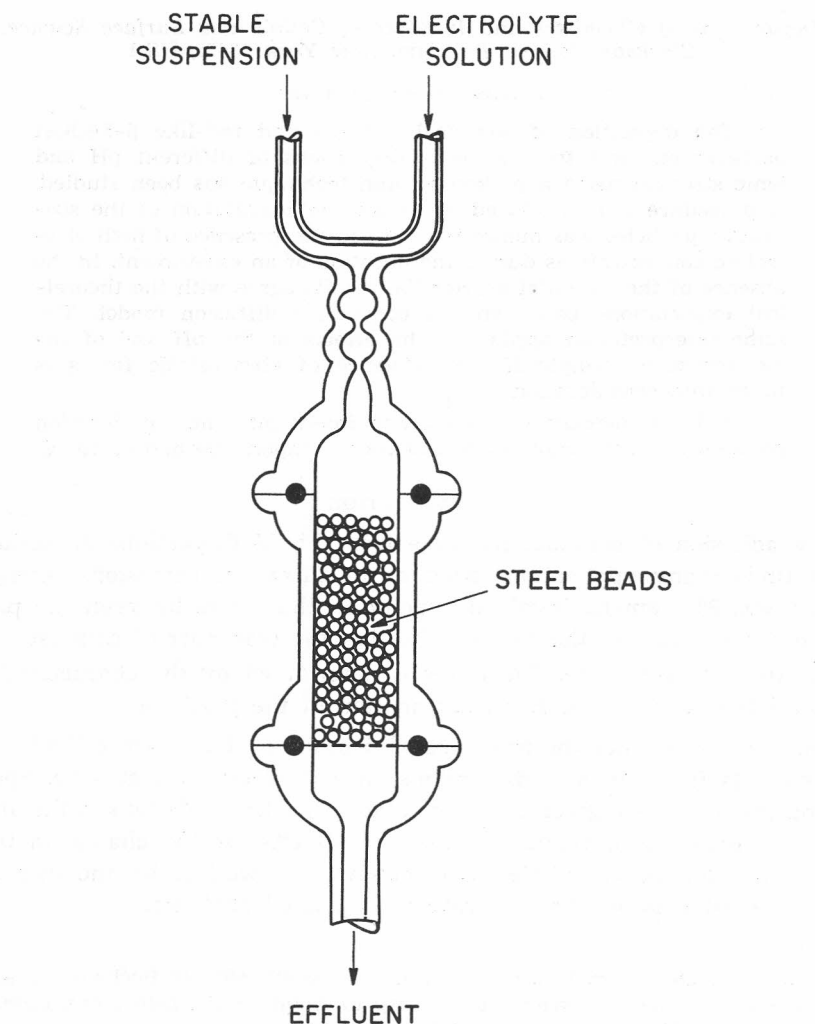

Figure 1. Schematic presentation of the mixing chamber and the packed bed column used in the deposition studies.

means of a peristaltic pump through separate tubes and thoroughly mixed in a chamber just above the column packed with spherical steel beads. Providing that the employed sol concentration was sufficiently low yet measurable in the effluent, the flow still laminar, and the void volume of the column as small as possible, the extent of coagulation was minimized. Indeed, under the conditions used in this work it was estimated that more than 95% of the particles were in dispersed state assuming the highest possible rate of coagulation.[2] Any aggregation of particles following the passage through the packed bed had no effect on the data as the sol could be redispersed by ultrasonic treatment or by the addition of an appropriate dispersant before the particle number concentration was measured.

B. Interpretation of the Results

The interpretation of the deposition results obtained by packed column technique is simple and accurate if no particle detachment occurs and if the deposited solids do not further influence the adhesion. The latter is the case only at the initial stage of the process; thus, the data should be extrapolated to zero surface coverage. For such a condition the rate of deposition can be described by

$$-\frac{dC}{dt} = \frac{A_s}{V} k_a C \tag{1}$$

where C is the particle number concentration, t time, A_s the total surface area of the substrate, V the volume of the liquid in contact with the substrate (void volume of the packed bed), and k_a the rate constant of deposition, often called the mass transfer coefficient, which is assumed to be independent of C and t.

Integration of Eqn (1) at constant k_a yields

$$\ln(C_{in}/C_{out}) = \frac{A_s}{V} k_a t_c \tag{2}$$

where C_{in} and C_{out} are the particle number concentrations in the influent and the effluent suspension, and t_c is the time required to pass the volume element of the sol through the bed, i. e.

$$t_c = V/\dot{V} \tag{3}$$

where $\dot{V}$ is the flow rate. Equation 2 enables the experimental evaluation of the rate constant k_a. Taking into account the properties of the column one obtains:

$$\ln(C_{in}/C_{out}) = \frac{3m}{\varrho r_s \dot{V}} k_a \tag{4}$$

where m is a total mass of the spherical beads of radius r_s and density ϱ.

C. Theoretical Considerations

As in the case of a single sphere collector, the particle deposition in the packed bed is governed by convective diffusion, interception, and sedimentation.[3] It was shown that the uptake of latex particles smaller than 1 μm in diameter on glass was governed by diffusion alone.[3] However, spherical Fe_2O_3

particle 0.5 μm in diameter had higher deposition rates than expected from diffusion theory while those of 0.15 μm in diameter agreed with the predicted values.[1]

When interaction forces do not influence the diffusion process the deposition of sufficiently small particles may be described by[4-9]:

$$k_a \text{ (diff)} = 0.624 \, D^{2/3} \, r_s^{-2/3} \, (\beta v)^{1/3} \tag{5}$$

where D is the diffusion coefficient of colloidal particles, and v the superficial velocity equal to the ratio of the flow rate and the cross-sectional area of the column. The porosity term for a column packed with spherical beads, β, is related to void volume fraction Φ by

$$\beta = [1 - (1 - \Phi)^{5/3}]/[1 - 1.5 \, (1 - \Phi)^{1/3} + 1.5 \cdot (1 - \Phi)^{5/3} - (1 - \Phi)^2] \tag{6}$$

When the diffusion process is influenced by the interactions forces (e. g., in the case of an electrostatic repulsion barrier), the rate constant of deposition differs from that calculated by Eqn (5). The discrepancy may be accounted for by introduction of the »collision efficiency«, a, or by the stability coefficient, W, defined as

$$W = a^{-1} = k_a \text{ (diff)}/k_a \tag{7}$$

The results obtained by the packed column technique can then be evaluated by combination of Eqns (4)—(7), which yields

$$\ln \frac{C_{in}}{C_{out}} = 1.87 \, D^{2/3} \, W^{-1} \, m \, r_s^{-5/3} \, \varrho^{-1} \, \beta^{1/3} \, S^{-1/3} \, \dot{V}^{-2/3} \tag{8}$$

where S is the cross-sectional area of the packed bed.

D. Results

In order to examine the validity of Eqn. (5) it is necessary to achieve conditions under which interaction forces do not influence the diffusion process while the attraction causes a permanent attachment of the incoming particles. The London-van der Waals force acts at short distances and always causes attraction. The electrostatic force could be either attractive or repulsive depending on the sign of the charges of particles and of the substrate; its range of action will depend on the ionic strength of the liquid medium. Using the rotating disk technique Hull and Kitchener[10] showed that the rate of deposition of negatively charged polystyrene latex particles ($d = 0.3$ μm) on a positively charged surface agreed with the theoretical expectations based on diffusion alone. The rate of deposition of positively charged spherical hematite particles ($d = 0.15$ μm) on negatively charged steel beads in a packed bed was also found to agree with theoretical predictions if the assumption was made that the attraction did not affect the rate of the process.[1] In both cases the homocoagulation in the dispersion was prevented by the charge on the particles. Since the substrates carried an opposite charge, no repulsion barrier was present to prevent the deposition process; indeed, the electrostatic attraction of the oppositely charged surfaces could have enhanced the deposition rate. In order to eliminate the latter possibility the packed column technique described
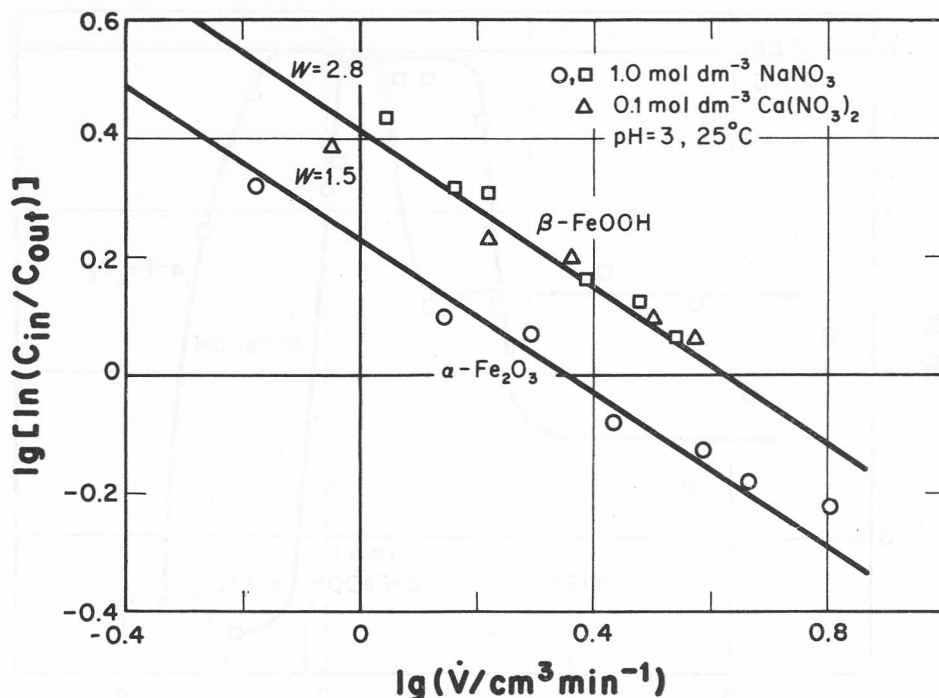
Figure 2. The effect of the flow rate on the deposition of spherical α-Fe$_2$O$_3$ (O) and rod-like β-FeOOH ($\square$, $\triangle$) particles on steel at pH = 3 and 25 °C. Diameter of α-Fe$_2$O$_3$: 0.15 μm, the length and the width of β-FeOOH rods: 0.25 μm and 0.02 μm. Concentrations of NaNO$_3$: 1.0 mol dm^{-3} (O, $\square$); and of Ca(NO$_3$)$_2$: 0.1 mol dm^{-3} ($\triangle$).

earlier permitted the experiments to be carried out with systems consisting of particles and substrates of like charges at high ionic strength, yet avoiding particle coagulation. Thus, despite the charges, only the short range van der Waals force was responsible for the particle attachment.[1,11]

Figure 2 presents data for the deposition of spherical Fe$_2$O$_3$ and rod-like β-FeOOH particles on steel beads in the packed column at various flow rates. The solid lines have the theoretical slope of — 2/3 as predicted by Eqn. 8 and are drawn by choosing the stability coefficients, W, which best fit the experimental points.

For the system of positively charged hematite particles and steel beads at high electrolyte concentrations W is close to unity ($W = 1.5$).[1] For the rod--like β-FeOOH particles[11] ($l = 0.25$ μm; $d = \sim 0.02$ μm) $W = 2.8$. In contrast, the rate of deposition in the same systems at pH values yielding oppositely charged particles and substrates[1,11] gave values of $W \sim 1$. Obviously, in the case of β-FeOOH the shape of the particles affects the adhesion rate. Apparently, in the absence of electrostatic attraction all collisions do not lead to adhesion; some particles approaching the surface with their ends are readily swept away; however if they are subjected to the electrostatic attraction they remain adhered.
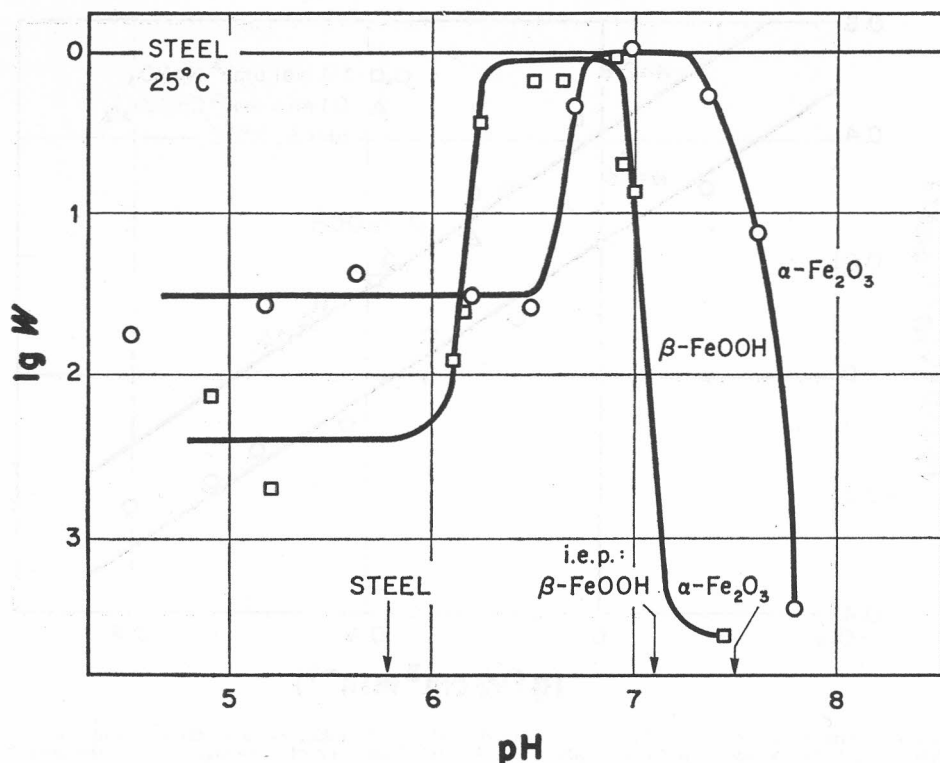
Figure 3. The effect of pH on the deposition of spherical α-Fe$_2$O$_3$ (O) and rod-like β-FeOOH ($\square$) particles on steel at 25 ^{0}C. Ordinate is given as the stability coefficient W. The size of the particles is the same as in Figure 2. The arrows indicate the corresponding isoelectric points.

E. The Effect of pH and Surface Saturation

Figure 3 shows the influence of pH on the deposition of spherical α-Fe$_2$O$_3$ and rod-like β-FeOOH particles on steel in a packed bed.[1,11] The arrows indicate the corresponding isoelectric points (i. e. p.) which lead to the conclusion that the deposition rate is high (W is small) over the pH range yielding particles and steel of opposite charges. The rapid deposition of α-Fe$_2$O$_3$ particles on steel ($W \sim 1$) does not occur over the entire region of oppositely charged surfaces.[1,12] This finding may be explained by the discharge of the collector due to gradual accumulation of the adhered hematite, which eventually leads to charge reversal. Thus, instead of electrostatic attraction, repulsion prevails.[1,13-16] In addition, it is necessary to consider the excluded area as well as the shadow effect. In the latter case it is assumed that the area of the collector inaccessible to adhesion of additional particles is larger than the geometric area of already deposited solids.[17,18] The upper part of Figure 4 gives the electrophoretic mobility of hematite particles as a function of pH as well as the product of the mobilities of these particles and of steel. The particle mobility is related to their surface charge, while the product of the mobilities is a measure of electrostatic interaction. In the lower part is given the corresponding change in the deposition rate constant (k_a) relative to the change in the surface
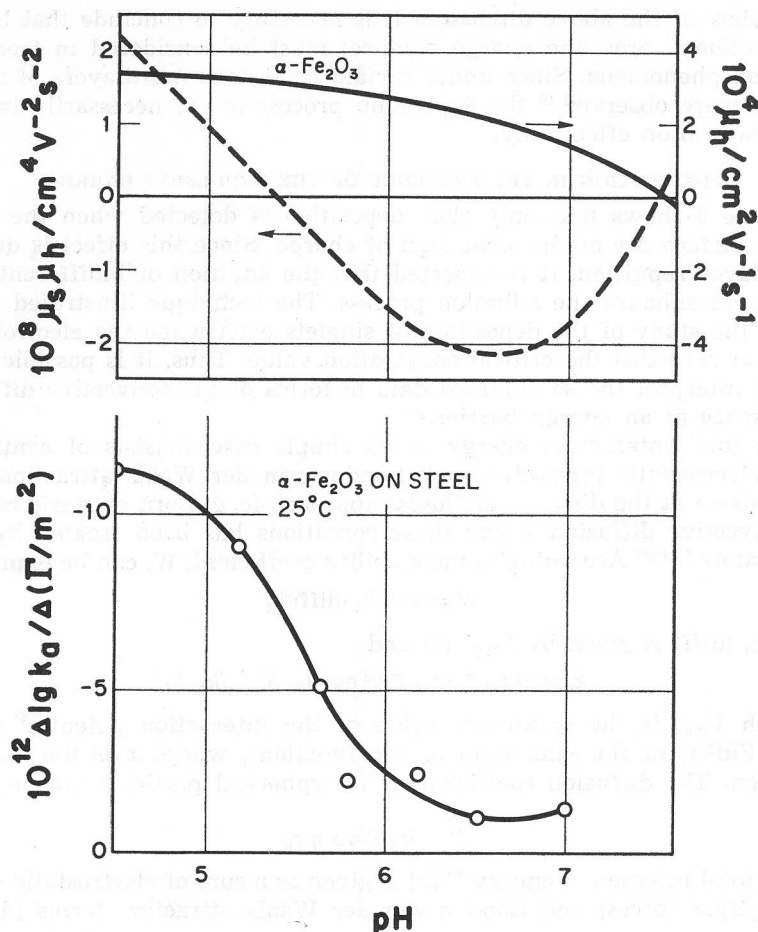
Figure 4. Upper: Electrokinetic mobilities of the α-Fe$_2$O$_3$ particles (solid line) and the product of mobilities of hematite particles and steel (dashed line) as a function of pH.
Lower: The change in the adhesion rate with the surface coverage of the steel by hematite particles as a function of pH. All data refers to the same system as in Figure 2.

concentration of adhered particles (Γ). It is noteworthy that a large change in the rates occurs even though the surface coverage by the adsorbed hematite does not exceed 1%. This evidence indicates that the effect of saturation of the collector surface by the deposited solids becomes more pronounced as the colloidal particles carry a higher charge while steel becomes less strongly charged[1]. Indeed, it was demonstrated experimentally that the deposition rate sharply decreases once the saturation by adhered particles brings about charge reversal of the substrate.[15] The saturation effect was found to be less pronounced as the ionic strength increased,[16] further pointing to the role of the double layer in the observed adhesion processes. Any theoretical interpretation of such data should take into consideration the inhomogeneity of the surface charge of the substrate caused by the adsorption of particles and consequent restructuring of the double layer.

In view of the above discussion it is necessary to conclude that both concepts (excluded area and charge balance) must be considered in treating the deposition phenomena. Since under certain conditions multilayers of deposited particles were observed,[19] the deposition process is not necessarily influenced by the saturation effect only.

DEPOSITION IN THE PRESENCE OF THE REPULSION BARRIER

Figure 3 shows that only slow deposition is detected when the particles and the surface are of the same sign of charge. Since this effect is due to the double layer repulsion, it is expected that the addition of indifferent electrolytes would enhance the adhesion process. The technique illustrated in Fig. 1 allowed the study of the deposition of singlets even when the electrolyte concentration exceeded the critical coagulation value. Thus, it is possible to theoretically interpret the so obtained data in terms of the convective diffusion in the presence of an energy barrier.

The total interaction energy in its simple case consists of contributions due to electrostatic interactions,[20,21] London-van der Waals attraction,[22,23] and the repulsion at the distance of closest approach (e. g. Born or steric repulsion). The convective diffusion under these conditions has been treated by several investigators.[4,24-27] Accordingly, the stability coefficient, W, can be expressed as[4]

$$W = 1 + k_a \, (\text{diff})/k_f \tag{9}$$

where k_a (diff) is given by Eqn (5) and

$$k_f = D \, (\omega/2 \, \pi \, k_B \, T)^{1/2} \exp \left(- V_{max}/k_B \, T \right) \tag{10}$$

in which V_{max} is the maximum value of the interaction potential and $\omega = = - \mathrm{d}^2 V/\mathrm{d}^2 \, x$, at the maximum of the function*, where x is the distance of separation. The diffusion coefficient D for spherical particles can be obtained from

$$D = k_B \, T/6 \, \pi \, \eta \, r_h \tag{11}$$

and the total interaction energy $V (x)$ is given as a sum of electrostatic repulsion (double layer forces) and London-van der Waals attraction terms (dispersion forces):

$$V (x) = V_{el} (x) + V_a (x) \tag{12}$$

The repulsion at the distance of closest approach need not be considered in the deposition process. However, it should be noted that in the particle removal this contribution is rather significant.

The term due to the dispersion force was calculated from[22,28,29]

$$V_a (x) = \frac{A}{6} \left[\ln \frac{x + 2}{x} - \frac{2 \, r_h \, (r_h + x)}{x \, (x + 2 \, r_h)} \right] \tag{13}$$

where A is the overall Hamaker constant which can be approximated by

$$A \approx (\sqrt{A_h} - \sqrt{A_w}) (\sqrt{A_s} - \sqrt{A_w}) \tag{14}$$

where subscripts h, s, and w apply to hematite particles, steel, and water, respectively.

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* Note that potential V is not to be confused with volume V in Eqns. (1)—(3) and (16).

The double layer interaction energy can be obtained from the BMRF theory[21]:

$$V_{el}(x) = \left(\frac{k_B T}{e}\right)^2 \left\{ -\pi r_h \varepsilon \, 2^{1/2} \int_0^{\varkappa r_s} \psi_h \left[(r_h \varkappa)^2 - R^2 \right]^{-1/2} \left[\cosh \psi_h - \varphi(R) \right]^{1/2} R \, dR - \right.$$

$$\left. -\pi r_s \varepsilon \, 2^{1/2} \int_0^{\varkappa r_s} \psi_s \left[(r_s \varkappa)^2 - R^2 \right]^{-1/2} \left[\cosh \psi_s - \varphi(R) \right]^{1/2} R \, dR \right\}, \tag{15}$$

where e is the elementary charge, and R is the product of the Debye-Hückel parameter $\varkappa$ and the radial coordinate of a cylinder with its axis connecting the centers of the two spheres, and ψ_h and ψ_s are the surface potentials of hematite and steel, respectively, which were approximated by the corresponding electrokinetic potentials.

Figure 5 shows the dependence of the stability coefficient on the concentration of added $NaNO_3$ for the hematite/steel system at pH 3.3 (circles). At these conditions the particle and the surface are positively charged.[1] The dashed line represents the calculated values based on the theoretical treatment given above. The Hamaker constant that best fits the detachment rates of hematite from steel[30,31] was found to be $A = 1.4 \times 10^{-20}$ J and therefore the same value is used in the calculation of deposition data. There is a rather good agreement between the experimental and theoretical value of the critical
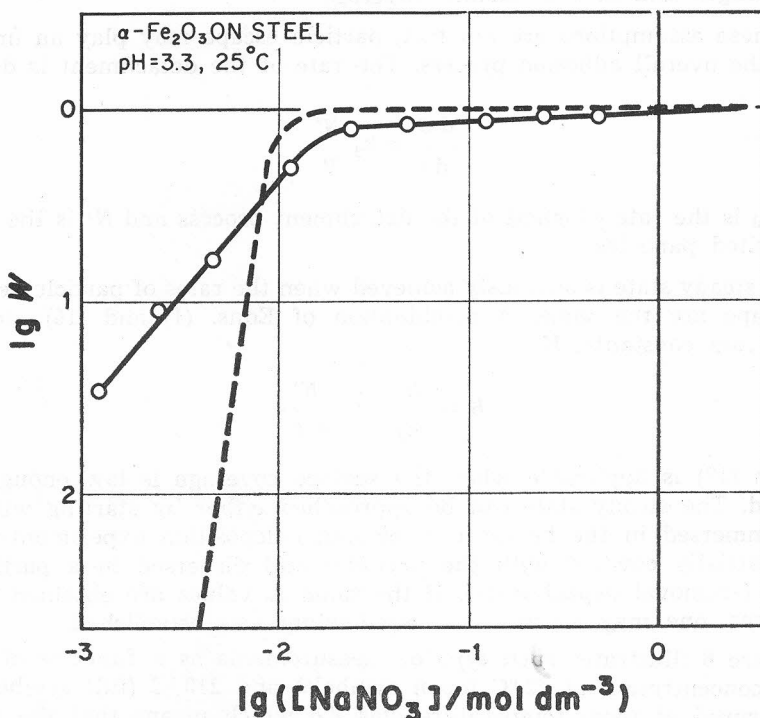

Figure 5. The effect of $NaNO_3$ on the deposition of spherical α-Fe_2O_3 particles (0.15 µm diameter) on steel at 25 °C and pH 3.3. The ordinate is given as the stability coefficient W. The theoretical dashed line was calculated assuming the value of the Hamaker constant $A = 1.4 \times 10^{-20}$ J.

salt concentration which leads to fast adhesion. At lower contents of $NaNO_3$ the data do not fit the predicted dependence although the trend is reasonable.

These results would indicate that the fundamental concepts applied to the processes in this system are essentially correct. The observed discrepancies may be due to oversimplifications, such as the neglect of retardation of the dispersion forces, double layer relaxation, inaccurate values of surface potentials, etc.

ATTACHMENT/DETACHMENT EQUILIBRIA

Adhesion studies were also carried out in a closed system (batch technique) in which the steel beads and dispersed particles remained in the same environment and the collector was kept in motion by slow tumbling. This procedure made it possible to compare the interactions at room and elevated (210 °C) temperatures. Furthermore, the exchange of particles in the dispersed state with those adhered could be followed until a steady state was established.[32] In such a system the relative movement of the individual beads in the suspension is subject to gravitational forces only which makes it possible to apply the Levich theory for diffusional transport towards a single sphere.[33] In this case the porosity term in Eqn. 5 equals unity. Using this treatment it was found[32] that the deposition rate constant agreed with the theory as long as particle detachment was insignificant. Such condition was achieved with the system consisting of oppositely charged particles and beads at low ionic strength and at low surface coverage.

If these assumptions are not met, particle escape may play an important role in the overall adhesion process. The rate of the detachment is described by[34-39]

$$\frac{dC}{d\tau} = k_d \frac{N^s}{V} \tag{16}$$

where k_d is the rate constant of the detachment process and N^s is the number of deposited particles.

The steady state is obviously achieved when the rates of particle deposition and escape are the same. A combination of Eqns. (1) and (16) yields the »equilibrium constant«, K:

$$K = \frac{k_a}{k_d} = \frac{N^s}{A_s C} \tag{17}$$

Equation (17) is applicable when the surface coverage is low enough to be neglected. The steady state can be approached either by starting with clean beads immersed in the hematite dispersion (»deposition experiment«) or by beads partially covered with the particles and dispersed in a particle-free solution (»removal experiment«). If the same K values are obtained by both procedures, one may assume that equilibrium was established.

Figure 6 illustrates such type of measurements as a function of sodium nitrate concentration at 22 °C (open symbols) and 210 °C (full symbols). The pH measured at room temperature was 8.6 which means that the particles and the beads were weakly negatively charged. Circles refer to »deposition« and squares to »removal« experiments. The apparent equilibrium constants,
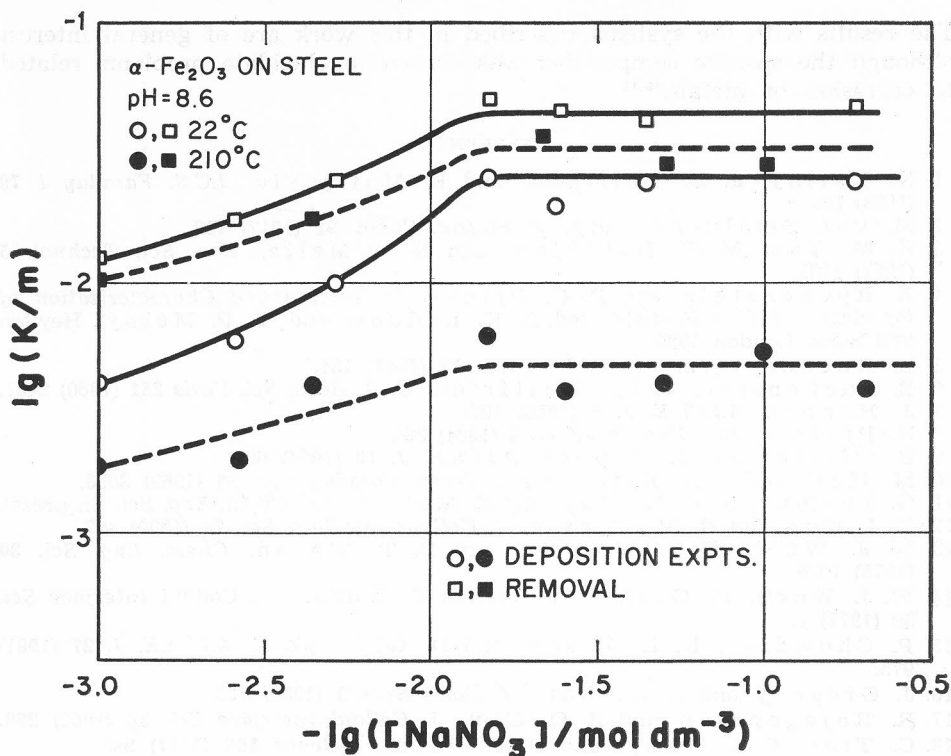
Figure 6. The apparent equilibrium constants, K, for the deposition of spherical α-Fe_2O_3 particles (0.15 μm in diameter) on steel as determined by the batch technique at pH 8.6 at different $NaNO_3$ concentrations. Attachment experiments (O, ●); detachment experiments (□, ■). Open symbols 22 °C, black symbols 210 °C.

K, increase with the ionic strength until a constant value is reached. At room temperature the values obtained by approaching the equilibrium from different directions are in much closer agreement than at 210 °C. Since the surface coverage amounted to less than 1%, the discrepancy may be attributed to still another reaction on the surface which seems to lead to stronger bonding. The latter is substantiated by the finding that the K values, obtained from the »removal experiments« are larger than those from the »deposition experiments«. Other works have shown that a lateral surface transfer of adhered particles takes place into sites of stronger bonding.[30,38,39] This effect is more pronounced at the higher temperature and is promoted by the flow of the liquid along the collector surface.[30,32]

CONCLUDING REMARKS

This work has shown that the deposition of colloidal particles on plane surfaces in the absence of shear is governed by convective diffusion whereby the charges on the particles and the substrate play a dominant role.

In its simplest form the adhesion process can be interpreted in terms of the existing theories of interactions of unlike particles combined with the kinetics of particle diffusion.

The results with the systems described in this work are of general interest although the specific composition was chosen to elucidate problems related to corrosion of metals.[40,41]

REFERENCES

1. N. Kallay, J. D. Nelligan, and E. Matijević, *J.C.S. Faraday I* **79** (1983) 65.
2. M. von Smoluchowsky, *Z. Physik. Chem.* **92** (1917) 129.
3. K. M. Yao, M. T. Habibian, and R. O'Melia, *Env. Sci. Technol.* **5** (1971) 1105.
4. E. Ruckenstein and D. C. Prieve, in *Testing and Characterization of Powders and Fine Particles,* (ed. J. K. Beddow and T. P. Meloy), Heydon and Sons, London 1980.
5. E. Ruckenstein, *Chem. Eng. Sci.* **19** (1964) 131.
6. E. Ruckenstein and F. Westfried, *C. R. Acad. Sci. Paris* **251** (1960) 2467.
7. J. Happel, *A.I.Ch.E. J.* **4** (1958) 197.
8. R. Pfeffer, *Ind. Eng. Fundam.* **3** (1964) 380.
9. R. Pfeffer and J. Happel, *A.I.Ch.E. J.* **10** (1964) 605.
10. M. Hull and J. A. Kitchener, *Trans. Faraday Soc.* **65** (1969) 3093.
11. G. Thompson, N. Kallay, and E. Matijević, *Chem. Eng. Sci.* (in press).
12. R. J. Kuo and E. Matijević, *J. Colloid Interface Sci.* **78** (1980) 407.
13. W. J. Wnek, D. Gidaspow, and D. T. Wasan, *Chem. Eng. Sci.* **30** (1975) 1035.
14. W. J. Wnek, D. Gidaspow, and D. T. Wasan, *J. Colloid Interface Sci.* **59** (1977) 1.
15. P. Chowdiah, D. T. Wasan, and D. Gidaspow, *A.I.Ch.E. J.* **27** (1981) 975.
16. J. Gregory and J. Wishart, *Colloids Surf.* **1** (1980) 313.
17. R. Rajagopalan and R. Q. Chu, *J. Colloid Interface Sci.* **86** (1982) 299.
18. C. Tien, C.-S. Wang, and D. T. Barot, *Science* **196** (1977) 983.
19. R. K. Iler, *J. Colloid Interface Sci.* **21** (1966) 569.
20. R. Hogg, T. W. Healy, and D. W. Fuerstenau, *Trans. Faraday Soc.* **62** (1966) 1638.
21. E. Barouch, E. Matijević, T. A. Ring, and M. Finlan, *J. Colloid Interface Sci.* **67** (1978) 1; **70** (1979) 400.
22. H. C. Hamaker, *Physica (Utrecht)* **4** (1937) 1058.
23. E. J. Clayfield, E. C. Lumb, and P. H. Mackey, *J. Colloid Interface Sci.* **37** (1971) 382.
24. J.-S. Kim and R. Rajagopalan, *Colloids Surf.* **4** (1982) 17.
25. E. Ruckenstein and D. C. Prieve, *J.C.S. Faraday II* **69** (1973) 1522.
26. L. A. Spielman and S. K. Friedlander, *J. Colloid Interface Sci.* **46** (1974) 22.
27. B. Dahneke, *J. Colloid Interface Sci.* **48** (1974) 520.
28. J. Visser, in *Surface and Colloid Science,* Vol. **8**, (ed. E. Matijević), Wiley-Interscience, New York, 1976.
29. J. Visser, *Adv. Colloid Interface Sci.* **3** (1972) 331.
30. N. Kallay and E. Matijević, *J. Colloid Interface Sci.* **83** (1981) 289.
31. J. D. Nelligan, N. Kallay, and E. Matijević, *J. Colloid Interface Sci.* **89** (1982) 9.
32. N. Kallay and E. Matijević, *Corrosion* **39** (1983) 15.
33. V. G. Levich, *Physicochemical Hydrodynamics,* Prentice Hall, Englewood Cliffs, N. J., 1962.
34. E. J. Clayfield and E. C. Lumb, *Disc. Faraday Soc.* **42** (1966) 285.
35. E. J. Clayfield and A. L Smith, *Env. Sci. Technol.* **4** (1970) 413.
36. J. E. Kolakowski and E. Matijević, *J.C.S. Faraday I* **75** (1979) 65.
37. R. J. Kuo and E. Matijević, *J.C.S. Faraday I* **75** (1979) 2014.
38. G. Thompson, N. Kalay, and E. Matijević, submitted.
39. E. Matijević, N. Kallay, and M. A. Hubbe, in preparation.

40. E. Matijević, in *Atmospheric Corrosion,* Chapter 8, Wiley, New York, 1982, pp. 123—127.
41. E. Matijević, *Pure Appl. Chem.* **53** (1981) 2167.

SAŽETAK

Kinetika prianjanja koloidnih čestica metalnih oksida na površinu čelika

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Kinetika prianjanja okruglih α-Fe_2O_3 i štapićastih čestica β-$FeOOH$ na čelik proučavana je kolonskom tehnikom. Eksperimenti su vođeni u vodenoj sredini pri različitim ionskim jakostima i pH-vrijednostima. Razrađen je postupak kod kojega je efekt koagulacije neznatan čak i uz visoku koncentraciju elektrolita. U odsutnosti energijske barijere pokazano je slaganje s teorijom utemeljenom na modelu konvekcijske difuzije. Utjecaj elektrolita i pH moguće je objasniti elektrostatskim silama. Povratnost i uravnoteženje procesa otcjepljivanje-prianjanje ispitivano je u zatvorenim posudama pri sobnoj temperaturi i 210 °C.