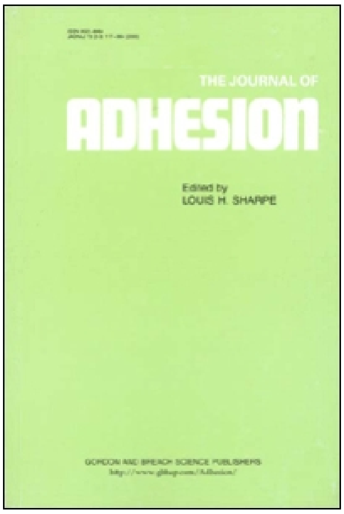
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Kinetics of Particle Deposition and Detachment

Egon Matijević[a]; Niels P. Ryde[ab]
[a] Center for Advanced Materials Processing, Clarkson University, Potsdam, New York, USA [b] Rohm & Haas Company, Pennsylvania, USA

To cite this Article Matijević, Egon and Ryde, Niels P.(1995) 'Kinetics of Particle Deposition and Detachment', The Journal of Adhesion, 51: 1, 1 — 14

To link to this Article: DOI: 10.1080/00218469508009985

URL: http://dx.doi.org/10.1080/00218469508009985

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1995, Vol. 51, pp. 1–14
Reprints available directly from the publisher
Photocopying permitted by license only

Kinetics of Particle Deposition and Detachment*

EGON MATIJEVIĆ** and NIELS P. RYDE†

Center for Advanced Materials Processing, Clarkson University, Box 5814, Potsdam, New York 13699-5814, USA

(Received March 26, 1994; in final form June 13, 1994)

The packed column technique serves as a useful tool in the investigations of the deposition and removal mechanisms of particles dispersed in a liquid in contact with a solid substrate. A model is presented which can be used to estimate explicitly the effects of multilayer deposition, which is based on three phenomenological parameters: two mass transfer coefficients, and one blocking parameter. The latter accounts for the area occupied by each adhered particle. The method can be used to evaluate the experimental results in terms of the particle-collector and particle-particle interactions. The former are related to heterocoagulation, and the latter to homocoagulation.

It is shown that the rate of deposition of hematite particles onto glass beads, in the absence of a repulsion barrier, is governed by a convective diffusion mechanism. If a repulsion barrier exists, the deposition rate depends on the ionic strength in a manner consistent with colloid stability. The adhered particles can be removed by rinsing the column with a solution of an appropriate pH, which renders both surfaces sufficiently strongly charged, if the ionic strength is kept low.

When gelatin is adsorbed onto the glass beads, irreversible deposition of hematite particles takes place, which is caused by chemical bonds between the collector beads and the metal oxide.

The effect of external force fields can also be analyzed using the packed column technique. It is shown how the deposition of hematite on steel is affected by a magnetic field. It is possible to induce deposition under conditions where particles and beads bear the same sign of charge, and thus repel each other. Under such conditions, a deep secondary minimum is generated, which can be controlled by the strength of the magnetic field.

KEY WORDS Adhesion of hematite on gelatin-coated glass; adhesion of iron oxide on glass; deposition of hematite on steel, magnetic effects on; kinetics of particle attachment; particle adhesion.

INTRODUCTION

Particle adhesion phenomena, which include deposition of dispersed matter from a liquid onto solid surfaces and their detachment from such substrates, are encountered in countless physical and biological situations[1] and need not be enumerated here. In addition to practical significance of the processes involved, the results of carefully executed experiments can yield useful information on interactions between solid surfaces, with special reference to the effects of the electrical double layers.[2–6] The

---

* Presented at the Seventeenth Annual Meeting of The Adhesion Society, Inc, in Orlando, Florida, U.S.A., February 21-23, 1994.

** Corresponding author.

† Current address: Rohm & Haas Company, Spring House, Pennsylvania, USA.

adhesion in such systems can be theoretically treated as heterocoagulation of unlike particles[7-14] with a large difference in their size. In multilayer deposition the heterocase converts to the equivalent of a homocoagulation process.[12-14]

In order to interpret the adhesion experiments properly, it is necessary to deal with well-defined systems, for which the necessary parameters can be evaluated. For this purpose the packed column technique is rather suitable, as long as the properties of the beads used as the collectors and of the particles passing through the column at a given flow rate are well defined.[7-9,11-17] The dispersion should consist preferably of spheres of narrow size distribution in a solution of controlled ionic strength and pH. In many cases the last variable can be used to alter the surface potential of the particles and of the collector beads.

The described system makes it also possible to investigate the effects of the imposed external forces, such as of a magnetic field,[18-20] which should greatly influence the deposition and the detachment of particles, if either or both interacting solids have finite magnetic moments.

In this work is discussed the kinetics of adhesion with systems consisting of monodispersed spherical hematite particles and a column loaded with uniform glass or steel beads. Special attention is given to the distinction between mono-and multilayer depositions as affected by a convective-diffusional mechanism.

THEORETICAL

In the packed column technique a dispersion of colloid particles suspended in a solution of known ionic strength, pH, etc., is passed through a bed of much larger beads. In the absence of any attraction between the two solids, the concentration of dispersed particles collected after passing through the column (C) equals their original concentration, C_0. Should deposition occur, one can follow the change in the quantity C/C_0 with time as a function of various experimental parameters (initial particle concentration, flow rate, ionic strength, pH, etc.).

It was shown elsewhere[12-14] that the values of C/C_0 can be calculated from the expression

$$\frac{C}{C_0}=\frac{(\alpha-\beta)\{1-\exp[-(\alpha a K_{th} C_0 G)]\}+\beta(\alpha a K_{th} C_0 G)}{(\alpha-\beta)\{1-\exp[-\alpha a K_{th} C_0 \tau]\}+\beta(\alpha a K_{th} C_0 \tau)} \tag{1}$$

that includes three adjustable parameters. The first is the mass transfer coefficient for transport of particles in solution to an unoccupied part of the bead surface, which in the normalized form reads

$$\alpha \equiv K_{\mathrm{exp}}^{(1)}/K_{th} \tag{2}$$

where

$$K_{th}=0.624\, D^{2/3} r_b^{-2/3} (\vartheta u)^{1/3} \tag{3}$$

as derived by Pfeffer and Happel[21–23] for a bed of packed spheres. D is the particle diffusion coefficient, r_b is the radius of beads, and u is the superficial velocity, which is defined by $(\Delta V/\Delta t)/S\Phi$, $\Delta V/\Delta t$ being the volume flow rate, S the column cross-sectional area, and Φ the column porosity. The quantity described by ϑ is a function dependent on the void volume fraction.[12]

The second parameter is the mass transfer coefficient for transport of suspended particles to an already-occupied part of the surface, defined as

$$\beta \equiv K_{\exp}^{n>1}/K_{th} \tag{4}$$

Finally, the third parameter is characteristic of the occupied area per particle, and normalized to the projected area of a suspended particle, it reads

$$\gamma \equiv a/\pi r_p^2 \equiv 1/\pi r_p^2 \Gamma_{\max}^{(1)} \tag{5}$$

where $\Gamma_{\max}^{(1)}$ is the saturation surface concentration of adhered particles in the first layer.

In equation (1) the quantity $\tau = t - z/u$, t being time and z the height of the column, with the G function defined elsewhere.[12] Strictly, $\tau = 0$ is the time that a particle exits the column. However, since z/u is insignificant in comparison with τ over the course of experiment, the times in the figures are given as t.

It is useful to define the stability ratio, W, in terms of mass transfer coefficients for rapid (r) and slow (s) particle deposition, both for monolayer and multilayer cases, in analogy to this experimental quantity used in the evaluation of the rates of (hetero) coagulation, as follows:

$$W_{\exp}^{(1)} = \alpha_r/\alpha_s \quad \text{and} \quad W_{\exp}^{(n>1)} = \beta_r/\beta_s \tag{6}$$

The theoretical stability ratio, W_{th}, can be calculated from:[24]

$$W_{th} = \frac{\int_0^\infty [(r_1+r_2)/(r_1+r_2+H_0)^2][\exp(V_{sp}^T/kT)]\mathrm{d}H_0}{\int_0^\infty [(r_1+r_2)/(r_1+r_2+H_0)^2][\exp(V_{sp}^A/kT)]\mathrm{d}H_0} \tag{7}$$

where r_1 and r_2 are the radii of the two spheres separated by the closest surface-to-surface distance, H_0, and the total interaction energy $V_{sp}^T = V_{sp}^{dl} + V_{sp}^A$, the rhs terms representing the double layer and van der Waals contributions, respectively.

It can be shown[14] that at the initial stage of the deposition process, when the entire collector surface is available for adhesion

$$C(x,0) = C_0\exp(-\alpha f K_{th} x) \tag{8}$$

while for long times

$$C(x,\tau=\infty) = C_0\exp(-\beta f K_{th} x) \tag{9}$$

where $x = z/u$ and $f = 3(1-\Phi)/\Phi r_b$.
The combination of equations (8) and (3) yields

$$\ln(C_0/C) = bu^{-2/3} \tag{10}$$

where b incorporates all constants. Thus, linear dependence of $u^{-2/3}$ on $\ln(C_0/C_0)$ is consistent with a convective diffusion controlled deposition mechanism.

EXPERIMENTAL

1. Hematite Particles on Glass

Systematic experiments have been carried out using uniform spherical hematite particles with the radius $r_p = 33 \pm 4$ nm, which had an isoelectric point at pH ~ 8.5 and glass beads (LaPine, radius $r_b = 55 \pm 9\ \mu$m), which were negatively charged over the entire pH range of interest. The particle deposition was evaluated as a function of the ionic strength at different pH values and flow rates.

Figure 1 verifies that for the deposition of these hematite particles on glass the plot of $-\ln[\ln(C/C_0)_{t=0}]$ against $\ln u$ yields a slope of $-2/3$ in accordance with equation (10).

It is expected that an increase in the ionic strength would promote multilayer adhesion. Figure 2 displays a series of experiments, which indeed show that the kinetics of adhesion is strongly dependent on the content of the neutral electrolyte. It is noteworthy that at pH = 3 the particles and the beads carry charges of opposite sign, which means that the deposition is taking place in the absence of a potential barrier.

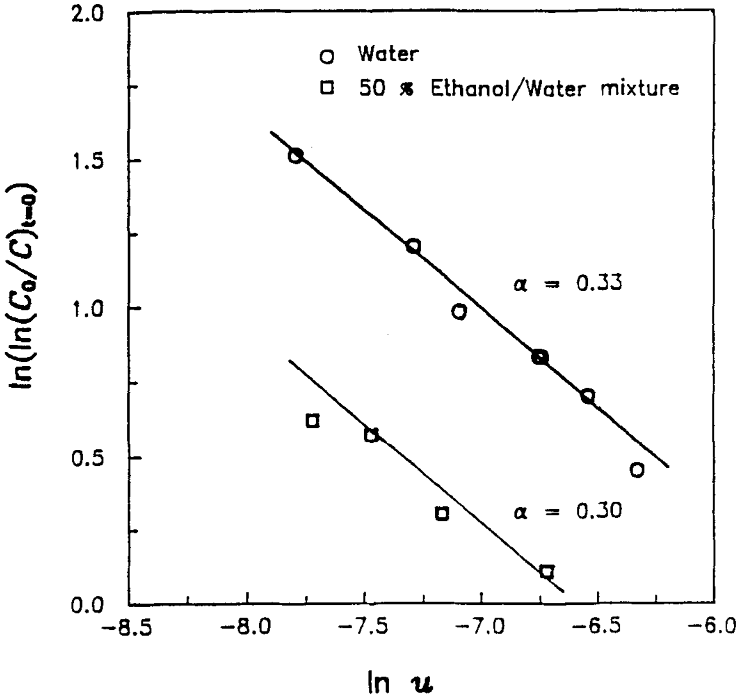


FIGURE 1 Plots showing the $u^{-2/3}$ dependence on $-\ln(C/C_0)_{t=0}$ in verification of Eq. (10) for the adhesion on glass beads of hematite particles deposited in aqueous (○), and the 50% ethanol/water media (□) in the presence 1.0×10^{-3} mol dm^{-3} HNO_3. The α values were calculated using Eq. (8).

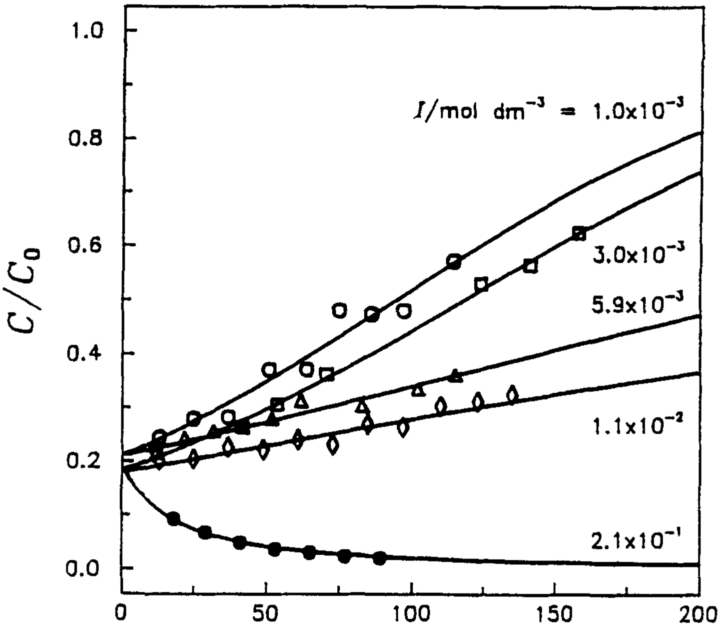


FIGURE 2 Experimental values of C/C_0 as a function of time for the adhesion on glass beads of hematite particles from a 50% ethanol/water solution, containing 1.0×10^{-3} mol dm^{-3} HNO_3, at the ionic strength of $I = 1.0 \times 10^{-3}$ (○), 3.0×10^{-3} (□), 5.9×10^{-3} (△), 1.1×10^{-2} (◇), and 2.1×10^{-1} mol dm^{-3} (●). Solid lines were calculated using Eq. (1) with fitted values α, β, and γ.

The solid lines represent calculated values using equation (1) with fitted values of α, β, and γ.

The similar intercepts for C/C_0 at $t = 0$ indicate that the deposition rates on the bare collector surface are essentially the same. The asymptotic behavior of curves at $I \leq 1.1 \times 10^{-2}$ mol dm^{-3} for $t \rightarrow \infty$ is characteristic of the monolayer case; *i.e.* $\beta = 0$. At $I = 2.1 \times 10^{-1}$ mol dm^{-3} the trend of the curve indicates multilayer deposition. In the last case the ionic strength is greater than the critical coagulation concentration of the hematite dispersion, and $\beta > \alpha > 0$, as concluded from the negative slope at initial times.

The calculated values of $\alpha \sim 0.4$ were found to be independent of the ionic strength, which is expected to be case in the absence of a potential barrier, when the flux is limited by convective diffusion only.

The values of β for systems of Figure 2, plotted in Figure 3, along with those of W^{-1} determined and calculated from coagulation experiments, indicate a good correlation between the two parameters. Obviously, multilayer deposition becomes significant once the ionic strength is sufficiently high to suppress the potential barrier on colloid particles.

Finally, the value of the γ parameter increases as the electrolyte concentration is lowered (Figure 4), which is caused by the lateral repulsion between the adhered particles on the collector surface.

In order to compare the experimental results with the theoretical predictions, the stability coefficients were calculated for the adhesion of hematite particles on glass

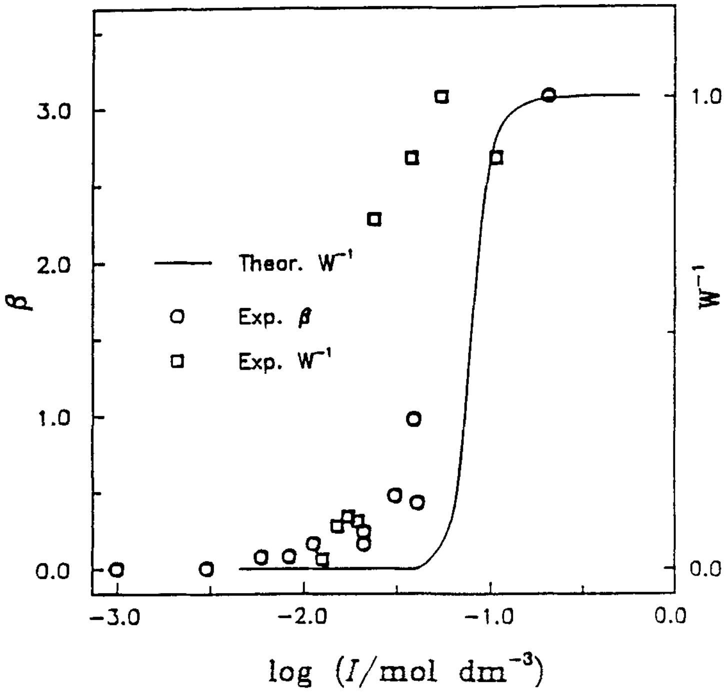


FIGURE 3 Fitted β parameter (○) as a function of the ionic strength for the system illustrated in Figure 2. The inverse stability ratio (□, W^{-1}) was determined from coagulation experiments, and the corresponding solid line was calculated from theory.

beads as a function of the ionic strength, and the results are reproduced in Figure 5. Also included in the diagram are data that refer to coagulation of the same hematite dispersion. The calculations were carried out using both the Hogg-Healy-Fuerstenau[25] and the Overbeek[26] expressions for homocoagulation, since under the given experimental conditions multilayer deposition takes place. Neither model describes the experimental data well and analogous discrepancies were observed with many other dispersions.[27–31] Considerable effort was invested in attempts to reconcile such experimental and theoretical results by varying different parameters of importance in the interactions between identical and different solids (the Hamaker constant, hydrophobic interaction, hydrodynamic retardation, Born repulsion, etc.), but all these attempts failed.[32] However, by assuming charge segregation on the particles of ~ 25–30%, the calculated curves could be brought into agreement with data obtained both in adhesion and coagulation measurements.[33]

Another essential aspect of adhesion deals with the removal of deposited particles. In order to achieve detachment, it is necessary to alter the charge characteristics of interacting solids. With many inorganic systems this change can be achieved by rinsing the column with solutions of adequate pH and sufficiently low ionic strength.[34–37] One example of such a process is given in Figure 6. The ascending curve represents the deposition of hematite particle on glass beads at pH = 4.0. At time intervals between 165 and 305 min the column was rinsed with a solution of pH 4.0, between 305 and

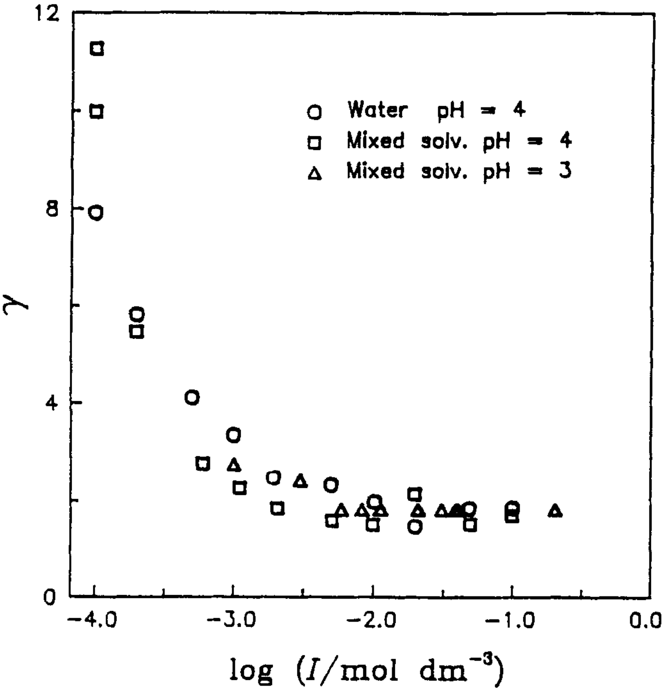


FIGURE 4 Fitted γ parameter for adhesion of hematite particles from different media on glass beads as a function of the ionic strength.

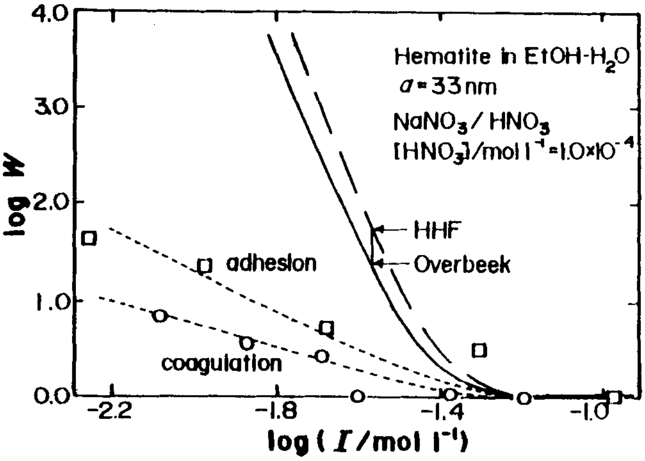


FIGURE 5 The stability coefficients (W) for homocoagulation (○) of hematite particles, and for their multilayer adhesion on glass beads (□) as a function of the ionic strength at $[HNO_3] = 1.0 \times 10^{-4}$ mol dm^{-3}. The Overbeek[26] and the Hogg, Healy, and Fuerstenau (HHF)[25] expressions are used in the calculation of the theoretical dependence of W on I.

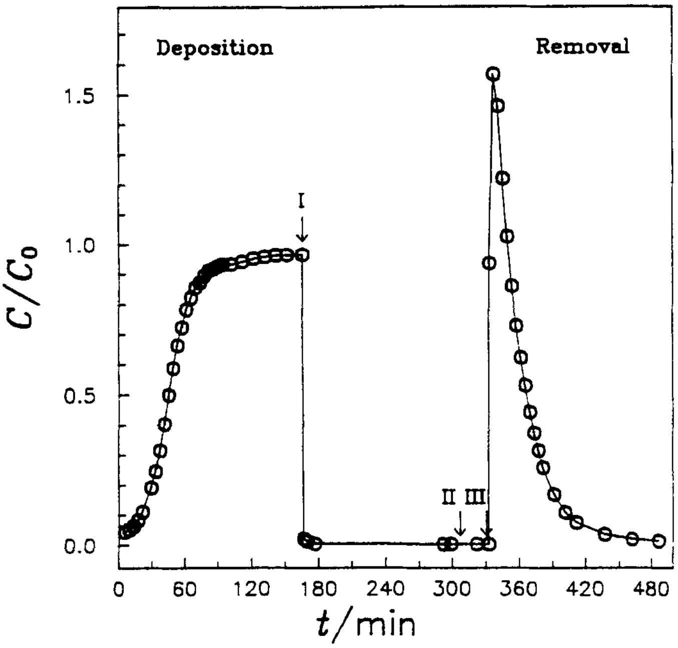


FIGURE 6 The plot of C/C_0 as a function of time for hematite particles on glass beads at the ionic strength $I = 1.0 \times 10^{-4}$ mol dm^{-3}. The deposition was carried out at pH = 4.0. Afterwards the column with adhered particles was rinsed with a solution of pH = 4.0 starting at 165 min (I), continued with a solution of pH = 9 at 305 min (II), and of pH 11.7 starting at 331 min (III).

331 min with a solution of pH 9.8, and afterwards with a solution of pH 11.7. Only during the last segment of the process did detachment of particles take place. The amount of adhered hematite can be evaluated from the area of the plot in Figure 6 related to the deposition sequence, and that of detachment particles by the corresponding area in the removal sequence. It was established that in this particular system ~ 92% of all deposited particles were removed when a solution of sufficiently high pH was used in washing the column to render both surfaces strongly negatively charged. This result, in turn, is consistent with the conclusion that only physical forces (electrostatic and van der Waals) control the particle adhesion *i.e.* no bonding between hematite particles and glass beads took place.

2. Hematite Particles on Gelatin-Coated Glass

Coating the glass beads with gelatin has two major effects on the adhesion process. The first is due to the different dependence of the surface potential on the pH, which is essentially determined by the properties of the protein, *i.e.* on its isoelectric point (i.e.p.), while the second is caused by chemical interactions between gelatin and the adhered particles.

Figure 7 displays the deposition on glass beads coated with gelatin of the same hematite particles, as used in the study described in the previous section, as a function of

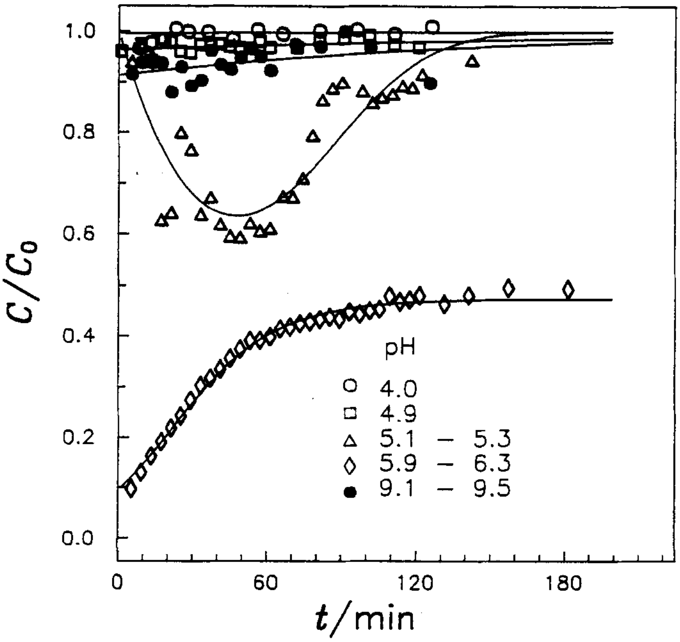


FIGURE 7 An analogous plot as in Figure 2 for hematite particles on gelatin-coated glass beads at different pH values.

time at several pH values.[37] In some samples, it was difficult to maintain a constant pH in the course of the experiments, since no buffers were used. The latter are avoided in this work, because such additives alter the ionic strength of the system and many constituents of a buffer can directly interact with the collectors and, as such, obscure the adhesion effects of interest. It is quite obvious that the conditions for deposition differ from those observed with untreated glass (Figure 2).

The gelatin glass-coated surface had an i.e.p. at pH ~ 5. As a consequence, the glass beads were positively charged below this pH value in contrast to the bare collectors, which remained negatively charged over the entire pH range investigated. The breakthrough curves at pH 4.0, 4.9, and 9.1 show essentially no particle deposition, which is readily explained by the electrostatic repulsion; *i.e.*, at the two lower pH values both interacting surfaces are positively charged, while at pH = 9.1 both bear negative charge. The solid lines were calculated using the equations given in the theoretical part.

In the run at the initial pH = 5.9 a slow initial deposition rate is observed and a limiting value of $C/C_0 < 1$ is attained, which indicates multilayer deposition. The latter is further substantiated by the evaluation of the parameters α, β, and γ, not shown here.

The somewhat unusual trend at the pH 5.1–5.3 may be due to a combination of effects. The initial pH is sufficiently low for particles and the collector to have the same sign of charge which, in the course of the experiment, changes sufficiently to cause attraction and later on again repulsion. This example clearly shows the great sensitivity of the adhesion process to the change in the sign of the charge, which can take place over a very narrow pH range under certain critical conditions. In this case, the solid line was calculated by allowing the parameter α to change with time, which is justified in view of the fact that the nature of the process is altered in course of a given experiment.

In contrast to the results with untreated glass beads, all efforts to detach hematite particles from the gelatin-coated collectors failed, regardless of the pH of the rinsing solutions. This finding supports the conclusion that iron oxide particles chemically interact with the substrate. The most obvious bond formation will occur by condensation of the surface $\equiv$ FeOH site with the carboxyl group of the protein molecule, as was demonstrated by adsorption measurements of different proteins on metal oxides.[38,39] Thus, the deposition of the particles is affected by both physical and chemical forces

3. Hematite Particles on Steel

The packed column technique was also used to study the adhesion phenomena of hematite dispersions in contact with steel beads, and it was again established that the electrostatics plays the dominant role in the deposition and detachment processes.

Figure 8 clearly shows that the uptake of hematite is essentially quantitative when the particles and steel beads are of opposite sign of charge.[8] The removal of deposited

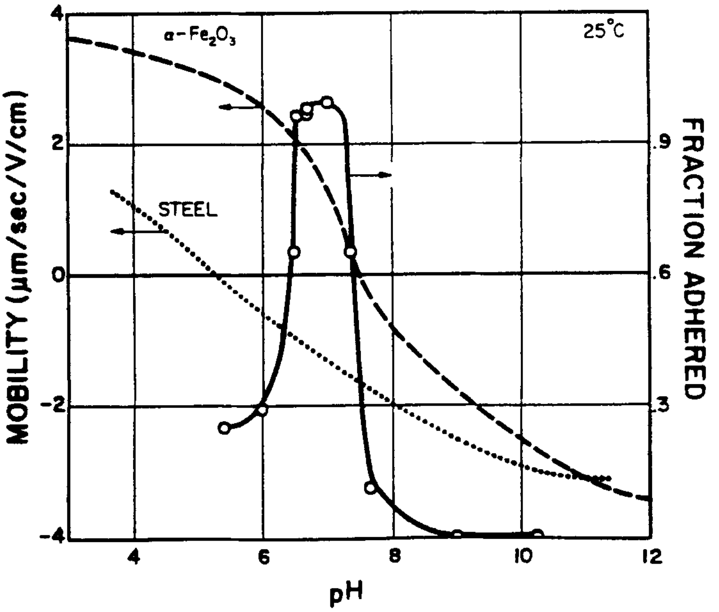


FIGURE 8 Fraction of α–Fe_2O_3 particles ($r_p = 0.041$ μm) deposited on steel ($r_b = 116$ μm) as a function of pH at 25°C. In each case 50 cm^3 of an α–Fe_2O_3 sol of $\sim 10^8$ particles/cm^3 was passed through the bed at a flow velocity of ~ 0.03 cm sec^{-1}. The corresponding electrophoretic mobilities of hematite particles and of steel beads are shown by dashed and dotted lines, respectively.[8]

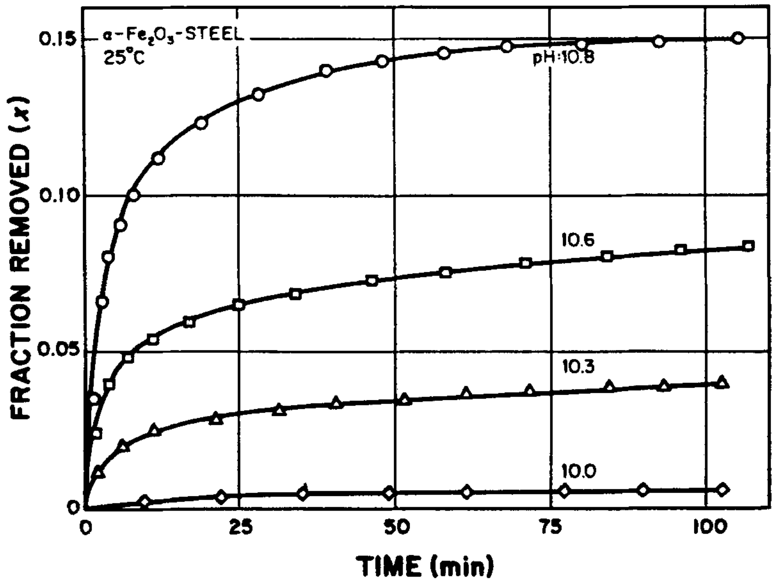


FIGURE 9 Fraction of hematite (α–Fe_2O_3) particles (x) removed from steel, as a function of time at 25°C, by rinsing the bed with NaOH solutions of pH: 10.8 (○), 10.6 (□), 10.3 (△), and 10.0 (◇). The initial number of adhered particles: 2.6×10^9 per gram of steel; aging time before rinsing 250 hr.[8]

particles does take place, and the rate of the process depends on the pH of the rinsing solution. Obviously, the latter must render both surfaces negatively charged as demonstrated in Figure 9.[8,34]

The same system lends itself for the investigation of another parameter, *i.e.* of the effect of the external magnetic field, both on deposition and detachment of particles. The magnetic force can be utilized to cause or enhance particle deposition when a potential barrier prevents such interaction in the absence of an imposed field. Obviously either the particles or the collector (or both) must have a finite magnetic moment for the adhesion to take place under the influence of the applied force, if electrostatic repulsion is to be overcome.

Figure 10 shows that, when a magnetic force is present, hematite particles can indeed be deposited on steel at pH 11,[18] which renders both surfaces strongly negatively charged. The extent of the uptake is dependent on the field strength and on the ionic strength. It is also expected that the size of collector beads would play a role in this case, as was confirmed experimentally.[18]

The calculation of the total interaction energy for the steel/hematite system, taking into consideration electrostatic, van der Waals, and magnetic contributions, showed the last to dominate, resulting in a deep secondary minimum, as illustrated in Figure 11. It is apparent that the attachment of particles under the influence of the magnetic field takes place at some distance from the collector surface.

It is to be expected that particles deposited in the secondary minimum, which is far from the bead surface, cannot interact directly with the sites on the collector's surface.

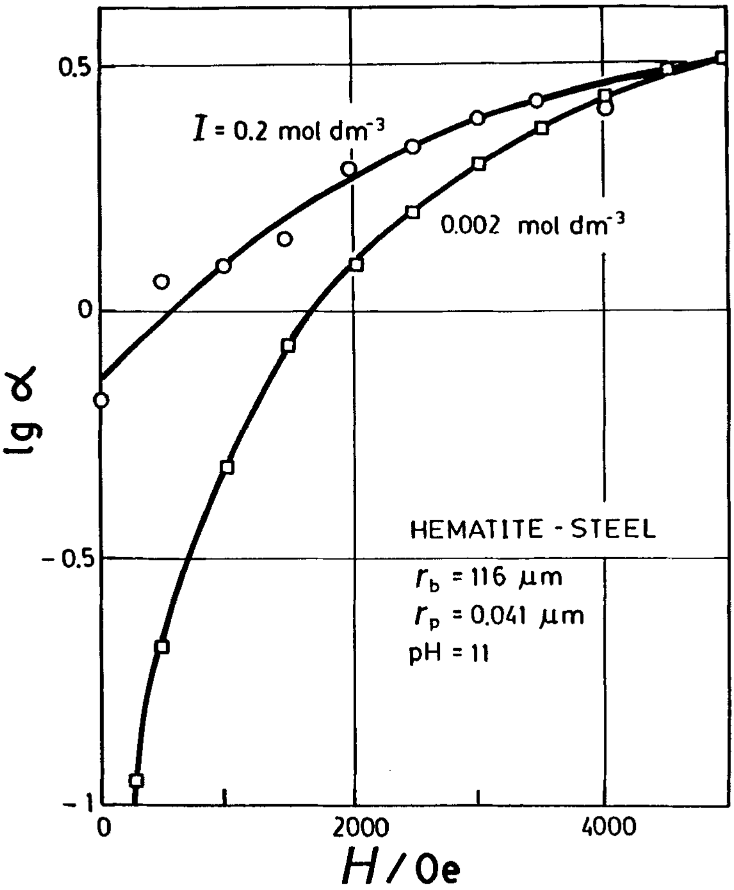


FIGURE 10 Effect of the magnetic field strength (H) on the collision efficiency (α) of hematite particles ($r_p = 0.041\,\mu m$) with steel beads ($r_b = 116\,\mu m$) at ionic strengths ($NaNO_3$) $I = 0.2\,mol\,dm^{-3}$ (○) and $I = 0.002\,mol\,dm^{-3}$(□), at pH 11 and 22°C.[18]

Consequently, on removing the external (in this case magnetic) force, the complete release of the adhered particles can be achieved. Such removal was indeed experimentally confirmed in several systems.[40]

CONCLUDING REMARKS

This limited survey has demonstrated the usefulness of the packed column technique in the investigation of the effects of various parameters on particle adhesion phenomena. Using monodispersed colloids makes it possible to quantify the data and to explain the observed phenomena by considering various contributions to the interactions between the collectors and the particles.

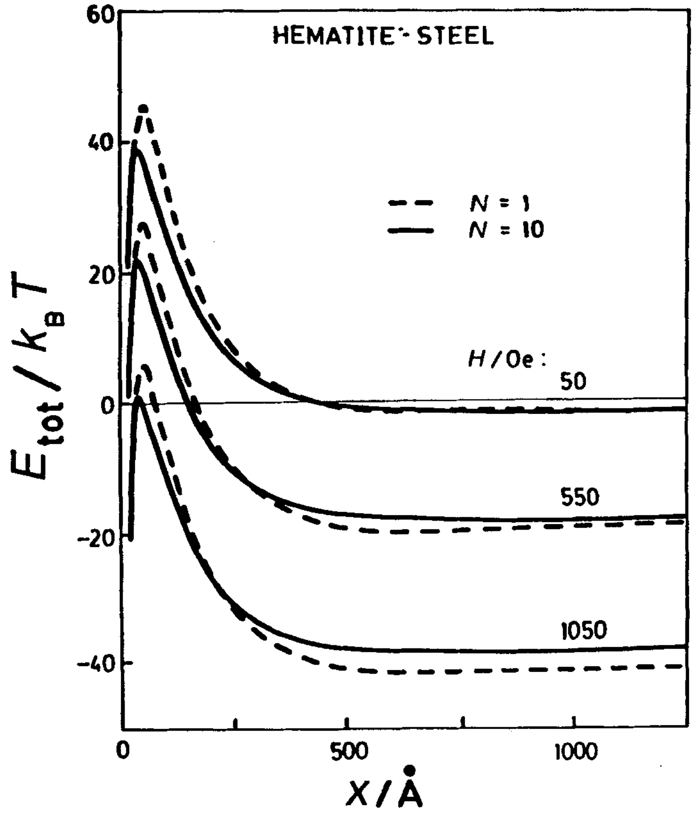


FIGURE 11 Total interaction energy as a function of distance at different magnetic field strength for the hematite/steel system shown in Figure 10, calculated for the deposition of one particle on the bead surface ($N = 1$), and for the 10th particle attached to a chain of nine particles ($N = 10$).[40]

One important aspect, which has not been dealt with in this study, is the surface roughness. The latter influences greatly the adhesion, if it is present either on the substrate or on the particles. The effect of the surface topography is especially noticeable in the particle detachment process, as was demonstrated elsewhere.[41]

Acknowledgement

This work was supported by NSF Grant CHE-9108420.

References

1. C. S. Hirtzel and R. J. Rajagopalan, *Colloidal Phenomena Advanced Topics* (Noyes Publications Park Ridge, New Jersey, 1985), Chap 5, pp. 119–159.
2. L. A. Spielman and S. K. Friedlander, *J. Colloid Interface Sci.* **46**, 22 (1974).
3. Z. Adamczyk, *Colloids Surf.* **39**, 1 (1989).
4. Z. Adamczyk, B. Siwek and M. Zembala, *Colloids Surf.* **62**, 119 (1992).
5. N. Kallay, *MRS Bulletin.* **15**, 41 (1990).

6. N. Kallay, E. Barouch and E. Matijević, *Adv. Colloid Interface Sci.* **27**, 1 (1987).
7. R. J. Kuo and E. Matijević, *J. Chem. Soc. Farady Trans. I.* **75**, 2014 (1979).
8. R. J. Kuo and E. Matijević, *J. Colloid Interface Sci.* **78**, 407 (1980).
9. N. Kallay, J. Nelligan and E. Matijević, *J. Chem. Soc. Faraday Trans. I.* **79**, 65 (1983).
10. G. Thompson, N. Kallay and E. Matijević, *Chem. Eng. Sci.* **38**, 1901 (1983).
11. E. Matijević and N. Kallay, *Croat. Chem. Acta.* **56**, 649 (1983).
12. V. Privman, H. L. Frisch, N. Ryde and E. Matijević, *J. Chem. Soc. Faraday Trans.* **87**, 1371 (1991).
13. N. Ryde, N. Kallay and E. Matijević, *J. Chem. Soc. Faraday Trans.* **87**, 1377 (1991).
14. N. Ryde, H. Kihira and E. Matijević, *J. Colloid Interface Sci.* **151**, 421 (1992).
15. M. Elimelech and C. R. O'Melia, *Env. Sci. Technol.* **24**, 1528 (1990).
16. M. Elimelech, *J. Colloid Interface Sci.* **146**, 337 (1991).
17. L. Song and M. Elimelech, *Colloids Surf. A.* **73**, 49 (1993).
18. M. F. Haque, N. Kallay, V. Privman and E. Matijević, *J. Adhesion Sci. Technol.* **4**, 205 (1990).
19. V. Privman, N. Kallay, M. F. Haque and E. Matijević, *J. Adhesion Sci. Technol.* **4**, 221 (1990).
20. N. Kallay and E. Matijević, *Colloids Surf.* **39**, 161 (1989).
21. J. Happel, *AIChE J.* **4**, 197 (1958).
22. R. Pfeffer and J. Happel, *AIChE J.* **10**, 605 (1961).
23. R. Pfeffer, *I&E C. Fundamentals.* **3**, 381 (1964).
24. N. Fuchs, *Z. Physik.* **89**, 736 (1934).
25. R. Hogg, T. W. Healy and D. W. Fuerstenau, *J. Chem. Soc. Faraday Trans. I.* **62**, 1638 (1966).
26. J. T. G. Overbeek, *Colloids Surf.* **51**, 61 (1990).
27. H. Reerink and J. T. G. Overbeek, *Discuss. Faraday Trans.* **18**, 74 (1954).
28. R. H. Ottewill and J. N. Shaw, *Discuss. Faraday Soc.* **42**, 154 (1966).
29. A. Lips, C. Smart and E. Willis, *Trans. Faraday Soc.* **67**, 2979 (1971).
30. A. Lips and E. Willis, *J. Chem. Soc. Faraday Trans. I.* **69**, 1226 (1973).
31. H. Kihira, N. Ryde and E. Matijević, *Colloids Surf.* **64**, 317 (1992).
32. H. Kihira, *Kinetics of Heterocoagulation* (Ph.D. Thesis, Clarkson University, 1992, available from UMI Microfilm Services), pp. 89–98.
33. H. Kihira, N. Ryde and E. Matijević, *J. Chem. Soc. Faraday Trans.* **88**, 2379 (1992).
34. N. Kallay and E. Matijević, *J. Colloid Interface Sci.* **83**, 289 (1981).
35. J. D. Nelligan, N. Kallay and E. Matijević, *J. Colloid Interface Sci.* **89**, 9 (1982).
36. N. Kallay, B. Biškup, M. Tomić and E. Matijević, *J. Colloid Interface Sci.* **114**, 357 (1986).
37. N. Ryde and E. Matijević, *J. Colloid Interface Sci.* (1994, in press).
38. J. E. Johnson and E. Matijević, *Colloid Polym. Sci.* **270**, 353 (1992).
39. J. E. Johnson and E. Matijević, *Colloid Polym. Sci.* **270**, 364 (1992).
40. M. F. Haque, N. Kallay, V. Privman and E. Matijević, *J. Colloid Interface Sci.* **137**, 36 (1990).
41. N. Kallay, M. Tomić, B. Biškup, I. Kunjašić and E. Matijević, *Colloids Surf.* **28**, 185 (1987).