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# Kinetics of Colloid Deposition onto Heterogeneously Charged Surfaces in Porous Media

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A general theoretical approach for the calculation of colloid deposition rate onto heterogeneously charged surfaces is presented. Patchwise and random distribution models are used to quantitatively describe surface charge heterogeneity and its effect on the kinetics of colloid deposition. It is shown that unfavorable surfaces with only minor amounts of charge heterogeneity have particle deposition rates that are orders of magnitude larger than similar surfaces having no charge heterogeneity. Furthermore, the sensitivity of particle deposition rate to solution ionic strength decreases as the degree of surface charge heterogeneity increases. Parameters characterizing the surface charge heterogeneity of collectors in porous media are identified from experimental data of colloid deposition by using the inverse procedure of parameter estimation. These heterogeneity parameters can be used in conjunction with current theories of particle deposition to explain experimental results of colloid deposition rates under chemical conditions that are unfavorable for particle deposition.

## Introduction

Suspended colloidal particles are ubiquitous in subsurface aqueous environments (1-5). Field and laboratory column studies demonstrate that colloids are mobile in porous media and that the transport of inorganic and organic contaminants sorbed onto mobile colloids can be enhanced significantly (1, 6-10). The enhancement in the transport of contaminants sorbed onto colloids is usually termed *facilitated transport* or *colloid-mediated transport*.

Suspended colloids interact with stationary surfaces in porous media. The extent of migration of colloids and sorbed contaminants in groundwaters and soils is determined in large part by the rate of colloid deposition onto stationary media. Slow deposition kinetics in porous media can result in the extensive transport of colloids while fast deposition kinetics result in a limited transport (10, 11). Hence, a fundamental understanding of the factors controlling the kinetics of colloid deposition onto solid surfaces in subsurface environments is of paramount importance.

The kinetics of colloid deposition under unfavorable chemical conditions have been studied extensively in the past 2 decades (12-16). These studies have shown that initial colloid deposition rates in the presence of repulsive double-layer interactions are sensitive to the solution chemistry (electrolyte concentration and type) and to the electrokinetic potentials of particles and collector surfaces, but not to the large extent predicted by theory. Observed particle deposition rates are usually many orders of magnitude larger than those predicted with electric double-

layer (EDL) theories that are based on uniform surface charge distribution (12-14, 17, 18). Consequently, theoretical deposition rates calculated with the use of current theories cannot be utilized directly to predict particle mobility in aquatic environments.

In previous theoretical studies of colloid deposition, uniform distribution of surface charge was assumed for particles and collectors. This assumption, however, is not valid since real surfaces, such as soil and stationary aquifer media or collectors used in controlled laboratory experiments, are heterogeneously charged at both the microscopic (molecular) and macroscopic levels. Microscopic surface charge heterogeneities arise from imperfections in the arrangement of ions within the crystal lattice whereas macroscopic heterogeneities are the result of differences in surface charge properties of adjacent crystal faces and the presence of bulk or surface-bound chemical impurities (19-28). In subsurface aquatic environments, the presence of iron and aluminum oxide patches on mineral surfaces is the main source of macroscopic surface charge heterogeneities (26, 28).

The interaction of colloidal particles with heterogeneously charged surfaces differs markedly from colloidal interactions with ideal surfaces having uniform charge distribution. Unlike an ideal surface where no particle deposition is predicted for like charges, local (preferential) deposition of colloidal particles may occur onto heterogeneously charged surfaces where the electric double-layer repulsion between colloidal particles and some sites on the collector surface is sufficiently small or on favorable sites which have charge opposite to that of the colloidal particles. This rather important feature of colloidal deposition has not as yet been systematically investigated.

The objectives of this paper are to develop a general theoretical approach for calculating the kinetics of colloid deposition onto heterogeneously charged surfaces in porous media and to evaluate this approach using data of colloid deposition rates from well-controlled column experiments. With the newly developed theoretical approach, the effect of surface charge heterogeneity on the initial deposition rate of colloidal particles in porous media is systematically investigated. The results of this study demonstrate the important role of surface charge heterogeneity in colloid deposition kinetics under unfavorable chemical conditions.

## Theoretical Analysis

**Nominal Surface Potential.** When determining the interaction of a spherical particle with a flat surface at a given solution chemistry, essential parameters include the surface potentials of the particle and the surface as well as the separation distance. For cases involving homogeneous surface charge distribution, the electric double-layer (EDL) interaction energy between the particle and the surface is readily obtained using conventional Derjaguin-

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Landau-Verwey-Overbeek (DLVO) theory and the above-mentioned parameters (29-32). For cases involving heterogeneous surface charge distribution, one may also use conventional DLVO theory to calculate EDL interaction energy between a spherical particle and a heterogeneous, flat surface by assigning a *nominal surface potential* to the heterogeneous surface.

The nominal surface potential of a heterogeneous surface is equivalent to the potential of a homogeneous surface which would produce the same EDL interaction with a particle as the heterogeneous surface, at an identical separation distance. A value for the nominal potential of a surface should not be taken as an attempt at describing the actual potential of a heterogeneously charged surface; instead, it is only intended to represent the homogeneous analog of a heterogeneously charged surface. By replacing the actual surface potential with a nominal surface potential, EDL interaction energies can be calculated between heterogeneous surfaces by using the general expressions developed for interaction between homogeneously charged surfaces.

**Models for Charge Heterogeneity of Collector Surfaces.** The EDL interaction between a particle and a flat surface can be fully characterized by the local surface potential  $\psi(x,y)$ , with  $x$  and  $y$  forming an orthogonal coordinate system on the surface. For cases involving particle deposition from dilute suspensions, the surface charge heterogeneity can be characterized by the distribution of potential on the surface. Generally, it is not possible to determine or assign exact values for variations in potential over the entire surface. However, a probability distribution of nominal potentials may be assigned according to *a priori* knowledge or assumptions about surface characteristics. Based on studies involving adsorption of gases and solutes (33), two models are considered when describing surface charge heterogeneity. They are the patchwise and random distribution models.

**(a) Patchwise Model.** Patchwise heterogeneity implies that surface sites of equal potential are grouped together in macroscopic patches, each of which can be treated as a homogeneous surface (34, 35). Both isolated and interacting patches are recognized and may be distinguished on the basis of size (35). The transition from interacting patches to isolated patches is around  $\kappa R = 1$ , with  $\kappa$  being the inverse Debye length and  $R$  being the size of the patch. When considering large patches (i.e.,  $\kappa R > 1$ ), it may be assumed that each patch behaves as a homogeneous, isolated surface in equilibrium with the bulk solution and that the interactions at patch boundaries can be neglected. In natural systems, such macroscopic surface heterogeneities as crystal planes and iron oxide patches on minerals are representative of large patchwise heterogeneities. For the patchwise model used in this study, we will assume that equipotential sites form large patches and that particles and patches are of an appropriate size such that individual particles interact with only one patch on the collector surface (36, 37).

For the patchwise model, the ratio of each type of patch to the entire area of the collector surface, denoted as  $p_i$  or as a probability density function  $p(\psi_i)$ , is given by

$$p_i = p(\psi_i) = \lambda_i \quad (1)$$

$$i = 1, 2, \dots, n$$

where  $\psi_i$  and  $\lambda_i$  are the surface potential and the surface

fraction of patches of type  $i$ , respectively, and  $n$  is the number of patch types. In cases where the heterogeneity of surface charge originates from one type of patch interspersed throughout a surface of otherwise uniform potential, the patches are taken to be the sites that are more favorable for particle deposition.

**(b) Random Distribution Model.** Continuous random heterogeneity indicates that sites of equipotential are randomly distributed over the entire surface. The random distribution model may be applied to collectors whose surfaces do not have an obvious patchwise arrangement of charge distribution, such as glasses and other amorphous substances. Since there is often no information available as to the distribution of surface potentials, a normal (Gaussian) distribution is generally assumed, i.e.

$$p(\psi) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\psi - \psi_0)^2}{2\sigma^2}\right] \quad (2)$$

where  $\psi_0$  and  $\sigma$  are the mean and standard deviation of the potential, respectively.

The patchwise and random distribution models can only be regarded as mathematical representations of surface charge heterogeneity since information about the topography of charge site distribution is generally unavailable. Despite their limited nature, these models are a sufficient means of describing the characteristics of surface charge heterogeneity as applied to particle deposition.

**Particle Deposition Rate onto Heterogeneously Charged Surfaces.** Experimentation has shown that a significant amount of particle deposition occurs onto collector surfaces under unfavorable chemical conditions, which is in direct contrast to theoretical predictions based on DLVO theory (12-18). This apparent failure of theory may be due, in part, to nonidealities that arise as a result of surface charge heterogeneity. Heterogeneities such as lattice imperfections and surface impurities may provide favorable deposition sites on what is otherwise an unfavorable surface for particle deposition. The rate of particle deposition onto favorable sites may be several orders of magnitude higher than that of unfavorable sites. Therefore, the proportion of favorable to unfavorable sites may actually determine the kinetics of particle deposition onto a collector surface.

**(a) Local Particle Deposition Rate.** Particle attachment to a collector surface is controlled by local interactions between the particle and a small area (or site) on the surface. For heterogeneously charged collector surfaces, the local particle deposition rate will vary depending on the local surface conditions. Using the concept of nominal surface potential introduced earlier, the local particle deposition rate may be calculated using the existing methods developed for ideal, homogeneous surfaces.

For colloid deposition onto favorable patches (i.e., negligible EDL interactions), the Smoluchowski-Levich (SL) approximation (38, 39) can be used to calculate the local particle deposition rate. When using this approximation, one assumes that hydrodynamic interaction (retardation) is balanced by the attractive van der Waals force. Analytical expressions for colloid deposition onto various collector geometries using the SL approximation can be found in Adamczyk *et al.* (39) and Jia and Williams (40). When calculating the deposition rate of non-Brownian particles onto favorable patches of spherical

collectors, the correlation equation of Rajagopalan and Tien (41) can be used.

For colloid deposition onto unfavorable surfaces (i.e., where repulsive EDL interactions exist), the interaction force boundary layer (IFBL) approximation (42, 43) can be used to calculate local particle deposition rate. When using the IFBL approximation, the effects of colloidal and hydrodynamic interactions on particle deposition rate are lumped into a boundary condition of the convective diffusion equation. This boundary condition takes the form of an irreversible first-order chemical reaction occurring on the collector surface. While the IFBL approximation is appropriate for Brownian colloids, no analytical approximations exist for calculating the deposition rate of non-Brownian particles under unfavorable chemical conditions.

Greater accuracy can be obtained in calculating the particle deposition rate by using a direct numerical solution of the convective diffusion equation with colloidal, hydrodynamic, and gravitational forces fully incorporated. The numerical solution of particle deposition onto favorable surfaces is relatively straightforward, requiring a simple grid point allocation strategy (44). Numerical calculation of particle deposition onto unfavorable surfaces is more intractable because of the singular behavior of the governing equation involved. A sophisticated numerical procedure developed for this condition is available (45).

**(b) Overall Particle Deposition Rate.** The overall particle deposition rate is the sum total of local particle deposition occurring over the entire collector surface. Generally, the kinetics of particle deposition onto a surface with charge heterogeneity can be described by the overall particle deposition rate,  $J$ , defined as follows:

$$J = \int_S J(\psi) p(\psi) d\psi \quad (3)$$

where  $J(\psi)$  is the local particle deposition rate,  $\psi$  is the nominal surface potential,  $S$  is the range of possible variations of nominal potential, and  $p(\psi)$  is the probability density function of the potential  $\psi$ . In cases where the patch model is used, eq 3 can be simplified to

$$J = \sum_{i=1}^n \lambda_i J_i \quad (4)$$

where  $J_i$  is the particle deposition rate onto patches of type  $i$ , and  $\lambda_i$  is the surface fraction of patches of type  $i$  (i.e., the ratio of total area of patches of type  $i$  to the entire collector surface).

When only one kind of favorable patch exists on an otherwise homogeneous surface which is unfavorable for particle deposition, eq 4 can be further simplified to

$$J = \lambda J_P + (1 - \lambda) J_R \quad (5)$$

where  $J_P$  and  $J_R$  are the particle deposition rates onto the patches and the rest of the collector surface, respectively; and  $\lambda$  and  $(1 - \lambda)$  are the area fractions of the patches and the rest of the collector surface, respectively. When  $\lambda \ll 1$ , the average collector surface potential is determined by the potential of the unfavorable part of the collector surface. However, the overall particle deposition rate is usually controlled by characteristics of the favorable patches; namely, the surface potential of patches and the patch fraction  $\lambda$ .

In cases where the Gaussian distribution model is used, eq 3 becomes

$$J = \int_{-\infty}^{\infty} \frac{J(\psi)}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\psi - \psi_0)^2}{2\sigma^2}\right] d\psi \quad (6)$$

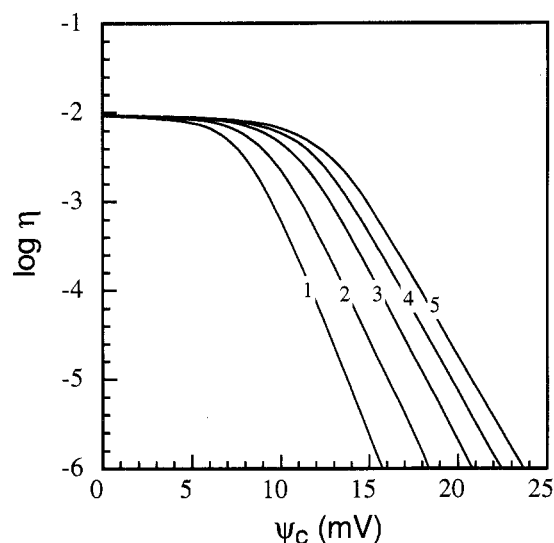
Because of the complex dependence of the local particle deposition rate on surface potential, a numerical calculation of eq 6 is necessary to obtain the overall particle deposition rate. The average value of the surface potential of the collector  $\psi_0$  cannot be used to exclusively determine the kinetics of particle deposition. The other necessary parameter is the standard deviation of the potential distribution  $\sigma$ , which may be conceptualized as a representation of the degree of surface charge heterogeneity.

**Effect of Surface Charge Heterogeneity on Overall Particle Deposition Rate.** Representative model simulations are presented in order to illustrate the effect of surface charge heterogeneity on overall particle deposition rate. These simulations were performed for deposition of spherical colloids in a porous medium composed of spherical collectors having surface heterogeneities.

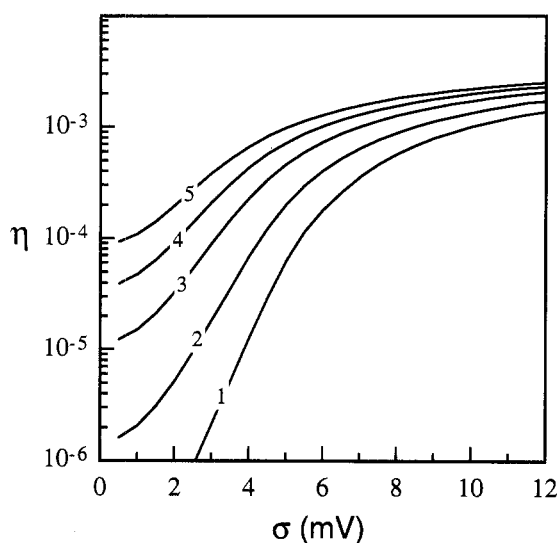
Before determining the overall particle deposition rate, the local particle deposition rate is first computed numerically for various collector surface potentials and ionic strengths. Gregory's expression (46) was used to determine van der Waals interactions, while the expression developed by Hogg *et al.* (30) was used to calculate EDL interactions. Using the concept of nominal surface potential, the local particle deposition rates may be represented as single collector removal efficiencies for a uniformly charged surface. The single collector removal efficiency is a dimensionless deposition rate; it is calculated by dividing the particle deposition rate of the entire collector surface by the total particle flux approaching the cross-sectional area of the collector (47). Particle deposition rates were calculated from a numerical solution of the complete convective diffusion equation as described by Song and Elimelech (45). Deposition rates expressed as single collector removal efficiencies  $\eta$  are shown in Figure 1. This figure illustrates the dependence of local particle deposition rate not only on surface potential but also on solution ionic strength.

Overall particle deposition rates,  $\eta$ , were calculated by numerical integration of eq 6 for the Gaussian distribution of the nominal potential, using various standard deviations and ionic strengths. The overall particle deposition rates, which are based on the local deposition rates shown in Figure 1, are plotted as a function of the standard deviation of surface potential in Figure 2. In general, it is evident that an increase in the standard deviation of local surface potential  $\sigma$  leads to an increase in the overall particle deposition rate. Furthermore, the overall particle deposition on surfaces which contain high standard deviations in surface potential is much less affected by changes in ionic strength than surfaces with low standard deviations of surface potential. Two separate regions are distinguishable in Figure 2, based on standard deviation  $\sigma$ . In the region having smaller  $\sigma$  (i.e.,  $\sigma$  below about 6 mV), the effect of  $\sigma$  on the overall particle deposition rate is more pronounced.

The overall particle deposition rates for the random distribution model are plotted against ionic strength for various standard deviations in Figure 3, with the bold line near the bottom of the figure representing uniform surface



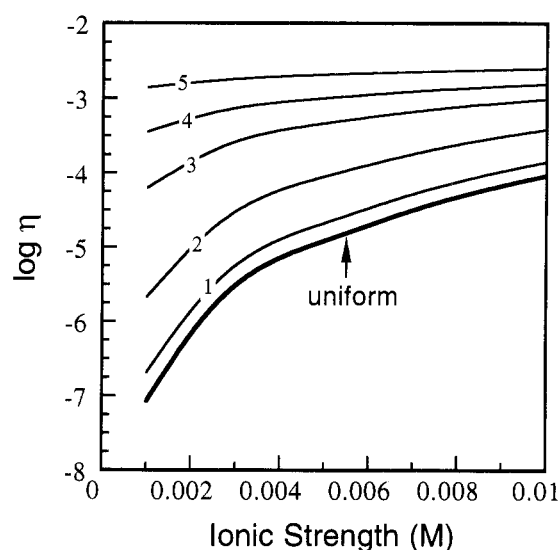
**Figure 1.** Colloid deposition rate (expressed as single collector removal efficiency) as a function of the surface potential of a uniformly charged collector for various ionic strengths (1:1 electrolyte). The labeled curves correspond to the following ionic strengths: (1)  $10^{-2.5}$ , (2)  $10^{-2.0}$ , (3)  $10^{-1.5}$ , (4)  $10^{-1.0}$ , and (5)  $10^{-0.5}$  M. The other parameters are surface potential of particles = 20 mV, particle radius =  $0.05 \mu\text{m}$ , collector radius = 0.1 mm, porosity = 0.4, Hamaker constant =  $1 \times 10^{-20}$  J, approach velocity = 0.1 cm/s, and temperature =  $25^\circ\text{C}$ .



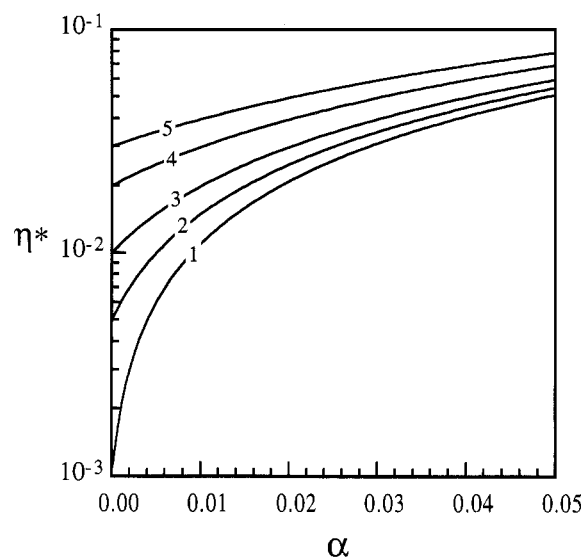
**Figure 2.** Overall colloid deposition rate as a function of the standard deviation of the collector surface potential for different ionic strengths (1:1 electrolyte). The labeled curves correspond to the following ionic strengths: (1)  $1 \times 10^{-3}$ , (2)  $2.5 \times 10^{-3}$ , (3)  $5 \times 10^{-3}$ , (4)  $7.5 \times 10^{-3}$ , and (5)  $1 \times 10^{-2}$  M. The other parameters are surface potential of particles = 20 mV, mean surface potential of collectors = 18 mV, particle radius =  $0.05 \mu\text{m}$ , collector radius = 0.1 mm, porosity = 0.4, Hamaker constant =  $1 \times 10^{-20}$  J, approach velocity = 0.1 cm/s, and temperature =  $25^\circ\text{C}$ .

charge. This figure illustrates the effect of surface heterogeneity on particle deposition, with homogeneous surfaces exhibiting the lowest particle deposition rates. As surface heterogeneity increases (i.e., an increase in standard deviation), the overall particle deposition rate increases. Furthermore, it is shown that deposition rates onto surfaces with a higher degree of charge heterogeneity display a much more moderate dependence on ionic strength.

The patchwise model of surface heterogeneity produces similar variations in particle deposition rate with changing



**Figure 3.** Overall colloid deposition rate as a function of ionic strength for various standard deviations in surface potential. The labeled curves correspond to the following standard deviations: (1) 1.0, (2) 3.0, (3) 5.0, (4) 7.0, and (5) 12.5 mV. The other parameters are similar to those used in Figure 2.



**Figure 4.** Normalized single collector removal efficiency ( $\eta^*$ ) as a function of the collision efficiency ( $\alpha$ ) for various patch sizes (expressed as  $\lambda$ ). The labeled curves correspond to the following fractions of favorable area ( $\lambda$ ): (1) 0.001, (2) 0.005, (3) 0.01, (4) 0.02, and (5) 0.03.

surface heterogeneity. For modeling purposes, we have assumed that patches favorable for deposition are superimposed on what would otherwise be a homogeneous collector surface. In this instance, surface charge heterogeneity may be represented by  $\lambda$ , the fraction of favorable patch area to the total area of the collector surface. Equation 5 is employed to calculate the single collector removal efficiencies, with  $\eta$ ,  $\eta_P$ , and  $\eta_R$  substituting for  $J$ ,  $J_P$ , and  $J_R$ , respectively. The results are presented in Figure 4 in the form of  $\eta^*$  as a function of the collision efficiency with the unfavorable surface fraction  $\alpha$ . The normalized single collector efficiency,  $\eta^*$ , is defined as the ratio of the actual single collector efficiency,  $\eta$ , to the patch removal efficiency,  $\eta_P$  (i.e.,  $\eta^* = \eta/\eta_P = \lambda + (1 - \lambda)\alpha$ ). The collision efficiency here is defined as  $\eta_R/\eta_P$ , with  $\eta_P$  and  $\eta_R$  being the dimensionless deposition rates onto the favorable patches and the rest of the collector, respectively. In these simulations, the collision efficiency shown by the

horizontal axis is equivalent to the use of ionic strength, with higher collision efficiencies representing higher ionic strengths. As was the case with the random distribution model, the overall deposition rate shows more variation with ionic strength at lower degrees of surface heterogeneity (i.e., at lower  $\lambda$ ).

**Significance.** The modeling results for random surface charge and patchwise heterogeneity help to illustrate the important role that surface charge heterogeneity plays in determining particle deposition. These results show that particle deposition onto an unfavorable surface is greatly enhanced with even a minor amount of surface heterogeneity. It has also been shown that the deposition rate onto surfaces containing a higher degree of charge heterogeneity is less sensitive to a change in solution ionic strength. These two features of particle deposition onto heterogeneously charged surfaces are very helpful in explaining the experimental observations discussed below.

### Results and Discussion

Two sets of previously published experimental data (14, 16) involving particle deposition kinetics have been reexamined using the patchwise and random distribution models developed for describing surface heterogeneities. These data sets were obtained from laboratory column experiments, which were performed under well-controlled physical and chemical conditions. The surface heterogeneity parameters  $\lambda$  and  $\sigma$  are enumerated and discussed for each data set. Experimental data of particle deposition are compared with theoretical predictions generated from DLVO theory using both the homogeneous and heterogeneous surface models. These comparisons help to illustrate the significant role that surface charge heterogeneities play in particle deposition.

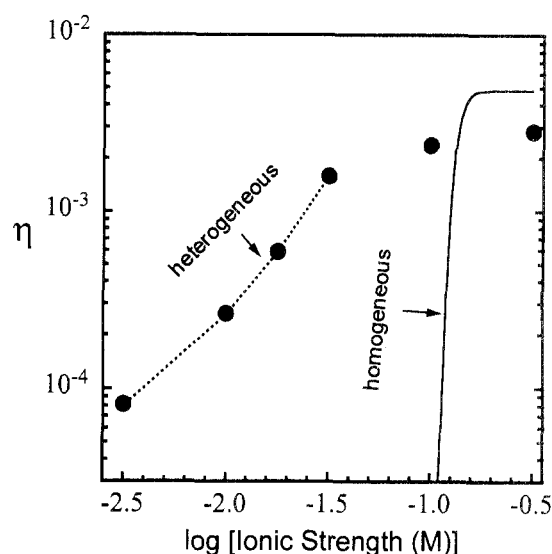
**Identification of Surface Heterogeneity from Experimental Data.** Although surface charge heterogeneity has been shown to be key parameter in controlling the overall particle deposition rate, no direct methods are available to measure the heterogeneity of surfaces. As a means of identifying surface heterogeneity, the following inverse problems for the Gaussian and patchwise distribution models, respectively, have to be solved:

$$\min_{\sigma} |\eta_{\text{exp}} - \int_S \eta(\psi) p(\psi_0, \sigma) d\psi| \quad (7)$$

$$\min_{\lambda} |\eta_{\text{exp}} - (\lambda \eta_P + (1 - \lambda) \eta_R)| \quad (8)$$

Here  $\eta_{\text{exp}}$  is the experimental single collector removal efficiency,  $\eta(\psi)$  is the theoretical single collector efficiency for surface potential  $\psi$ ,  $\sigma$  is the standard deviation in the Gaussian (random) distribution model, and  $\eta_P$  and  $\eta_R$  are the calculated single collector efficiencies of patches and the rest of the collector, respectively. The deposition rate onto the patches was assumed to be favorable, that is, transport limited deposition. The theoretical single collector efficiencies  $\eta(\psi)$ ,  $\eta_P$ , and  $\eta_R$  were calculated from a numerical solution of the convective diffusion equation as described earlier in this paper. Equation 7 is used to identify the heterogeneity parameter  $\sigma$  for the random distribution model, and eq 8 yields the parameter  $\lambda$  for the patchwise model. The inverse problems are readily solved using the golden section search method (48).

**Effect of Ionic Strength on Particle Deposition Rate.** The results of an investigation conducted by



**Figure 5.** Comparison of theoretical calculations with experimental data of overall colloid deposition rate as a function of ionic strength. The symbols (●) are for experimental data points. The solid line represents theoretical values based on homogeneous surface charge while the dashed line connects the calculated points based on the optimized heterogeneity parameters. The heterogeneity parameters used are given in Table 1. Experimental data points were taken from ref 14.

Elimelech and O'Melia (14) involving particle deposition under varying ionic strength were used to obtain heterogeneity parameters for the patchwise and random distribution models. In their study, uniformly-sized latex particles having sulfate functional groups and a mean diameter of 0.121  $\mu\text{m}$  were used as model colloids, and soda-lime glass beads packed in vertical columns served as collectors. The solution pH during the column experiments was about 6, the approach velocity was 0.14 cm/s, and the bed porosity was 40%. More details about these experiments, including the cleaning procedure for the glass beads, can be found elsewhere (49).

The glass beads were composed primarily of  $\text{SiO}_2$ , but trace amounts of  $\text{Fe}_2\text{O}_3$  (0.3%) and  $\text{Al}_2\text{O}_3$  (0.2%) were also reported by the manufacturer (49). The composition of the glass beads is worth noting due to the presence of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , which carry a surface charge opposite of the other components present at the solution pH maintained during experimentation. Consequently, surface charge heterogeneity is expected for the glass bead collectors which is manifested as higher experimental deposition rates than what is predicted from DLVO theory based on homogeneous surfaces.

A comparison of experimental particle deposition results with theoretical predictions based on homogeneous surface charge is presented in Figure 5. Also presented in this figure are the calculated values based on the parameters obtained for the surface charge heterogeneity models (dashed line). In all theoretical calculations, the reported  $\zeta$  potentials of particles and collectors were used as mean surface potentials in calculating EDL interactions. Furthermore, a Hamaker constant of  $1 \times 10^{-20}$  J was used in the calculation of the van der Waals attraction energy. It is shown in Figure 5 that calculated deposition rates based on surface charge heterogeneity clearly give a match to the experimental data which are superior to theoretical predictions based on ideal homogeneous surfaces. The presence of surface heterogeneities seems to provide a

**Table 1. Identified Heterogeneity Parameters of Glass Bead Collectors Used in Ref 14**

ionic strength (M)	$\zeta_p$ (mV) <sup>a</sup>	$\zeta_c$ (mV) <sup>b</sup>	$\sigma$ (mV)	favorable area (%) <sup>c</sup>	$\lambda$ (%)
10 <sup>-2.5</sup>	-76.3	-56.8	28.2	2.2	1.1
10 <sup>-2.0</sup>	-60.8	-47.0	26.5	3.8	3.2
10 <sup>-1.75</sup>	-48.0	-43.0	29.6	7.4	7.3
10 <sup>-1.5</sup>	-36.9	-38.6	50.0	20.3	19.5
10 <sup>-1.25</sup>	-30.0	-34.0	ND <sup>d</sup>	ND	ND
10 <sup>-1.0</sup>	-26.9	-28.7	ND	ND	ND
10 <sup>-0.5</sup>	-22.5	-12.9	ND	ND	ND

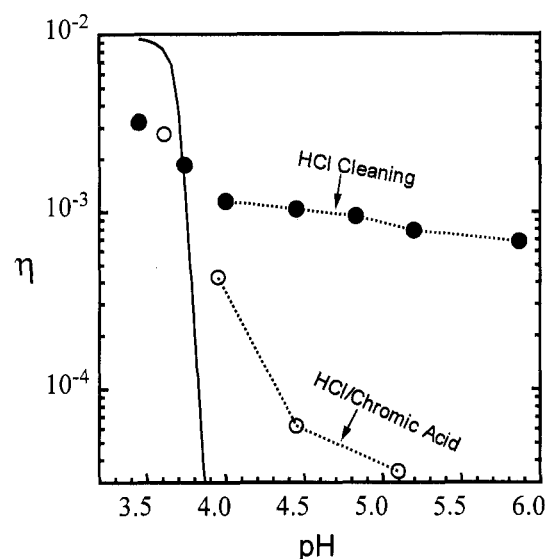
<sup>a</sup>  $\zeta$  potential of particles (from refs 14 and 49). <sup>b</sup>  $\zeta$  potential of collectors (from refs 14 and 49). <sup>c</sup> Calculated from the normal distribution,  $N(\zeta_c, \sigma)$ , as the percentage of collector surface that is positively charged. <sup>d</sup> ND, not determined for colloid deposition under favorable conditions (high ionic strengths).

plausible explanation for the vast discrepancy between experimental particle deposition data and theoretical predictions based on conventional DLVO theory.

The parameters for surface charge heterogeneity were obtained *a posteriori* from the experimental data of unfavorable deposition (i.e., ionic strengths smaller than 10<sup>-1.5</sup> M) by solving the inverse problem. Heterogeneity parameters were determined for both the random distribution and the patchwise models of surface heterogeneity. Table 1 provides a comparison of the two parameters  $\sigma$  and  $\lambda$ , which were determined for varying ionic strengths. Also included in this table are the  $\zeta$  potentials of particles ( $\zeta_p$ ) and collectors ( $\zeta_c$ ), which were used as mean surface potentials in the theoretical calculations.

For the random distribution model, the surface heterogeneity parameter  $\sigma$  maintains a fairly constant value below ionic strengths of 10<sup>-1.75</sup> M (i.e., for deposition under unfavorable conditions). This is in direct contrast to  $\lambda$ , the surface heterogeneity parameter for the patchwise model. Unlike  $\sigma$ , the parameter  $\lambda$  shows a direct correlation with ionic strength variations. This seemingly inconsistent behavior of the two heterogeneity parameters is a result of the inherent differences in what each parameter represents. The parameter  $\lambda$  is a measure of the relative amount of collector surface having favorable characteristics for particle deposition, which in this instance is the percentage of surface area having a negligible charge or a charge opposite in sign to that of the particles. In contrast, the parameter  $\sigma$  is a measure of the standard deviation of surface potential values about the mean surface potential of the collector. The two parameters may be compared for a given ionic strength by using the value of  $\sigma$  along with the mean surface potential of the collector to determine the percentage of collector surface having a positive charge. This generates a value for the percentage of favorable sites which may then be directly compared to  $\lambda$  from the patchwise model. These calculated values are tabulated alongside the values of  $\lambda$  in Table 1. For the most part, there is good agreement between the percentage of favorable deposition sites calculated using the random distribution model and the value of  $\lambda$  from the patchwise model, which strengthens the validity of the methods underlying both models.

It is of interest to compare the minimum value of  $\lambda$  with the percentage of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> present on the glass bead collector surface. On a molar basis, 0.3% of the collector surfaces contain Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> whereas the



**Figure 6.** Comparison of theoretical calculations with experimental data of overall colloid deposition rate as a function of solution pH. The solid line represents theoretical values based on homogeneous surface charge while the dashed lines connect the calculated points based on the optimized heterogeneity parameters. The heterogeneity parameters used are given in Tables 2 and 3 for the HCl and HCl/chromic acid cleaning solutions, respectively. Experimental data points (shown by the filled and open circles) were calculated from ref 16.

minimum percentage of favorable sites generated from experimental data is 1.1%. This may suggest that charge heterogeneities other than those arising from bulk chemical impurities are present on the collector surfaces.

**Effect of pH on Particle Deposition Rate.** The effect of solution pH and surface cleaning techniques on particle deposition was examined experimentally by Litton and Olson (16, 50). Their results have been used to identify parameters for the two surface heterogeneity models. Experimentation was carried out in a fashion similar to that described in the previous section, with soda-lime glass beads and carboxyl latex particles serving as collectors and model colloids, respectively. The diameters of the latex particles and glass bead collectors were 0.245  $\mu$ m and 0.275 mm, respectively. In these experiments, the ionic strength was fixed at 10<sup>-3</sup> M, while the pH was varied systematically from 3.5 to 5.9. The approach velocity in the column experiments was maintained at 0.03 cm/s, and the bed porosity was kept at 39%.

The composition of the glass beads used by Litton and Olson is similar to that of the previous study of Elimelech and O'Melia (14). As stated earlier, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are expected to provide favorable deposition sites on what is otherwise an unfavorable surface for deposition, especially in the higher pH ranges explored during experimentation. This is because Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> have positive surface charge at the pH range used, whereas the other components produce negatively charged surfaces above pH 3.

Two separate cleaning solutions were examined, and their effects on deposition rate were compared. It was noted that glass bead surfaces cleaned with an HCl/chromic acid mixture behaved quite differently in colloid deposition experiments than similar glass beads cleaned only with HCl. Experimental results are presented in Figure 6, along with a theoretical deposition curve based on homogeneous collector surfaces. Again, it is noted that theory and experimentation differ markedly; however, the collectors cleaned with chromic acid more closely match the theo-



**Table 2. Identified Heterogeneity Parameters of Glass Bead Collectors Used in Ref 16 (HCl Cleaning)**

pH	$\zeta_p$ (mV) <sup>a</sup>	$\zeta_c$ (mV) <sup>b</sup>	$\sigma$ (mV)	favorable area (%) <sup>c</sup>	$\lambda$ (%)
3.45	0	-42	ND <sup>d</sup>	ND	ND
3.74	-5	-47	ND	ND	ND
4.00	-18	-52	46.1	12.9	12.2
4.45	-36	-57	48.4	11.9	11.0
4.83	-45	-62	50.7	11.1	10.1
5.20	-55	-66	50.3	9.5	8.3
5.87	-66	-70	50.9	8.4	7.2

<sup>a</sup>  $\zeta$  potential of particles (from ref 16). <sup>b</sup>  $\zeta$  potential of collectors (from ref 16). <sup>c</sup> Calculated from the normal distribution,  $N(\zeta_c, \sigma)$ , as the percentage of collector surface that is positively charged. <sup>d</sup> ND, not determined for colloid deposition under favorable conditions (low pH).

**Table 3. Identified Heterogeneity Parameters of Glass Bead Collectors Used in Ref 16 (HCl/Chromic Acid Cleaning)**

pH	$\zeta_p$ (mV) <sup>a</sup>	$\zeta_c$ (mV) <sup>b</sup>	$\sigma$ (mV)	favorable area (%) <sup>c</sup>	$\lambda$ (%)
3.61	0	-41	ND <sup>d</sup>	ND	ND
3.95	-16	-50	30.8	5.3	4.5
4.45	-36	-59	29.2	2.2	0.7
5.10	-52	-68	33.2	2.0	0.4

<sup>a</sup>  $\zeta$  potential of particles (from ref 16). <sup>b</sup>  $\zeta$  potential of collectors (from ref 16). <sup>c</sup> Calculated from the normal distribution,  $N(\zeta_c, \sigma)$ , as the percentage of collector surface that is positively charged. <sup>d</sup> ND, not determined for colloid deposition under favorable conditions (low pH).

retical predictions than the collectors cleaned with HCl. Litton and Olson attribute the reduced deposition rate on the chromic acid-cleaned beads to the strong oxidizing ability of chromic acid. This makes chromic acid a better reagent for removing organic contaminants sorbed to collector surfaces. The organic contaminants may provide additional surface area having favorable deposition characteristics; their removal from surfaces by chromic acid is equivalent to reducing the degree of surface heterogeneity present on the collector surfaces.

Tables 2 and 3 document the variation in surface potentials and heterogeneity parameters with changing pH for the two cleaning methods. The heterogeneity parameters were determined only for chemical conditions which are unfavorable for deposition (i.e., above pH 3.9). Variations in  $\sigma$  and  $\lambda$  are similar to those noted in the previous section involving changing ionic strength. The parameter  $\sigma$  is once again fairly steady as pH rises, while  $\lambda$  shows a decline as pH is increased. The percent of favorable surface area calculated using  $\sigma$  compares well to  $\lambda$  for both cleaning methods above pH 3.9.

Due to the ability of chromic acid to remove organic surface impurities from the collectors, one would expect fairly good agreement between the minimum  $\lambda$  value and the molar percent of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  present on the glass surfaces. The values do compare well with one another, with  $\lambda$  being 0.4% and the molar percent of  $\text{Al}_2\text{O}_3$  plus  $\text{Fe}_2\text{O}_3$  being 0.3%. This striking agreement not only strengthens the assertion that sorbed impurities introduce additional charge heterogeneity to collector surfaces but also implies that bulk chemical impurities introduce surface heterogeneities which are structurally intact and not subject to removal.

## Conclusion

The solids which comprise natural and synthetic porous media contain surface charge heterogeneities. The effect of surface charge heterogeneity on the kinetics of colloid deposition in porous media can be quantitatively investigated with the concept of nominal surface potential and a distribution model for this potential. Using either the patchwise or random distribution models, we have demonstrated that surface charge heterogeneity is one of the key factors controlling the kinetics of colloid deposition under unfavorable chemical conditions.

The results of this study demonstrate that colloid deposition rate onto surfaces having charge heterogeneity is moderately dependent on solution ionic strength. This behavior has been observed experimentally in the past 2 decades but could not be explained theoretically. In addition to solution ionic strength, surface charge and charge heterogeneity of solids in natural environments are affected by other chemical factors, including solution pH and the presence of dissolved organic matter and anionic surfactants. When adsorbed on mineral surfaces, dissolved organic matter and anionic surfactants may mask underlying surface charge heterogeneity, thereby reducing particle deposition rates and enhancing colloidal mobility. Knowledge of the relationship between surface charge heterogeneity and these chemical factors is necessary for a thorough understanding of colloidal transport in subsurface environments.

Colloid deposition under unfavorable chemical conditions is a rather transient (dynamic) phenomenon. Particle deposition kinetics apply only to the initially 'clean' surfaces, before deposited colloidal particles start to block favorable deposition sites. The transient behavior of particle deposition, though beyond the scope of this paper, should be considered in future investigations of colloidal transport.

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