# Relative Insignificance of Mineral Grain Zeta Potential to Colloid Transport in Geochemically Heterogeneous Porous Media

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The role of  $\zeta$ -(zeta)potential of mineral grains in the initial deposition kinetics of colloidal particles in geochemically heterogeneous porous media is investigated. Colloid deposition experiments with colloidal silica particles flowing through columns packed with chemically heterogeneous sand were carried out. Patchwise chemical heterogeneity was introduced to the granular porous medium by modifying the surface chemistry of a fraction of the quartz sand grains via reaction with aminosilane. Experimental initial colloid deposition rates and resulting collision efficiencies were compared to theoretical predictions based on the measured average  $\zeta$ -potential of the chemically heterogeneous sand. It is shown that colloid deposition kinetics are controlled by the degree of patchwise chemical heterogeneity and that use of the measured  $\zeta$ -potential of the granular porous medium in theoretical predictions leads to erroneous results.

#### Introduction

The transport of colloidal particles in subsurface environments is limited by particle–grain collisions resulting in attachment (deposition). The fate of these collisions is influenced by the density and sign of the electrostatic charge on the particle and grain surfaces. Grain surfaces are inherently heterogeneous because of the presence of a variety of constituent minerals, coatings, crystal faces, and physical and chemical imperfections. Recent laboratory, field, and modeling studies have demonstrated that these geochemical heterogeneities are a major factor controlling the transport of colloidal particles in subsurface porous media (1-4).

When discussing the effect of charge heterogeneity on colloid transport, a distinction between macroscopic and microscopic heterogeneity must be made (*3*). Colloid transport behavior is influenced predominantly by macroscopic chemical (charge) heterogeneities. A surface with microscopic charge heterogeneity at the molecular level will appear uniform to a colloidal particle and may thus be modeled as a homogeneous surface. In contrast, surfaces with macroscopic charge heterogeneity may be modeled as a patchwork mosaic, with individual patches treated as isolated homogeneous entities having uniform electrostatic potential (3). Iron, aluminum, and manganese oxide coatings on mineral grains, which are quite common in groundwater aquifers (2, 4-8), are representative of patchwise chemical heterogeneity.

An important parameter for the characterization of the electrostatic charge and the resulting electrostatic repulsion between colloidal particles and solid surfaces is the  $\zeta$ -(electrokinetic) potential. Several techniques are available for determining the electrokinetic properties of colloids and surfaces. Microelectrophoresis is most commonly used for suspended colloidal particles, and streaming potential or electroosmosis are often used for coarse solid surfaces, such as mineral grains (*10*).

The  $\zeta$ -potentials of colloids and mineral grain surfaces are commonly used in quantitative and semiquantitative analyses of colloid deposition in granular porous media (2, 6, 7, 9, 11). These potentials are essential parameters for prediction of colloid deposition kinetics with the framework of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (12, 13). While the  $\zeta$ -potential of collector surfaces may be useful for analyses of colloid deposition kinetics onto homogeneously charged surfaces, rather erroneous results can be obtained when used for quantifying the deposition kinetics onto solid surfaces with patchwise chemical heterogeneity. For heterogeneously charged solid surfaces, the  $\zeta$ -potential represents the average electrokinetic charge of the entire surface and, thus, fails to account for the local heterogeneity of mineral grains that may have a dramatic effect on colloid deposition kinetics. Other parameters for determining the deposition kinetics of colloids onto chemically heterogeneous solid surfaces are needed.

**Objective and Scope.** The objective of this paper is to demonstrate the insignificance of the measured  $\zeta$ -potential of mineral grains in controlling the deposition kinetics of colloidal particles in patchwise, geochemically heterogeneous porous media. Colloid deposition experiments were designed with dilute colloidal silica suspensions flowing through columns packed with chemically heterogeneous granular porous medium. Patchwise chemical heterogeneity was introduced to the granular porous medium by modifying the surface chemistry of a fraction of the quartz grains via anhydrous silvlation with aminosilane. The silvlation reaction was successful in converting the surface charge of the quartz grains from negative to positive. Modifying the grain surface charge by silvlation for introducing chemical heterogeneity in colloid transport studies is advantageous over other methods, such as iron oxyhydroxide coating. The latter results in several complicating effects, including nonuniform and incomplete surface coverage, significant alteration of the surface morphology, and abrasion of iron oxyhydroxide colloids onto clean sand grains during the mixing of the modified and clean sand and the column packing process. Experimental colloid deposition rates and resulting collision efficiencies were compared to theoretical predictions based on the measured average  $\zeta$ -potential of the chemically heterogeneous sand. It is shown that colloid deposition kinetics are controlled by the degree of patchwise chemical heterogeneity and that use of the measured  $\zeta$ -potential of the granular porous medium in theoretical predictions, as commonly used, leads to erroneous results.

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## Materials and Methods

**Preparation of Chemically Heterogeneous Porous Medium.** Uniform quartz sand was used as the granular porous medium (Aldrich Chemical, Milwaukee, WI). The sand grains were thoroughly cleaned prior to use. Cleaning consisted of ultrasonication for 30 min in deionized (DI) water, followed by immersion in sodium dithionite solution (0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) for 2 h to remove surface-bound metal impurities such as iron and manganese oxides. The sand was then immersed in a cleaning solution (mixture of chromic and sulfuric acids) (Fisher Scientific, Pittsburgh, PA) overnight, followed by ultrasonication for 30 min. Organic impurities were removed by soaking the sand in hydrogen peroxide  $(5\% H_2O_2)$  for 3 h, followed by a wash with DI water. The sand was immersed again in the sulfuric/chromic acid cleaning solution overnight, followed by ultrasonication for 30 min. Last, the sand was soaked overnight in hydrochloric acid (12 N HCl). The sand grains were treated with a final rinse in DI water, followed by additional ultrasonication for 30 min. Between each of the above steps, the sand was washed repeatedly with DI water. The cleaning proceeded to the next step only when the conductivity of the supernatant in the DI washing dropped below 2  $\mu$ S/cm.

Visual examination of the quartz sand was performed at various magnifications using both petrographic and scanning electron microscopy. The petrographic examinations revealed the sand grains to be prolate spheroidal in shape. The quartz grains were well sorted, with a nominal grain diameter of 0.32 mm. The nominal grain diameter was determined by averaging the major and minor axes of 35 separate quartz grains. High magnification SEM images of individual quartz grain surfaces revealed a substantial amount of surface roughness. The surfaces appear highly irregular, having sharp, angular terminations, jagged protrusions, and deep crevices.

Some of the cleaned quartz grains were subjected to anhydrous silylation with aminosilane. The surface charge of the aminosilane-modified grains was reversed from negative to positive at the solution pH range relevant to the colloid transport experiments. To produce a chemically heterogeneous porous medium, aminosilane-modified and clean quartz grains were mixed in the columns in varying proportions.

Anhydrous silylation was employed to avoid polysilane formation that occurs in aqueous silvlation (14). The chosen silvlation agent was 3-aminoethyl-3-aminopropyl dimethoxy methyl (AADM) silane (United Chemical Technologies Inc., Bristol, PA) due to its enhanced hydrolytic stability as compared to triethoxy derivatives (15). Cleaned grains were dried at 110 °C under vacuum for 2 h to remove adsorbed water from grain surfaces. The AADM (20 mL) was added to 20 mL of 12 N HCl solution to prevent condensation. The acidified AADM solution was then added to 980 mL of boiling toluene in a reflux condenser at 130 °C to remove water and methanol formed during the silvlation reaction. Clean quartz grains (500 g) were added to the reflux condenser for 6 h; the grains were then washed several times with toluene and allowed to cure overnight at 110 °C under vacuum. Before use, the aminosilane-modified grains were incubated in DI water for 24 h.

**Colloidal Particles.** Silica microspheres (PST-3, Nissan Chemicals, Terrytown, NY) were used as the colloidal phase. The silica colloids are reported by the manufacturer to be monodisperse, with a mean diameter of  $0.30 \,\mu$ m. The nominal size of the silica was verified using dynamic light scattering (Nicomp model 370, Particle Sizing Systems, Santa Barbara, CA). Gravimetric measurements were used to determine a particle density of 2.28 g/cm<sup>3</sup> for the colloidal silica. An indifferent, monovalent electrolyte (reagent-grade NaCl) was used to control the solution ionic strength.

**Characterization of Granular Porous Medium and** Colloids. Streaming potentials of the chemically heterogeneous granular porous medium (i.e., varying mixtures of the aminosilane-modified and clean sand grains) were determined by a streaming potential analyzer (BI-EKA, Brookhaven Instruments Corp., Holtsville, NY). The analyzer is equipped with Ag-AgCl electrodes and a cylindrical cell with an inner diameter of 2.0 cm to house the granular porous medium. Heterogeneous porous media having a porosity of 0.38 were wet-packed in the cylindrical cell to a length of 3 cm in a solution having the same chemical composition as the solution used during the corresponding column experiment. Before the start of each measurement, the cell was equilibrated by circulating the solution in alternate directions for a period of 10 min. Streaming potentials were converted to  $\zeta$ -potentials using the Helmholtz–Smoluchowski equation and the Fairbrother and Mastin approach (16, 17). Electrophoretic mobilities and the corresponding  $\zeta$ -potentials of the silica colloids as a function of pH and ionic strength were reported in our previous work (Figure 1 of ref 1).

**Column Colloid Transport and Deposition Kinetics Experiments.** Colloid transport experiments were carried out using chromatography columns packed with various ratios of aminosilane-modified and clean quartz grains. Adjustable-height glass columns with 1 cm i.d. were used (Omnifit USA, Toms River, NJ). The columns were adjusted to a height of 7.8 cm. Polyethylene meshes (125  $\mu$ m) were placed at both ends of the column. Columns were wet-packed with a solution having the same chemical composition as the solution used during the subsequent deposition experiment. Column packing porosity for each experiment was determined to be 0.39 based on a measured quartz grain density of 2.59 g/cm<sup>3</sup>.

A typical column experiment involved pumping an aqueous particle suspension (10 mg/L) through the packed column at a constant approach velocity of  $2 \times 10^{-4}$  m/s. To ensure accurate and smooth flow throughout the experiments, high-performance liquid chromatography (HPLC) pumps (Accuflow series II, Fisher Scientific, Pittsburgh, PA) were used. One HPLC pump was used to deliver the appropriate concentration of silica particles suspended in deionized water, and a second HPLC pump was used to deliver the appropriate dosage of NaCl solution at a flow rate identical to the first pump. The colloid suspension and the NaCl solution were mixed in-line just ahead of the column to avoid particle aggregation. Particle concentrations in the column effluent were monitored at 1-s intervals with a UV/ Vis spectrophotometer (Hewlett-Packard model 8452A) and a 1-cm flow-through cell. Room temperature was maintained during experimentation (about 21 °C). The solution pH of influent and effluent showed little or no variation during the experiments, remaining between 5.6 and 5.8. All column apparatus and accessories were carefully cleaned between experimental runs with a strong acid (HCl) and a final rinse with DI water.

Two sets of column experiments were carried out. The first set was designed to investigate the effect of chemical heterogeneity on colloid deposition kinetics. Various mixtures of aminosilane-modified and clean quartz grains were used to represent various degrees of geochemical heterogeneity. Solution ionic strength was maintained at  $10^{-3}$  M using NaCl as a background electrolyte. Chemical heterogeneity was varied from 0 to 100% by packing the column with the appropriate mixture of aminosilane-modified and clean quartz grains. The second set of experiments was designed to investigate the effect of solution ionic strength on colloid deposition kinetics at a fixed surface charge heterogeneity of 25% (i.e., the percentage of the aminosilane-modified quartz grains). Solution ionic strength was varied from  $10^{-4}$  to  $10^{-2}$  M NaCl.

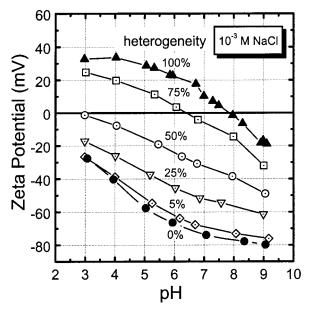


FIGURE 1.  $\zeta$ -Potential as a function of solution pH for clean sand grains (filled circles), aminosilane modified sand grains (filled triangles), and various mixtures of aminosilane-modified and clean sand grains (open symbols).  $\zeta$ -Potentials were calculated from measured streaming potentials. Experiments were conducted with  $10^{-3}$  M NaCl as a background electrolyte at a temperature of 21 °C.

#### **Results and Discussion**

**ζ-Potential of the Chemically Heterogeneous Sand.** ζ-Potential versus pH curves for the clean sand grains, silanemodified sand, and various ratios (mixtures) of silanemodified and clean sand are presented in Figure 1. The sand grains are negatively charged at the pH range investigated, with the  $\zeta$ -potential becoming more negative as the pH increases in accord with previously reported electrokinetic measurements for quartz sand grains (1, 18). The aminosilane-modified sand (100% ratio curve) is positively charged up to pH 8 and then becomes negatively charged. Protonated amino functional groups of the covalently bonded silane molecules provide the pH-dependent positive charge. Similar trends of  $\zeta$ -potential versus pH have been reported for aminosilane-modified silica surfaces (19). The positive charge of the chemically modified sand is indicative of the successful anhydrous silvlation of the sand grains. Our attempts of hydrous silvlation of the quartz grains were not as successful in converting the grain surface charge from negative to positive, most likely due to the formation of polysilanes during the aqueous silvlation reaction (20, 21). Steric hindrance of these large polysilane molecules may limit the surface coverage and lead to nonuniform silvlation and low yields (14)

At various ratios of aminosilane-modified and clean quartz grains, the measured  $\zeta$ -potential of the heterogeneous mixture becomes less negative as the fraction of the chemically modified quartz grains increases. However, even at a 50% ratio, the  $\zeta$ -potential is still negative over the entire pH range investigated (from 3 to 9). A close inspection of the curves reveals that, at a given pH, the  $\zeta$ -potential of the chemically heterogeneous porous medium (i.e., the mixture of clean and chemically modified quartz) is a linear combination of the  $\zeta$ -potentials of the clean and the aminosilanemodified grains:

$$\zeta = \lambda \zeta_{\text{silane}} + (1 - \lambda) \zeta_{\text{quartz}}$$
(1)

where  $\lambda$  is the ratio of the mass of aminosilane-modified quartz grains to the total mass of quartz grains, and  $\zeta_{quartz}$ 

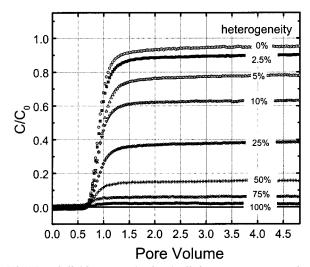


FIGURE 2. Colloid transport in chemically heterogeneous granular porous medium. Colloid breakthrough curves are expressed as normalized colloid concentration at the column effluent as a function of pore volume for various mixtures of aminosilane-modified and clean sand grains (ranging from clean sand, 0%, for the top curve to 100% for the bottom curve). Experimental conditions were as follows: silica colloid concentration = 10 mg/L, solution ionic strength =  $10^{-3}$  M NaCl, solution pH = 5.6-5.8, column length = 7.8 cm, grain diameter = 0.32 mm, bed porosity = 0.39, approach velocity 2  $\times 10^{-4}$  m/s, and temperature = 21 °C.

and  $\zeta_{silane}$  are the  $\zeta$ -potentials of the clean and silane-modified sand grains, respectively. A similar linear relationship has been recently reported for a mixture of clean sand and iron oxide-coated sand (*22*). It should be noted that, for small ratios of chemically modified to clean sand grains, the  $\zeta$ -potential of the heterogeneous mixture is only slightly less negative than that of a clean sand. Although small values of  $\lambda$  have only a minor effect on the  $\zeta$ -potential of the chemically heterogeneous granular porous medium, we will show later that the presence of such a small chemical heterogeneity has a marked effect on the colloid deposition rate.

**Colloid Deposition Rate Dependence on Geochemical** Heterogeneity. The colloid breakthrough curves of column experiments with various ratios of chemically modified and clean sand are depicted in Figure 2. The results demonstrate the paramount role of chemical heterogeneity in controlling colloid transport and deposition in heterogeneous porous media. The initial ("clean bed") removal efficiency increases as the degree of chemical heterogeneity (or the fraction of aminosilane-modified sand) increases. At the initial stages of deposition, the colloid removal efficiency for the given conditions increases from 8% (i.e., 92% breakthrough) for the clean quartz grains to 98% (i.e., 2% breakthrough) for the aminosilane-modified quartz grains. At the pH maintained during the column experiments (5.6-5.8), the aminosilanemodified quartz grains are positively charged and thus provide favorable surfaces for the deposition of the negatively charged silica colloids.

The colloid breakthrough curves can be used to determine the single collector efficiency and the colloid deposition rate coefficient for the various degrees of chemical heterogeneity. The experimental single collector efficiency can be obtained from (9)

$$\eta = -\frac{2d_g}{3L(1-\epsilon)}\ln\left(C/C_0\right) \tag{2}$$

where  $d_g$  is the grain diameter, L is the column length,  $\epsilon$  is the porosity, and  $C/C_0$  is the value of the normalized column effluent concentration at the initial stages of deposition (taken

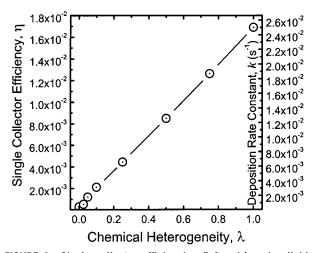


FIGURE 3. Single collector efficiencies (left axis) and colloid deposition rate coefficients (right axis) for various degrees of chemical heterogeneity ( $\lambda$ ), calculated from the colloid breakthrough data shown in Figure 2, using eqs 2 and 3, respectively. (Note that  $\lambda = 1.0$  corresponds to 100% aminosilane-modified sand whereas  $\lambda = 0$  corresponds to clean sand grains.)

at 2 pore vols). The experimental colloid deposition rate constant *k*, a necessary parameter for modeling colloid transport (*6*, *23*, *24*), is related to the single collector efficiency  $\eta$  and the approach velocity *U* by the following relationship (*23*):

$$k = -\frac{3}{2} \frac{1 - \epsilon}{\epsilon d_g} U\eta = -\frac{U}{\epsilon L} \ln \left( C/C_0 \right)$$
(3)

The single collector efficiencies and colloid deposition rate coefficients for the various degrees of chemical heterogeneity  $\lambda$  are presented in Figure 3. The results show that the colloid deposition rate increases linearly with the degree of chemical heterogeneity. The single collector efficiency increases from 3.09  $\times$  10<sup>-4</sup> to 1.69  $\times$  10<sup>-2</sup> when  $\lambda$  increases from 0 to 1 (or 0 to 100%), respectively. Of particular interest is the increase in the colloid deposition rate at the low range of  $\lambda$ , which is the range of patchwise chemical heterogeneity of sandy aquifers with iron oxide coatings (1, 2, 5, 7, 8). For instance, the colloid deposition rate increases by more than 1 order of magnitude when the degree chemical heterogeneity  $\lambda$  increases from near-zero (clean sand) to 0.1 (i.e., 10%). Note that such an increase in  $\lambda$  has only a slight effect on the  $\zeta$ -potential of the chemically heterogeneous granular porous medium (Figure 1).

The data for the single collector efficiency in Figure 2 follow closely the following relationship for patchwise heterogeneous porous media surfaces (3):

$$\eta = \lambda \eta_{\rm f} + (1 - \lambda) \eta_{\rm u} \tag{4}$$

where  $\eta_f$  and  $\eta_u$  are the single collector efficiencies for favorable (aminosilane-modified sand) and unfavorable (clean sand) surfaces. The values of  $\eta_f$  and  $\eta_u$  for our experiments are  $1.69 \times 10^{-2}$  and  $3.09 \times 10^{-4}$ , respectively. Because  $\eta_f \gg \eta_u$  for patchwise heterogeneous surfaces, eq 4 can further be simplified to

$$\eta \approx \lambda \eta_{\rm f} \tag{5}$$

This expression should be accurate for  $\lambda$  values greater than a few percent. The very good linear relationship shown in Figure 3 strongly supports this simplified expression.

To further investigate the role of colloidal interactions, the colloid deposition experiments described above are

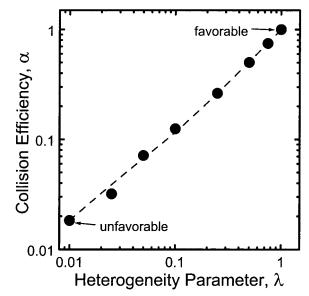


FIGURE 4. Overall collision (attachment) efficiency for the colloid transport experiments at various degrees of chemical heterogeneity ( $\lambda$ ) presented in Figure 2. The collision efficiency is defined as the ratio of the single collector efficiency,  $\eta$  (from Figure 3), to the single collector efficiency of aminosilane-modified sand,  $\eta_f$ . The dashed line represents predictions based on eq 6.

analyzed in terms of the commonly used collision (attachment) efficiency (Figure 4). The overall collision efficiency was obtained by normalizing the single collector efficiency  $\eta$  by the measured favorable single collector efficiency  $\eta_{\rm f}$ , i.e.,  $\alpha = \eta/\eta_{\rm f}$ . The overall collision efficiency displays a linear dependence on the degree of chemical heterogeneity and follows the following relationship:

$$\alpha = \lambda + (1 - \lambda)\alpha_{\rm u} \approx \lambda \tag{6}$$

where  $\alpha_u$  (=  $\eta_u/\eta_t$ ) is the collision efficiency for the unfavorable surface fraction (i.e., the clean sand grains). The results suggest that the collision efficiency is determined by the fraction of favorable surfaces,  $\lambda$ , for patchwise, chemically heterogeneous surfaces, and that other factors such as ionic strength and the average  $\zeta$ -potential of mineral grains do not play an important role in colloid deposition kinetics.

For the chemical conditions employed in the column experiments (pH = 5.7 and  $10^{-3}$  M ionic strength), the  $\zeta$ -potential of the heterogeneous sand grains changes from -64 to -21 mV (Figure 1) when the degree of chemical heterogeneity increases from 0 to 50%. Not accounting for the patchwise chemical heterogeneity of the sand grains and use of the measured (average)  $\zeta$ -potentials of the heterogeneous sand as well as the solution ionic strength and  $\zeta$ -potentials of colloidal particles to calculate the collision efficiency with the framework of the DLVO theory result in rather erroneous results. For the above colloid deposition conditions, the collision efficiency was calculated using the interaction force boundary layer approximation (25, 26). In these calculations, we used the measured  $\zeta$ -potentials of the sand grains shown in Figure 1; the  $\zeta$ -potentials of the silica colloids were taken from ref 1, the Hamaker constant was set to a typical value of  $10^{-20}$  J (6, 7, 9), and the solution ionic strength was 10<sup>-3</sup> M. The results showed that the predicted collision efficiencies for the colloid deposition experiments at  $\lambda$  of 0, 0.025, 0.05, 0.1, 0.25, and 0.50 are practically 0; that is, the predicted collision efficiencies varied from  $\sim 10^{-265}$  to  $10^{-54}$  when  $\lambda$  increased from 0 to 0.5 (0 to 50%), respectively. For the deposition experiments at  $\lambda$  of 0.75 and 1.0, the predicted collision efficiencies were 1, because the average  $\zeta$ -potential of the heterogeneous sand is positive (+7 and

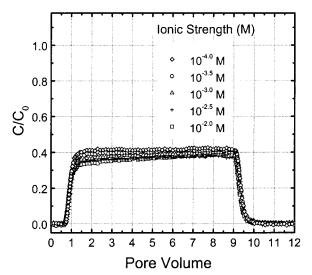


FIGURE 5. Colloid breakthrough curves at different background electrolyte (NaCl) concentrations using columns packed with 25% aminosilane-modified sand (i.e.,  $\lambda = 0.25$ ). Curves from top to bottom correspond to ionic strengths ranging from  $10^{-2}$  M (top) to  $10^{-4}$  M (bottom). Experimental conditions were as follows: silica colloid concentration = 10 mg/L, solution pH = 5.6–5.8, column length = 7.8 cm, grain diameter = 0.32 mm, bed porosity = 0.39, approach velocity 2  $\times 10^{-4}$  m/s, and temperature = 21 °C.

+24 mV, respectively) and the colloidal particles are negatively charged (-54 mV as reported in ref 1). These results clearly demonstrate the insignificance of the average  $\zeta$ -potential of patchwise heterogeneous porous media in controlling the colloid deposition kinetics. It is the degree of patchwise chemical heterogeneity that controls colloid deposition kinetics and appropriate means to determine this heterogeneity are the key for successful predictions of colloidal behavior in chemically heterogeneous porous media.

**Colloid Deposition Rate Dependence on Solution Ionic Strength.** To further demonstrate the insignificance of the average  $\zeta$ -potential of patchwise heterogeneous porous media in colloid deposition kinetics, column experiments at a fixed chemical heterogeneity ( $\lambda = 0.25$ ) and different ionic strengths (ranging from  $10^{-4}$  to  $10^{-2}$  M) were carried out. The corresponding colloid breakthrough curves are shown in Figure 5. As the ionic strength increases by 2 orders of magnitude, the clean bed removal and the colloid breakthrough profiles barely change. The slight increase in the clean bed removal with decreasing ionic strength is due to enhanced silica colloid deposition onto the positively charged aminosilane-modified sand grains due to the longer range of the attractive double layer interactions at lower ionic strengths (27).

Figure 6 depicts the variation of the collision efficiency with solution ionic strength as calculated from the corresponding colloid breakthrough curves. The results show that the collision efficiency is nearly constant over the entire ionic strength range. Under these conditions, colloid deposition occurs predominately on the aminosilane-modified sand grains. Thus, the degree of chemical heterogeneity controls the colloid attachment efficiency (i.e.,  $\alpha \approx \lambda$  as shown in eq 6).

Theoretical collision efficiencies were calculated for the colloid deposition runs shown in Figures 5 and 6 using the interaction force boundary layer approximation and the DLVO interaction potential as described in the previous subsection. Using the measured  $\zeta$ -potential of the chemically heterogeneous porous medium, the predicted collision efficiencies for the conditions maintained during the colloid

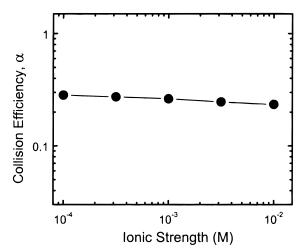


FIGURE 6. Experimental overall collision (attachment) efficiency ( $\alpha$ ) as a function of ionic strength for the colloid breakthrough data shown in Figure 5.

deposition experiments were practically zero, ranging from  $\sim 10^{-265}$  for  $10^{-4}$  M ionic strength to  $\sim 10^{-70}$  for  $10^{-2}$  M ionic strength. These erroneous predictions are again an outcome of the improper consideration of the role of patchwise chemical heterogeneity, which cannot be represented adequately using classical DLVO theory. These results demonstrate that for patchwise heterogeneous porous media, the colloid deposition kinetics are insensitive to solution ionic strength and are controlled by the patchwise chemical heterogeneity.

**Significance and Implications.** The key factor controlling the deposition kinetics of colloidal particles in patchwise heterogeneous subsurface porous media, such as iron oxidecoated sand aquifers, is the fraction of mineral grain surfaces coated with iron oxide. Other factors that usually control colloid deposition kinetics for homogeneous surfaces under unfavorable chemical conditions, namely, the  $\zeta$ -potential of mineral grains and solution ionic strength, play an insignificant role for patchwise heterogeneous subsurface porous media. Hence, advanced methods for quantifying the chemical heterogeneity of patchwise heterogeneous surfaces are most desirable.

The presence of dissolved organic matter complicates the analysis of colloid transport in chemically heterogeneous porous media. When adsorbed on mineral surfaces, natural organic matter and other ionogenic organic compounds may mask underlying geochemical heterogeneity, thereby altering the surface charge characteristics and colloid deposition kinetics. Although the effects of natural organic matter are not included in the present analysis, they should be considered in future investigations pertaining to colloidal transport in subsurface aquatic environments.

## Acknowledgments

The authors acknowledge the support of the National Science Foundation under Research Grants BES-9996240 (formerly BES 9705717) and EAR-9418472.

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Received for review September 8, 1999. Revised manuscript received February 16, 2000. Accepted March 3, 2000.

ES9910309