Prediction of Colloid Detachment in a Model Porous Media: Thermodynamics

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Detachment of polystyrene latex colloids was studied in a model porous media system comprised of a packed column of glass beads. The polystyrene colloids were attached and subsequently detached from the glass beads by varying solution pH and ionic strength. It was found that classical-DLVO theory could not predict detaching conditions. Extended-DLVO theory was used to determine the median detaching pH for deionized water, and solutions of 0.01 and 0.1 M NaCl. Although both the colloids and porous media were macroscopically homogeneous, detachment was observed at a variety of pH values. The pH distribution of detachment and the energy distribution of the interaction between the polystyrene latex colloids and the glass beads followed gamma distributions. This work has provided a technique to quantitatively predict the aqueous chemistry changes that induce colloid detachment in porous media.

Introduction

Porous media systems are used in many engineering operations such as filtration, heterogeneous catalysis, and activated carbon adsorption. In addition, groundwater traveling through an aquifer is a natural process of fluid flow through porous media. In these engineered and natural systems, colloidal particles may detach from substrate surfaces and become entrained in the fluid flow. The desirability of having these colloidal particles in the fluid is system dependent. For example, the backwash efficiency of a sand filter is dependent on particles being re-entrained in the flow. Conversely, colloid-facilitated transport in the environment may mobilize otherwise sparingly soluble contaminants. The study of the mechanisms and conditions promoting particle detachment from porous media is of significance in these, as well as many other applications. This work focuses on the prediction of chemistry-induced colloid detachment from packed or ‘‘fixed’’ granular beds.

Colloids in solution characteristically scatter light, and are operationally defined at having at least one dimension between 1 nm and 1 μm (Hiemenz, 1986; Stumm and Morgan, 1996). Because of their small size, colloids are primarily affected by surface forces and Brownian (thermal) motion and not significantly influenced by external forces such as gravity. Colloids can adhere to surfaces if the interfacial interactions and hydrodynamics are sufficiently favorable. The attachment and detachment of colloidal particles in packed beds of porous media has been extensively studied (Vaidyanathan and Tien, 1988; Tobiason, 1989; Rijnaarts et al., 1993; Elimelech, 1994; Liu et al., 1995; Rijnaarts et al., 1996; Grolimund et al., 1998).

For attached particles in saturated porous media to become detached from the substrata, a disturbance to the system must occur. This perturbation can be a change in either the chemistry of the aqueous solution (that is, pH, ionic strength), or the hydrodynamics of the system. Detachment of particles from porous media, in both natural and model systems, has been studied by many investigators and is discussed below. Generally, the data reported (Nightingale and Bianchi, 1977; Khilar and Fogler, 1984; Kia et al., 1987; Rosario et al., 1996; Roy and Dzombak, 1996) compare qualitative trends to those expected by Derjaguin-Landau-Verwey-Overbeek (*classical*-DLVO) theory for solution chemistry changes (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948).

While colloid attachment may be predicted through filtration models (such as trajectory modeling), detachment of colloids in porous media has yet to be predicted quantitatively.

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This work is part of a larger effort to quantitatively study the impact of both solution chemistry and system hydrodynamics on colloid detachment. Here, polystyrene latex colloids were attached in the primary energy minimum to substrata in a model porous media and subsequently detached with perturbations in solution chemistry. The hydrodynamic shear on the attached colloids was determined to be low and inconsequential in this experimental system (Bergendahl and Grasso, 1999). An *extended*-DLVO model was developed to quantitatively predict the requisite pH to detach 50% of the colloids from the media for ionic strengths ranging from essentially zero (deionized water) to 0.1 M NaCl.

Background

Field scale observations

Increases in effluent turbidity as a result of changes in solution chemistry have been noted by many researchers. Nightingale and Bianchi (1977) reported significant increases in turbidity in monitoring wells as a result of recharging an aquifer with lower ionic strength water. The increase in turbidity was reportedly due to the mobilization of particles from the media. Subsequent tests with bench-scale columns and *in situ* tests showed that the addition of gypsum ($CaSO_4 \cdot 2H_2O$) to the column eluent and on the ground surface resulted in turbidity reductions. This turbidity reduction may be qualitatively explained through *classical*-DLVO theory. Addition of gypsum raised the ionic strength of the groundwater, thereby compressing the electrostatic double layers surrounding the soil grains and the colloids in the groundwater. Resultant reductions in electrostatic interactions allowed attractive van der Waals forces to dominate the soil grain-to-particle interaction, and the colloids destabilized and attached to the surrounding soil grains.

Laboratory scale observations

The detachment of particles from laboratory-scale packed beds has been studied extensively. Fogler and co-workers (Khilar and Fogler, 1984; Kia et al., 1987) reported on experiments where the permeability of porous media was measured with changing solution chemistry. As a saline water flow through sandstone was changed to fresh water, at higher pH values, permeability decreased. The decrease in permeability was attributed to mobilized colloids becoming trapped in the sandstone pore "throats." Rosario et al. (1996) also noted permeability reductions with increased pH, using a consolidated alumina-kaolin media. Roy and Dzombak (1996) found an increase in colloid release from packed columns with decreasing ionic strengths of eluant.

Kallay et al. (1986) reported an increase in total particle removal from solid media as the ionic strength increased. This data is contrary to the pattern of release with solution chemistry change predicted by *classical*-DLVO theory. Most data reported in the literature can be qualitatively explained with DLVO theory: as pH increases (surface ionization increases concomitantly), particle release increases, and as ionic strength decreases (surface shielding decreases concomitantly), particle release increases.

The detachment of particles from surfaces in porous media may derive from the following mechanisms:

- A change in surface interactions that result in a net repulsive surface force. These surface forces may be comprised of van der Waals, electrostatic, and other non-DLVO forces (see below).
- An increase in the fluid-phase (external) hydrodynamic shear acting on the attached particle. This aspect of colloid release is not addressed here and is the subject of a subsequent article.

Theoretical Development

In *classical*-DLVO theory, the total interaction energy between two surfaces is the sum of van der Waals and electrostatic interaction energies. At very close separation distances, Born repulsion due to overlapping electron orbitals of the molecules comprising the separate surfaces also occurs. The incorporation of additional energies of interaction into the DLVO paradigm is often called *extended*-DLVO theory. These additional interactions may include: hydration pressure, hydrogen bonding forces, hydrophobic effects, solvation forces, disjoining pressure, structural forces, or Lewis acid-base forces (van Oss et al., 1988; Gutowski, 1991; van Oss, 1994; Swanton, 1995; Israelachvili and Wennerstrom, 1996). It has been reported that these non-DLVO forces can play a significant role in particle detachment (Raveendran and Amirtharajah, 1995). Short-range repulsive forces are usually termed hydration forces, while longer-range attractive forces between hydrophobic bodies are considered hydrophobic interactions. Non-DLVO interactions are poorly understood, but are thought to arise out of interactions between the solvent boundary layer and interface (Israelachvili, 1992; Elimelech et al., 1995). It has been reported that this non-DLVO interaction energy decays exponentially with distance from the surface (Israelachvili, 1992; van Oss, 1994). In order to estimate the non-DLVO interaction, we have employed the Lewis acid-base approach developed by van Oss and co-workers (van Oss et al., 1988; van Oss, 1994) using contact angle measurements to find the acidic and basic properties of surfaces. This technique has been reported to subsume various non-DLVO interactions (van Oss, 1994). Recent work (Kwok et al., 1994, 1998; Morra, 1996) indicates that this approach may not be an exact predictor, but can be used as a preliminary estimation of the magnitude of the Lewis acid-base interaction.

Here, we consider the total interaction energy between surfaces as the sum of the electrostatic, van der Waals, Born repulsion, and Lewis acid-base interaction energies

$$\Delta G^{\Sigma} = \Delta G^{\mathrm{EL}} + \Delta G^{\mathrm{VDW}} + \Delta G^{\mathrm{Born}} + \Delta G^{\mathrm{AB}} \tag{1}$$

A negative ΔG indicates an attractive interaction where the colloids will be attached to the substrata, while a positive ΔG indicates a repulsive interaction and colloid detachment.

The magnitude of the electrostatic interaction energy for dissimilar surfaces can be predicted with an equation developed by Gregory (1975) based on the linear superposition approximation (LSA). The LSA equation predicts values for ΔG^{EL} that are between those determined from electrostatic equations based on constant charge and constant potential assumptions (Elimelech et al., 1995). The following sphere-plate LSA equation was used (Gregory, 1975). (The relative colloid/collector size disparity allows the use of sphere-plate geometry)

$$\Delta G^{\mathrm{EL}} = 64\pi\epsilon a_c\left(\frac{kT}{z_j e}\right)^2 \gamma_1\gamma_2 \exp\left(-\kappa s\right) \tag{2}$$

where

$$\gamma_i = \tanh\left(\frac{z_j e\psi_{\mathrm{o,i}}}{4kT}\right) \quad \text{and} \quad \kappa = \sqrt{\frac{e^2\sum n_{jo}z_j^2}{\epsilon kT}}$$

The retarded van der Waals interaction energy was predicted from (Gregory, 1981)

$$\Delta G^{\mathrm{VDW}} = -\frac{A_{132}\cdot a_c}{6\cdot s}\left[1-\frac{5.32\cdot s}{\lambda}\ln\left(1+\frac{\lambda}{5.32\cdot s}\right)\right] \tag{3}$$

The combined Hamaker constant can be estimated from the Hamaker constant of the individual materials (Israelachvili, 1992)

$$A_{132} = \left(\sqrt{A_{11}}-\sqrt{A_{33}}\right)\left(\sqrt{A_{22}}-\sqrt{A_{33}}\right) \tag{4}$$

A_{11} is the Hamaker constant for polystyrene and is taken from Lifshitz theory as 6.6×10^{-20} J (Israelachvili, 1992). A_{33} is for water and is also found from Lifshitz theory as 3.7×10^{-20} J (Israelachvili, 1992). The constant for glass A_{22} is calculated from (van Oss, 1994)

$$A = 24\pi\gamma d_o^2 \tag{5}$$

γ for glass is reported as 33.7 mJ/m^2 (Wu et al., 1996), yielding A_{22} as 6.34×10^{-20} J. This compares favorably with the Hamaker constant cited for fused quartz, 6.5×10^{-20} J (Israelachvili, 1992), which is a similar material. The result from Eq. 4 for the combined Hamaker constant for the PS-water-glass system is 3.79×10^{-21} J.

Born repulsion can be calculated from (Ruckenstein and Prieve, 1976)

$$\Delta G^{\mathrm{Born}} = \frac{A\cdot\sigma_c^{6}}{7{,}560}\left[\frac{8a_c+s}{(2a_c+7)^7}+\frac{6a_c-s}{s^7}\right] \tag{6}$$

The collision diameter was varied to achieve a primary minimum depth at 0.158 nm, a commonly accepted distance of closest approach d_o (van Oss, 1994). Israelachvili (1992) reported a value of 0.165 nm, very close to that used here.

The Lewis acid-base interaction energy was determined with a method developed by van Oss and coworkers (van Oss et al., 1988; van Oss, 1994). Contact angles with three probe liquids (two polar and one nonpolar) were measured and each were used in the following equation to yield three equations with three unknowns which were solved simultaneously (van Oss et al., 1988; van Oss, 1994)

$$\gamma_l(1+\cos\theta_{ls}) = 2\sqrt{\gamma_l^{\mathrm{LW}}\gamma_s^{\mathrm{LW}}}+2\sqrt{\gamma_l^{+}\gamma_s^{-}}+2\sqrt{\gamma_l^{-}\gamma_s^{+}} \tag{7}$$

Once the γ^+ and γ^- parameters were determined for each surface, the Lewis acid-base free energy of interaction at d_o could be calculated from (van Oss et al., 1988; van Oss, 1994)

$$\begin{aligned}\Delta G_{d_0}^{\mathrm{AB}} = 2\Big[&\sqrt{\gamma_3^{+}}\left(\sqrt{\gamma_1^{-}}+\sqrt{\gamma_2^{-}}-\sqrt{\gamma_3^{-}}\right)\\ &+\sqrt{\gamma_3^{-}}\left(\sqrt{\gamma_1^{+}}+\sqrt{\gamma_2^{+}}-\sqrt{\gamma_3^{+}}\right)\\ &-\sqrt{\gamma_1^{+}\gamma_2^{-}}-\sqrt{\gamma_1^{-}\gamma_2^{+}}\Big]\end{aligned} \tag{8}$$

The AB interaction energy between a sphere and flat plane decays exponentially with distance with the following relation (van Oss, 1994)

$$\Delta G^{\mathrm{AB}} = 2\pi a_c\lambda_{\mathrm{AB}}\Delta G_{d_0}^{\mathrm{AB}}\exp\left[\frac{d_0-s}{\lambda_{\mathrm{AB}}}\right] \tag{9}$$

The decay length of water λ_{AB} (nm) is the subject of much research and discussion and has been reported to range from 0.4 to 32 nm (Yoon et al., 1997). However, it is typically accepted to be between 1 and 2 nm (Israelachvili, 1992). Sposito (Sposito and Prost, 1982; Sposito, 1984) reported an adsorbed water layer thickness on smectites of approximately 1.0 nm using infrared spectroscopy, X-ray diffraction, neutron diffraction, and nuclear magnetic resonance. For this work, we used a value of 1 nm (van Oss et al., 1990).

As a comparison to the van Oss method, an approach developed by Yoon et al. (1997) for determining the degree of hydrophobicity from water contact angles was also explored. In this approach, a power law decay with distance is assumed

$$F_h = -\frac{K\cdot a_c}{s^2} \tag{10}$$

Taking the integral from the distance of closest approach d_o to infinity, the interaction energy can be determined in lieu of force

$$\Delta G = \int_{d_o}^{\infty} -\frac{K\cdot a_c}{s^2}ds = -K\frac{a_c}{d_o} \quad (\text{in J}) \tag{11}$$

At the minimum separation distance d_o, substituting the above expression into Eq. 9

$$-K\frac{a_c}{d_0} = 2\pi a_c\lambda_{\mathrm{AB}}\Delta G_{do}^{\mathrm{AB}} \tag{12}$$

and solving for $\Delta G_{do}^{\mathrm{AB}}$ yields

$$\Delta G_{do}^{\mathrm{AB}} = -\frac{K}{2\pi d_o\lambda_{\mathrm{AB}}} \tag{13}$$

The coefficient K was predicted from their experimentally derived correlation (Yoon et al., 1997)

$$\log K = -7.0\left(\overline{\cos\theta}\right)-18.0 \tag{14}$$

The value for $(\overline{\cos\theta})$ is the average cosine of the water contact angles for each interacting surface. While this expression was developed from atomic force microscope measurements between glass and silica, and glass and hydrophobized silica, it was used here as an additional estimate of ΔG_{do}^{AB} for our system.

Others have found the existence of non-DLVO forces through direct measurement. Israelachvili and Adams (1978) experimentally determined a repulsive force between mica surfaces that was not explained through *classical*-DLVO theory. Using an atomic force microscope, Ducker et al. (1994) reported a strong attractive interaction between hydrophobic surfaces that was similarly not explained by *classical*-DLVO theory. The decay of this non-DLVO force with distance has been found to follow an exponential function (Israelachvili, 1992; Kirchner and Cevc, 1994) in agreement with Eq. 9. In contrast to direct force measurements which determine the surface forces *a posteriori* experimentally, the van Oss approach described above allows the estimation of these non-DLVO interactions *a priori.*

Materials and Methods

Colloids

1.0 μm diameter (standard deviation = 0.017 μm) polystyrene latex microspheres from Interfacial Dynamics Corporation (Portland, OR) were used in this study. The microspheres have carboxyl surface groups with a surface charge density of 27.0 $\mu C/cm^2$ (as reported by Interfacial Dynamics Corporation). The density of the polystyrene is 1.055 g/cm^3 at 20°C. All colloidal solutions were sonicated for 60 s before use.

Glass beads

Glass columns packed with 425 to 600 μm diameter soda lime glass beads (Sigma Chemical Company, St. Louis, MO) were used as the porous media substrate. The glass beads were cleaned by rinsing sequentially with acetone, hexane (both Fisher Scientific, Pittsburgh, PA), concentrated HCl (Fisher Scientific, Pittsburgh, PA; soak approximately 12 h), repeated rinsings with deionized water from a Milli-Q water system (Millipore Corporation, Bedford, MA), 0.1 M NaOH (J.T. Baker, Phillipsburg, NJ; soak approximately 12 h), and deionized water (repeated rinsings). The beads were dried overnight at 105°C after cleaning and stored in a dessicator until use.

Experimental setup

The apparatus illustrated in Figure 1 was used for all detachment experiments. Dual off-set peristaltic pumps (Cole Parmer, Chicago, IL) with a pulsation dampener were used to reduce pressure and flow transients. The optical density of the effluent from the columns was continuously monitored with a Varian Cary spectrophotometer (Varian Techtron, Victoria, Australia) set to a wavelength of 500 nm, using a 5 cm pathlength cell. A calibration curve was developed for the conversion of optical density measurements to colloid concentrations. A Pacific Scientific Hiac/Royco particle counter (Pacific Scientific, Silver Spring, MD) was used to develop the calibration curves. The particle counter sensor utilized a 5 mW laser light source and was a dual-mode type: utilizing the principle of light scattering for smaller particles, and light extinction for larger particles.

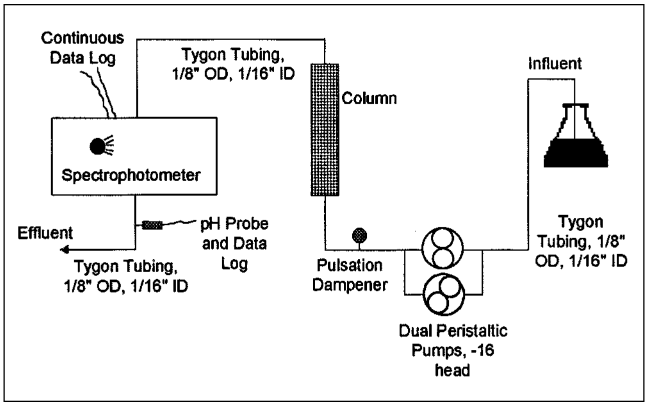

Figure 1. Experimental flowing columns setup.

Inner diameter = 25 mm; effective length = 155 mm; flow rate = 5 mL/min.

A glass column (inner diameter = 25 mm, effective length = 155 mm, from Ace Glass, Vineland, NJ) was packed by slowly pouring 100 gm glass beads into the water-filled column while constantly tapping to settle the beads and remove air. The resulting porosity was 0.42.

Experimental procedure

The polystyrene colloids were attached at pH = 3.5, $I = 0.1$ M NaCl at 5 mL/min for 10 pore volumes. The ionic strength was not raised above the critical coagulation concentration of the colloids, which was experimentally determined to be 0.158 ± .004 M NaCl (triplicate experiments). Particle size analyses confirmed a monodisperse distribution of influent particles. Following the attachment step, the column was flushed with pH = 3.5, $I = 0.1$ M solution (with no colloids) at 5 mL/min for another 10 pore volumes. For each ionic strength condition tested (0.1 M, 0.01 M, 1 mM, and DI), the pH was increased: 5.0, 7.0, 9.0, 10.0 (each for at least 20 pore volumes), and finally rinsed with deionized water at pH 11.0 to remove all remaining colloids and ensure mass balance. Experiments showed an average 94% total colloid recovery. Results from effluent particle size analyses indicated a monodisperse distribution with a similar shape factor as the influent particle size distribution. This supports the hypothesis that the particles are individually detached and do not self-aggregate in solution. All solutions were prepared with water from a Milli-Q water system (Millipore Corp., Bedford, MA) and were deaerated with 15 cm Hg vacuum for a minimum of 15 min prior to use.

Electrophoretic mobility

Electrophoretic mobilities of the polystyrene colloids were measured with a Malvern Zetasizer II (Malvern Instruments, Southborough, MA) over a pH range from approximately 3 to 11, with I from deionized water ($10^{-5.5}$ M) to $I = 0.1$ M NaCl. The glass beads used as the porous media were crushed and sonicated to produce smaller particles for measurement. Field strengths were adjusted to 20–30 V/cm. The pH was

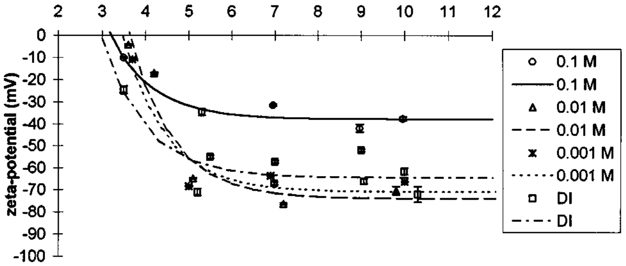

Figure 2a. Polystyrene latex ζ-potentials determined from EM measurements and Henry's equation.

Data points are the averages of 10 measurements and the error bars indicate 95% confidence intervals (25°C, field strength = 20 to 30 V/cm).

adjusted with HCl (0.01, 0.1, or 10 M; Fisher Scientific, Pittsburgh, PA), and/or NaOH (0.01, 0.1, or 6 M; J.T. Baker, Phillipsburg, NJ). The mobility was converted to ζ-potentials using Henry's equation (Henry, 1931; Hunter, 1981). The ζ-potentials are shown in Figure 2. The curves shown were fit to the data points for each I

$$y = a + b \cdot \exp(-x) \tag{15}$$

The ζ-potentials found for glass are similar to values reported by others (Elimelech and O'Melia, 1990; Rijnaarts et al., 1993, 1995), and those found for the polystyrene colloids are also similar to other literature values (Litton and Olson, 1993, 1996).

Contact angles

Table 1. Contact Angles (deg) with Probe Liquids

Surface	Water	Formamide	Diiodomethane
Polystyrene latex*	87.6 ± 1.7	71.9 ± 1.4	27.9 ± 1.4
Glass slide†	9.0 ± 1.2	14.7 ± 1.0	53.0 ± 0.4
Ground glass†	49.4 ± 2.2	48.4 ± 1.8	58.7 ± 1.4
Ground glass†,‡	50.9 ± 1.8	35.2 ± 2.4	58.3 ± 2.0

*Measured on spin-coated polystyrene at 24 ± 1°C.
†From Wu et al. (1996) at 20°C.
‡After exposure to water vapor.

The polystyrene latex colloids were spin-coated on a glass side with a procedure reported by Neumann (Neumann and Good, 1979). In this procedure, the PS colloids are dissolved in toluene (J.T. Baker, Phillipsburg, NJ), and spread on a spinning slide on a centrifuge rotor (International Clinical Centrifuge, Arthur H. Thomas Co., Philadelphia, PA). The rotational velocity of the rotor is adjusted to thinly and evenly spread the material on the slide. The prepared slides were kept in a dessicator until use. Three probe liquids were used to characterize the PS surface: deionized water, formamide, and diiodomethane. The contact angles were measured at 24 ± 1°C on a Ramé Hart goniometer (Model 100-00-115, Mountain Lake, NJ). The liquids were placed in a sessile drop on the slides with 10 μL stainless steel Hamilton syringes. A total of 20 contact angles were measured for each liquid. Measured contact angles are reported in Table 1. The surface tension components for the liquids used are summarized in Table 2. The contact angles for glass were abstracted from the literature (Wu et al., 1996) and are reported in Table 1. The preparation of the glass surfaces for contact angle measurements were significantly different, varying from glass slides, to dry ground glass, to hydrated ground glass.

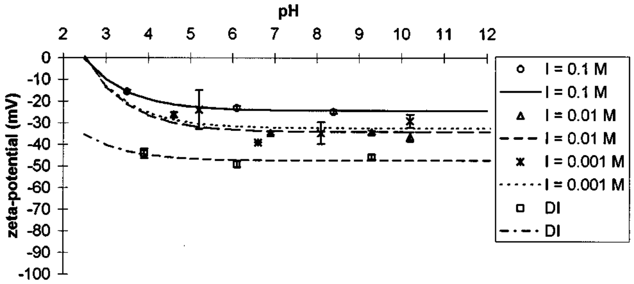

Figure 2b. Glass ζ-potentials determined from EM measurements and Henry's equation.

Data points are the averages of 10 measurements and the error bars indicate 95% confidence intervals (25°C, field strength = 20 to 30 V/cm).

Microscopy

Colloid attachment morphology was investigated by carefully disassembling columns after attachment runs and imaging with a scanning electron microscope (AMRAY, Inc., Bedford, MA, Model 1000). Glass beads were placed on two-sided carbon tape mounted on a stub, and imaged at 20 kV.

Results and Discussion

Colloid detachment

The attached colloids were removed from the porous media substrate via ionic strength and pH perturbations. All detachment experiments indicated qualitative agreement with the DLVO theory (as pH increased and/or ionic strength decreased, detachment increased). Results of a typical attachment and detachment experiment are depicted in Figure 3. To determine the cumulative removal for each pH change, the area under each portion of the curve was determined by the trapezoid rule (Shenk, 1979) with $\Delta t = 5$ s (Figure 4). The pH values of the median (50% cumulative) removal for each I were determined with the following equation (Ott, 1993), and are listed in Table 3

$$\text{median} = L + \frac{w}{f_m}\left(\frac{n}{2} - cf_b\right) \tag{16}$$

Table 2. Surface Tension Components for Probe Liquids Used to Measure Contact Angles on Polystyrene (van Oss, 1994)

Liquid	γ_L^T (mJ/m^2)	γ_L^{LW} (mJ/m^2)	γ_L^+ (mJ/m^2)	γ_L^- (mJ/m^2)
Water	72.8	21.8	25.5	25.5
Formamide	58.0	39.0	2.28	39.6
Diiodomethane	50.8	50.8	0	0

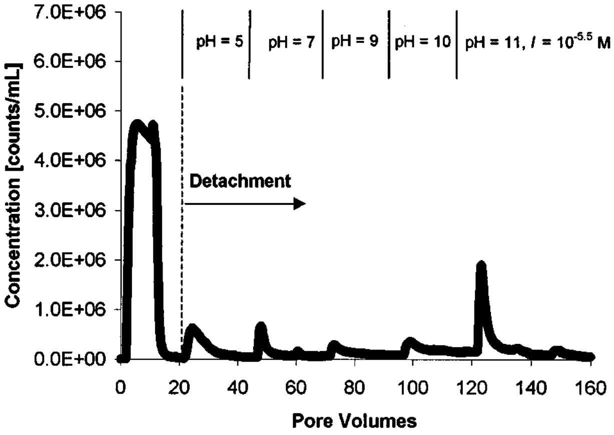

Figure 3. Typical attachment and detachment run.

Attaching at pH 3.5 and $I = 0.1$ M NaCl, detaching at $I = 1$ mM NaCl with increasing pH.

Lewis acid-base interactions

The Lewis acid and base parameters were determined using van Oss' method (van Oss et al., 1988; van Oss, 1994) (Table 4). There is a significant difference in the acid and base parameters for glass depending on the preparation method (glass slide vs. dry ground glass vs. hydrated ground glass). From these different values for glass, ΔG_{do}^{AB} values were determined for PS-water-glass interaction. The three values for ΔG_{do}^{AB} are also listed in Table 4. The range of values for ΔG_{do}^{AB} was too large for predictive purposes, but was expected to bracket the true Lewis acid-base interaction energy for this system. Values for ΔG_{do}^{AB} were also predicted with the Yoon et al. (1997) approach and are listed in Table 5. The range is substantially smaller, but still not accurate enough for predictive purposes.

Detachment experiments (performed in duplicate) in 1 mM NaCl solutions were used to determine a more accurate value for ΔG_{do}^{AB}. A value of $\Delta G_{do}^{AB} = -2.13$ mJ/m^2 was found to yield a $\Delta G^{\Sigma} = 0$ at the observed detachment pH (7.5). This is consistent with the values reported in Tables 4 and 5, and is depicted graphically in Figure 5. A significant hydrophobic interaction energy (negative ΔG_{do}^{AB}) may be expected for this system based on the work of others. We measured a water contact angle on PS of 87.6 degrees. Yoon and co-workers (Yoon and Ravishankar, 1996; Yoon et al., 1997) suggest that long-range hydrophobic forces are of quantitative significance when water contact angles are in this region.

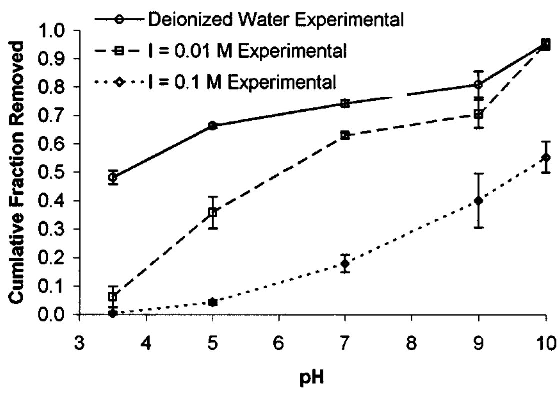

Figure 4. Cumulative removal of colloids with increasing pH.

Error bars indicate the range of duplicate runs.

Table 3. Actual and Predicted Median Removal pH Values

Ionic Strength (M) NaCl	Exp. Median Removal pH	Pred. Median Removal pH with *Extended*-DLVO*	Pred. Median Removal pH with *Classical*-DLVO
$10^{-5.5}$ (DI)	3.6	4.3	< 3.5
0.01	6.0	6.5	3.9
0.1	9.6	> 12	4.1

*$\Delta G_{do}^{AB} = -2.13$ mJ/m^2; $d_o = 0.158$ nm, $\lambda = 1$ nm.

The pre-exponential portion of Eq. 9 ($= 2 \cdot \pi \cdot a_c \cdot \lambda_{AB} \cdot \Delta G_{d_o}^{AB}$) was then calculated to be -6.69×10^{-15} mJ. When divided by the interaction area, which was $2 \cdot \pi \cdot a_c \cdot d_o$ from the Langbein approximation (Israelachvili, 1992), a value of -13.5 mJ/m^2 was found. This is consistent with typical pre-exponential values given by Israelachvili for stronger hydrophobic interactions, -20 to -100 mJ/m^2 (from Eq. 13.10, Israelachvili, 1992).

Extended-DLVO predictions

The *extended*-DLVO model was used to generate potential energy profiles. The interaction between PS latex and the glass surface at attaching conditions (pH 3.5 and $I = 0.1$ M)

Table 4. Solid Surface Tension Parameters (Calculated with Eq. 7 and Values from Tables 1 and 2), and ΔG_{do}^{AB} Using van Oss' Method

Surface	γ_s^+ (mJ/m^2)	γ_s^- (mJ/m^2)	ΔG_{do}^{AB} for PS-Water-Glass* (mJ/m^2)
Polystyrene latex	0	5.9	—
Glass slide	$1.3^{\ddagger}$	$62.2^{\ddagger}$	8.160
Ground glass	$0.4^{\ddagger}$	$37.1^{\ddagger}$	−12.638
Ground and hydrated glass†	$2.3^{\ddagger}$	$26.2^{\ddagger}$	−17.824

*Calculated with Eq. 8.
†After exposure to water vapor.
‡From Wu et al. (1996).

Table 5. Values of ΔG_{do}^{AB} Using Eq. 13 Derived from Yoon et al. Approach

Surface	$\overline{(\cos\theta)}$ with Polystyrene*	Hydrophobic Force Constant,† K (J)	ΔG_{do}^{AB} for PS-Water-Glass‡ (mJ/m^2)
Glass slide	0.515	2.48×10^{-22}	−0.250
Ground glass	0.346	3.78×10^{-21}	−3.81
Ground and hydrated glass††	0.336	4.45×10^{-21}	−4.48

*From Table 3.
†Calculated with Eq. 14.
‡Calculated with Eq. 13, $\lambda_{AB} = 1$ nm, $d_o = 0.158$ nm.
††After equilibrium with water vapor.

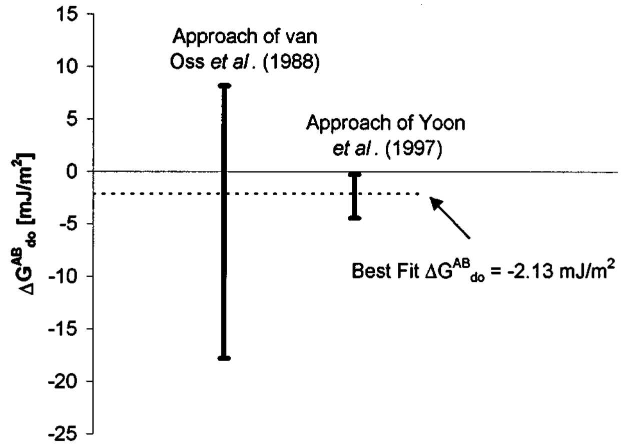

Figure 5. Comparison of van Oss et al. (1988) approach and Yoon et al. (1997) approach to predict the range of ΔG_{do}^{AB} values.

A value of -2.13 mJ/m^2 of ΔG_{do}^{AB} was found from the experimental detachment data and is represented by the dashed line.

is illustrated in Figure 6. Note the deep primary minimum of attachment ($\sim -1{,}700$ kT). In contrast, since ionic strength was maintained below the colloid critical coagulation concentration of 0.158 M NaCl (see Experimental Procedure), the colloid-colloid interactions were repulsive (positive) at all experimental conditions (Figure 6).

For ionic strengths of 0.1 M, 0.01 M, and deionized water ($I = 10^{-5.5}$ M), pH values for median, or 50%, removal, using *extended*-DLVO (where $\Delta G^{\Sigma} = 0$) are summarized in Table 3. For comparison purposes, *classical*-DLVO predictions are also reported. There was significant detachment both above and below the median removal pH. Except for the $I = 0.1$ M solution, the *extended*-DLVO model closely predicted the median detachment pH. The underprediction of detachment with 0.1 M ionic strength may be attributable to a failure of *extended*-DLVO to accurately characterize the Lewis acid-base interaction at higher ionic strengths. Butkus and Grasso (1998) reported increases in the nonelectrostatic interfacial energies of organically-coated sodium montmorillonite and polytetrafluoroethylene systems at ionic strengths above 0.001 M. Reported experiments with a surface force apparatus (Yoon and Ravishankar, 1996) indicated a decrease in the hydrophobic force of monolayer-covered mica surfaces with increasing electrolyte concentration (as low as 10^{-4} M KCl). The deviation from detachment prediction seen here is most likely caused by an overestimate of the hydrophobic interaction at 0.1 M NaCl.

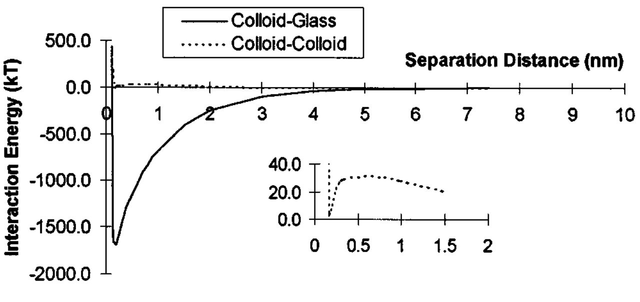

Figure 6. Ex-DLVO interaction energy plot at attaching conditions.

pH = 3.5, $I = 0.1$ M NaCl; colloid-colloid interaction (dashed line, shown in insert), colloid-glass interaction (solid line).

Removal distribution

Deterministic potential models are typically limited to predicting only one pH value for complete detachment at each ionic strength—colloids would be attached below this pH, and detached above this pH. However, Figure 4 clearly illustrates that portions of the attached colloids detach at a variety of pH values.

Work reported in the literature supports this removal distribution (Kallay and Matijevic, 1981; Hubbe, 1985). In experiments similar to ours but with flat surfaces, Hubbe (1985) performed detachment experiments on colloids with increasing fluid flow and found a distribution of fraction detached with increasing shear stress. Kallay and Matijevic (1981) reported a similar detachment distribution with pH for the removal of hematite from steel.

Scanning electron micrographs confirm the presence of many singlet colloids on glass bead surfaces with the presence of some surface aggregation. The repulsive colloid-colloid interaction is evidently overcome by the affinity of the colloids for certain surface domains of the glass. Local surface aggregation derives, in large measure, from heterogeneous glass surface functional groups: silanol, siloxane, geminal hydroxyls attached to silicon surface atoms, and adsorption of various other constituents (such as metals) to the silanol groups (Snoeyink and Weber, 1972). Despite this apparent surface site heterogeneity, colloids appear to detach individually, albeit with disparate detachment energies, as evidenced by monodisperse (1 μm) aqueous-phase distributions in the effluent. A paired t test showed no statistical difference (at $s = 0.05$) between influent and effluent colloid-size distributions; both were monodisperse with modes in the 0.89–1.02-μm channel (influent average = 1.1 μm; effluent average = 1.2 μm).

The two parameter gamma probability distribution is commonly used in engineering and science, and has been used to describe surface site energy distributions (Sposito, 1994)

$$y = \frac{(\beta \cdot x)^{\alpha - 1} \cdot e^{(-\beta \cdot x)}}{\frac{1}{\beta} \cdot \Gamma(\alpha)} \tag{17}$$

The two parameter gamma distribution can be simplified to one parameter by letting $\beta = 1$

$$y = \frac{x^{\alpha - 1} \cdot e^{-x}}{\Gamma(\alpha)} \tag{18}$$

When α approaches ∞, the two parameter gamma distribution becomes the Gaussian distribution (Sposito, 1994)

$$y = \frac{1}{\sqrt{2\pi} \cdot \sigma} \cdot e^{-(x-\mu)^2/2\sigma^2} \tag{19}$$

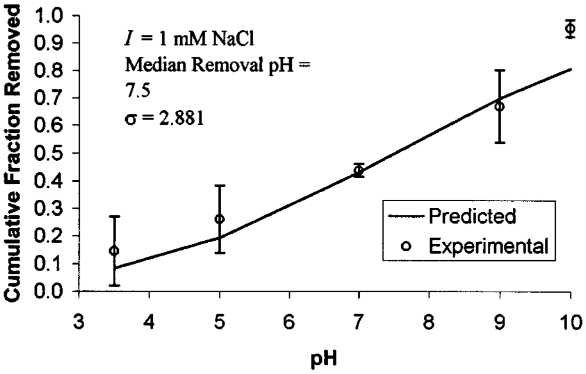

Figure 7. Cumulative density function prediction of experimental data using Eq. 18.

The pH standard deviation for detachment is 2.881 at $I = 1$ mM. Error bars represent the range of duplicate runs—data points are the averages of those runs.

Using results from the 1 mM detachment experiments, the standard deviation for a Gaussian distribution around the detachment pH was found by a least-squares approach. The best fit σ for 1 mM was determined to be 2.881 (Figure 7). This value was used for predicting the detachment pH distribution for deionized water, $I = 0.01$ M, and $I = 0.1$ M (Figure 8). The σ determined for 1 mM predicted the removal distribution for deionized and 0.01 M water fairly well. The similar removal distribution for $I = 0.01$ M, $I = 1$ mM, and deionized water was indicative of a similarity in heterogeneity of interaction energy.

The removal distribution for $I = 0.1$ M was not accurately predicted (Figure 8). This is not surprising as the median removal pH was not well-predicted for $I = 0.1$ M using *extended*-DLVO theory. As discussed above, the Lewis acid-base interaction at this high ionic strength may not have been accurately characterized with *extended*-DLVO.

Even for this model system (polystyrene colloids and glass beads), a removal distribution exists. Simple deterministic models (*classical*-DLVO and *extended*-DLVO) predict a singular detachment pH (for each ionic strength) and do not address the detachment distribution. To properly model real systems, the stochastics of removal must be addressed.

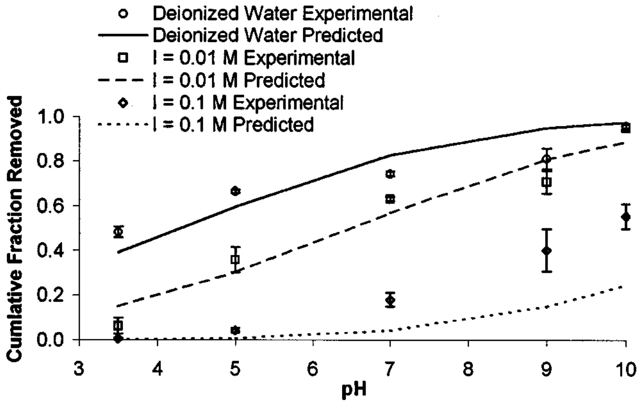

Figure 8. Stochastic predictions of detachment pH using a Gaussian distribution (σ = 2.881) around the median predicted with *extended*- DLVO.

Error bars represent the range of duplicate runs—data points are the average of those runs.

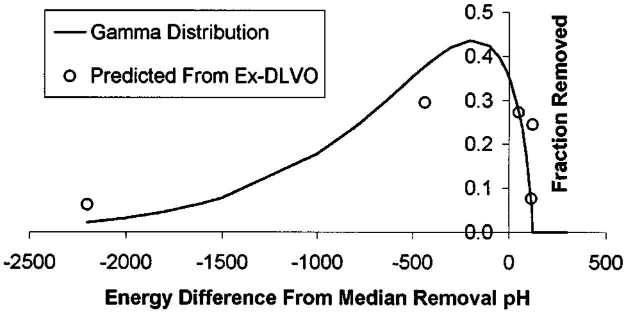

Figure 9. Typical predicted energy distribution at I = 0.01 M.

Gamma distribution shape parameter = 1.66 (estimated by normalizing the abscissa to non-negative values from 0 to 5). Points represent energy differences predicted from *extended*-DLVO.

Energy distribution

The distribution of particle removal as a function of pH indicated a strong possibility of a distributed interfacial energy structure between the PS colloids and the glass surfaces. The colloids detached at pH values lower than the median removal pH must have been attached with lower total interaction energies than predicted (a smaller pH change, or energy change, was needed to yield a zero interaction energy). Similarly, colloids detaching at higher pHs were attached with higher total interaction energies than predicted. By determining the energy for each detachment pH in relation to the energy at the median detachment pH, energy distributions as a function of pH were predicted. A representative plot (for $I = 0.01$ M) is illustrated in Figure 9. The energy at the median pH was predicted to be zero with *extended*-DLVO. The values reported on the abscissa correspond to energy deviations from the median required to detach the stated fraction of colloids. A one parameter gamma distribution was found to represent the energy distribution data well as shown for $I = 0.01$ M in Figure 9. Other ionic strengths were fit to the gamma distribution as well. A shape parameter of 1.66 was found from least-squares analysis by normalizing the energy values from 0 to 5 (the gamma distribution requires non-negative arguments). The data is skewed to the right (Figure 9) with most of the removal occurring within ±500 kT of the median removal pH.

The removal distribution with pH was found to be approximated with a Gaussian distribution while interaction energy followed by a gamma distribution. The fact that these interrelated parameters (pH and energy) follow different distributions may be attributed to the shape of the ζ-potential profiles reported in Figure 2. There is little change above approximately pH 5. But, at a pH lower than about 5, the change in ζ-potential (and surface potential) with pH is much greater

$$\left.\frac{\partial \psi_{o,i}}{\partial \mathrm{pH}}\right|_{\mathrm{pH} < 5} \gg \left.\frac{\partial \psi_{o,i}}{\partial \mathrm{pH}}\right|_{\mathrm{pH} > 5}$$

This manifests itself in a much reduced electrostatic interaction energy (see Eq. 2) and therefore a deeper primary minimum (Figure 6).

Conclusions

The objective of this work was to develop a predictive model for determining aqueous chemistry conditions promoting colloid detachment in porous media. Experiments were performed using a model PS-water-glass system in which colloid detachment was measured as a function of solution chemistry. *Classical*-DLVO theory was unable to predict detaching conditions for this system. An *extended*-DLVO theory was found to predict the median colloid detachment pH for all ionic strengths except 0.1 M NaCl where hydrophobic interactions were overpredicted.

Removal of colloids from the porous media was found to increase as a function of pH. The fraction removed with pH could be modeled with a Gaussian distribution. The standard deviation of the distribution was determined for 1 mM ionic strength, and applied to ionic strengths of 0.1 M, 0.01 M, and deionized water to successfully predict the removal distributions for those ionic strengths. From an *extended*-DLVO model and a gamma distribution, an interaction energy distribution was predicted for the polystyrene colloid and glass bead interaction.

Although colloid-colloid interaction was determined to be repulsive at all experimental conditions, some surface aggregation was confirmed through SEM analysis. This was thought to result from favorable attachment domains on the chemically heterogeneous glass surfaces. This may explain the observed dependence of removal on pH. The presence of potential energy distributions in this model system has serious implications for colloid detachment modeling of significantly more heterogeneous real systems. Potential energy models must incorporate the removal stochastic description of surface interactions to accurately predict detachment.

Notation

a_c = colloid radius, m
A_{132} = Hamaker constant between surfaces 1 and 2 across medium 3, J
cf_b = sum of frequencies (cumulative detachment) for all classes below the median
d_o = distance of closest approach (nm), taken as 0.158 nm (van Oss, 1994)
e = electron charge, C
f_m = frequency of interval-containing class
k = Boltzmann's constant, J/K
K = hydrophobic force constant, J
L = lower class limit of interval-containing median
n = total frequency (total cumulative detachment)
n_{jo} = number concentration of ions in bulk solution, ions/m^3
s = surface separation distance, m
T = temperature, K
w = interval width
z_j = ion valance
α = gamma distribution shape parameter
β = gamma distribution scale parameter
ϵ = permittivity of the medium, $C^2 \cdot J^{-1} \cdot m^{-1}$
$\psi_{o,i}$ = surface potential of each surface, V
λ = characteristic wavelength, taken as 100 nm
σ = Gaussian distribution standard deviation
σ_c = collision diameter, nm
γ_i^+ = Lewis acid surface component of material i
γ_i^- = Lewis base surface component of material i
μ = average
ΔG_{do}^{AB} = Lewis AB interaction energy at d_o, mJ/m^2
$\overline{(\cos\theta)}$ = average of cosine of water contact angles
λ_{AB} = decay length of water, nm

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