

Experimental determination of colloid deposition rates and collision efficiencies in natural porous media

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Abstract. Mobile colloids in groundwater aquifers and soils can serve as carriers for strongly sorbing contaminants and thereby facilitate contaminant transport. Therefore mobile colloids may have to be considered in modeling the fate of strongly sorbing contaminants in subsurface environments. In this study we present a chromatographic short-pulse technique for measuring colloid deposition rate coefficients and experimental collision efficiencies in natural porous media. The method was evaluated using four different experimental systems of increasing complexity. Short pulses (equivalent to 0.002 to 0.03 pore volumes) of latex or humic-coated hematite suspensions were injected under saturated flow conditions into laboratory columns packed with glass beads, soil, or aquifer materials. Colloid breakthrough curves were measured on-line using fluorescence and UV-VIS spectrophotometers. Deposition rate coefficients determined with the short-pulse method were in excellent agreement with results from step-input experiments. Experiments with different flow rates and column dimensions showed that colloid deposition generally followed a first-order kinetic rate law. On the basis of experimental fast deposition rates, collision efficiencies for colloid deposition can be calculated. The results demonstrate that the short-pulse method can be used very efficiently for studying the effects of solution chemistry and flow velocity on the kinetics of colloid deposition in natural porous media. The short-pulse method has several advantages over the more traditionally used step-input experiment and allows running several experiments on a single column without significant blocking or filter ripening effects.

Introduction

Mobile colloids in groundwater aquifers and soils can facilitate the translocation of strongly sorbing contaminants or, as in the case of certain bacteria or viruses, can be considered hazardous pollutants themselves [McDowell-Boyer *et al.*, 1986; McCarthy and Zachara, 1989; McCarthy and Degueldre, 1993; Grolimund *et al.*, 1996]. Therefore mobile colloids are recently being considered in modeling the fate of strongly sorbing contaminants in subsurface environments [Corapcioglu and Jiang, 1993; Kim and Corapcioglu, 1996]. In field studies, mobile colloids have been reported to consist of submicron-sized clay particles, iron oxyhydroxides, silica, natural organic matter, viruses, or bacteria [McDowell-Boyer *et al.*, 1986; McCarthy and Degueldre, 1993]. Potential sources of mobile colloids are (1) in situ mobilization of colloidal particles under geochemical conditions that favor dispersion, for example, low electrolyte concentration and high sodium adsorption ratio [Roy and Dzombak, 1996; Kaplan *et al.*, 1996]; (2) formation of colloids from supersaturated solutions, for example, along a chemical gradient due to wastewater infiltration [Gschwend and Reynolds, 1987]; and (3) colloids originating from external sources, for example, colloid injection for remediation purposes [McCarthy, 1993].

The transport and deposition of colloidal particles during flow through porous media have been studied extensively using well-characterized model systems [Fitzpatrick and Spielman,

1973; Elimelech and O'Melia, 1990; Elimelech, 1991]. Early research was driven by the need to understand the performance of deep-bed filters used in chemical engineering and wastewater treatment [Iwasaki, 1937; Yao *et al.*, 1971; Tien and Payatakes, 1979]. Filtration theories have been developed from theoretical considerations and experimental results for the transport of monodisperse microspheres through columns packed with spherical collector grains [Yao *et al.*, 1971; Rajagopalan and Tien, 1976]. More recently, the focus of interest has shifted to the transport of mobile colloids in natural subsurface porous media [McDowell-Boyer *et al.*, 1986; Ryan and Elimelech, 1996]. However, application of filtration theory to colloid transport in subsurface systems seems limited by the fact that most natural porous media have wide pore and particle size distributions, complex pore geometry, and rough surfaces with considerable surface charge heterogeneities [Kretzschmar *et al.*, 1994]. Moreover, current theories often do not accurately predict surface charge effects even in simple model systems [Elimelech and O'Melia, 1990]. Evaluating the mobility of colloids in a particular subsurface porous medium therefore strongly relies on empirical results. Improved experimental techniques are needed in order to systematically study the influence of chemical and physical parameters on colloid transport and deposition in heterogeneous natural porous media. Such studies will ultimately contribute to a better understanding of colloid behavior in subsurface environments.

A limited number of experimental studies have been published to date on the transport and deposition of colloids in heterogeneous, natural porous media [Lahav and Tropp, 1980; Vinten and Nye, 1985; Puls *et al.*, 1993; Higgo *et al.*, 1993;

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Kretzschmar *et al.*, 1994]. Studies attempting to measure colloid collision efficiencies in natural porous media are lacking. In most studies, step-input experiments were conducted and the resulting colloid breakthrough data were not evaluated in terms of deposition kinetics. Step-input experiments have the disadvantage that often relatively large amounts of colloids are introduced into the column. As a result, blocking or filter ripening effects can occur and lead to severe changes in colloid deposition rates with time [Song and Elimelech, 1993a; Kretzschmar *et al.*, 1995; Liu *et al.*, 1995]. Recently, Rodier and Dodds [1993] applied a short-pulse chromatographic technique to study the transport of latex colloids through columns packed with glass beads. Yan *et al.* [1995] analyzed pulse breakthrough curves of latex colloids through glass beads to determine colloid deposition and release rates. Short-pulse experiments have recently also been used to study bacteria transport through porous media [Hornberger *et al.*, 1992; McCaulou *et al.*, 1994].

The aim of this study was to evaluate a short-pulse chromatographic technique for determining colloid deposition rates and collision efficiencies in natural soil and aquifer materials. The term short-pulse is used here to indicate that the injected pulse is much smaller than 1 pore volume; in this study it was between 0.002 and 0.03 pore volumes. To demonstrate the applicability of the method, we present experiments using four different experimental systems of increasing complexity, ranging from a simple model system consisting of glass beads and latex colloids to a more "natural-like" system consisting of soil columns and Fe oxide colloids coated with adsorbed humic acid. The results demonstrate that the short-pulse method can be used very effectively for studying flow rate and ionic strength effects on the deposition kinetics of colloids in heterogeneous natural porous media.

Theoretical Considerations

Under steady state, saturated flow conditions the transport of colloids through porous media can be described by a convective-dispersive transport equation including a term for first-order colloid deposition:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v_p \frac{\partial C}{\partial x} - kC \quad (1)$$

where C is the colloid concentration in solution, t is the elapsed time, x is the travel distance, D is the dispersion coefficient for colloidal particles, v_p is the average travel velocity of colloidal particles, and k is the colloid deposition rate coefficient. In this equation, colloid release is neglected, which is justified if the kinetics of colloid release is very slow in the timescale of a colloid breakthrough experiment. This has, in fact, been observed in many colloid transport experiments conducted at constant flow rate and solution chemistry [McDowell-Boyer, 1992; Kretzschmar *et al.*, 1995]. Based on the assumption of first-order deposition kinetics, colloid breakthrough curves resulting from step-inputs are often evaluated by calculating a clean-bed filter coefficient as

$$\lambda_0 = -\frac{1}{L} \ln \left(\frac{C_f}{C_0} \right) \quad (2)$$

where L is the column length, C_0 is the influent colloid concentration, and C_f is the final effluent colloid concentration after the breakthrough curve has reached a plateau [Iwasaki,

1937; McDowell-Boyer *et al.*, 1986]. For columns with high Peclet numbers the colloid deposition rate coefficient k can then be estimated as

$$k = \lambda_0 v_p = \lambda_0 L / t_p \quad (3)$$

and thus

$$k = -\frac{1}{t_p} \ln \left(\frac{C_f}{C_0} \right) \quad (4)$$

where t_p is the average travel time of the colloidal particles through the column. Here k represents a time- and distance-averaged parameter. The term C_f/C_0 corresponds to the fraction of colloids recovered at the column outlet after the breakthrough curve has reached a plateau.

For breakthrough curves resulting from short-pulse inputs, the colloid deposition rate coefficient can, analogously, be estimated from the fraction of colloids recovered in the effluent as

$$k = -\frac{1}{t_p} \ln \left(\frac{q}{N_0} \int_0^{t_f} C(t) dt \right) \quad (5)$$

where q is the volumetric flow rate, N_0 is the total amount of colloids injected into the column, and t_f is the time at which the colloid pulse has completely moved through the column. The term in brackets of equation (5) corresponds to the fraction of colloids recovered at the column outlet following a pulse input of colloids.

The colloid deposition rate coefficient can also be estimated by fitting a solution of the transport equation (1) to the experimental data using a nonlinear least squares procedure [Parker and van Genuchten, 1984]. For columns with high Peclet numbers and ideal tracer breakthrough behavior, both methods yield practically identical results. However, with soil or aquifer materials, ideal column packing is sometimes difficult to achieve, so that the tracer pulse is not adequately described by a simple convective-dispersive transport equation. In such cases, the integration method (5) yields more reliable results because it is based on mass balance, i.e., the fraction of colloids recovered in the effluent.

The deposition kinetics of colloids in porous media is generally limited by two factors: (1) the frequency of collisions between colloids and matrix surfaces and (2) the fraction of collisions resulting in colloid attachment to the matrix surfaces (collision efficiency, α). The frequency of collisions is mainly a function of physical parameters such as flow velocity, pore size distribution, colloid size, and colloid density. The collision efficiency is largely controlled by the surface chemistry of the colloids and the matrix surfaces. In the absence of a repulsive energy barrier between the colloids and matrix surfaces, every collision results in attachment ($\alpha = 1$) and the deposition kinetics is called fast, or transport-limited. In the presence of a repulsive energy barrier due to electrostatic repulsion of similarly charged surfaces, not every collision results in attachment ($\alpha < 1$) and the deposition kinetics is called slow, or reaction-limited [Elimelech *et al.*, 1995]. If the fast deposition rate (k^{fast}) is known, collision efficiencies can be calculated by normalizing the experimental colloid deposition rates to the rate of fast deposition:

$$\alpha = \frac{k}{k^{\text{fast}}} \quad (6)$$

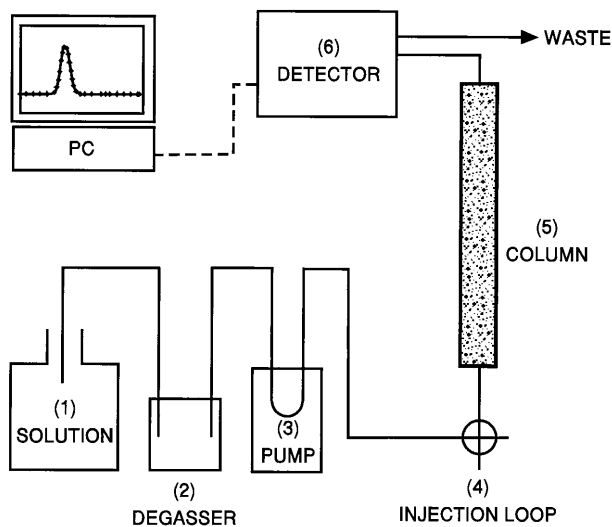


Figure 1. Schematic drawing of the experimental setup used for breakthrough experiments: 1, solution reservoir containing the background electrolyte solution; 2, degasser; 3, high-pressure liquid chromatography pump controlling flow rate; 4, pulse injection loop; 5, glass chromatography column packed with soil or aquifer material; and 6, on-line detection system for colloidal particles connected to a PC for data acquisition.

For simple model systems the fast deposition rate is often estimated theoretically [Elimelech *et al.*, 1995]. However, at present this is not possible for heterogeneous natural porous media, and the fast rates must also be determined experimentally.

Materials and Methods

Column Setup

The column setup used to determine colloid deposition rates (Figure 1) consisted of the following components: (1) a solution reservoir containing the background electrolyte solution, (2) a degasser, (3) a high-pressure liquid chromatography (HPLC) pump controlling the steady state flow rate, (4) a pulse injection loop, (5) a glass chromatography column (Omnifit, Cambridge, England) packed with the porous medium, and (6) an on-line detection system for colloidal particles connected to a PC for data acquisition. A back-pressure regulator was included between the pump and the injection loop to prevent pulsing. The exact flow rates were determined from the weight of effluent collected over a given time period, taking the specific gravity of the salt solutions into account. The column dimensions were varied between 6 and 45 cm length and between 1 and 2.5 cm inner diameter.

After saturating the packed columns with electrolyte solution (NaCl or CaCl₂), tracer breakthrough experiments were conducted to determine the pore volume and column Peclet number, $Pe = \nu L/D$, where ν is the average pore water velocity. Short pulses of electrolyte solutions containing 2.0 mM NO₃⁻ as a conservative tracer were injected using a 0.1-mL injection loop, and the NO₃⁻ concentration in the effluent was monitored on-line using a flow-through UV-VIS detector at a wavelength of 220 nm. From the calculated first and second moments of the NO₃⁻ breakthrough curve, the average travel time of the tracer and the dispersion coefficient were calculated [Villiermaux, 1981]. Fitting the convective-dispersive

transport equation to the NO₃⁻ breakthrough data using a nonlinear least squares procedure gave very similar results [Parker and van Genuchten, 1984]. That NO₃⁻ behaved as a truly conservative tracer in the soil and aquifer materials used was verified in several ways: (1) NO₃⁻ breakthrough experiments in 0.01 and 0.5 M CaCl₂ background electrolyte solutions gave identical results; (2) the breakthrough of NO₃⁻ was independent of the nitrate concentration injected; (3) the peak areas of NO₃⁻ breakthrough curves agreed well with those of bypass experiments (same setup but without column); and (4) the pore volumes determined from NO₃⁻ breakthrough curves agreed well with those calculated from the soil dry weight, soil particle density, and column dimensions.

For measuring colloid deposition rate coefficients, 0.1-mL pulses (equivalent to 0.002 to 0.03 pore volumes) of well-dispersed, dilute colloidal suspensions were injected at the column entrance under steady state, saturated flow conditions. The colloid concentrations in the effluents were monitored on-line using flow-through detection systems. Pulse breakthrough curves were analyzed by numerical integration and calculation of the colloid deposition rate coefficients according to (5). The total amounts of colloids injected (N_0) were determined from bypass experiments using the same setup but excluding the column. Some experiments were also analyzed by fitting the transport equation (1) to the experimental data using a nonlinear least squares procedure [Parker and van Genuchten, 1984]. Both methods gave practically identical results for the colloid deposition rate coefficients.

In addition, step experiments were conducted and the resulting deposition rates were compared with those from pulse experiments. For the step experiments the influent was switched to a continuous input of a dilute colloidal suspension using a two-way valve instead of a pulse injection loop. The plateau values C_f/C_0 were used to calculate the deposition rate coefficients according to (4).

Colloid breakthrough experiments were conducted using four different experimental systems of increasing complexity: columns packed with glass beads and latex colloids (system 1); packed soil columns and latex colloids (system 2); columns packed with calcareous aquifer material and latex colloids (system 3); and packed soil columns and humic-coated Fe oxide (α -Fe₂O₃) colloids (system 4). The first two systems were used to demonstrate that short-pulse and step-input experiments yield identical colloid deposition rate coefficients. Systems 2–4 were used to evaluate the short-pulse method for studying the effects of electrolyte concentration (system 2) and flow velocity (systems 3 and 4) on the kinetics of colloid deposition kinetics in calcareous and noncalcareous natural porous media. In the following sections, the four experimental systems are described in greater detail.

System 1: Glass Beads/Latex Colloids

A first set of experiments was conducted on the transport of negatively charged latex colloids through columns packed with glass beads, i.e., a simple and well-defined model system which has frequently been used in colloid filtration studies [Fitzpatrick and Spielman, 1973; Elimelech and O'Melia, 1990; Elimelech, 1991; Rodier and Dodds, 1993; Yan *et al.*, 1995]. Both step-input and short-pulse experiments were conducted at different solution ionic strengths to directly compare the results of both methods.

Soda-lime glass beads (Sovitec, Florange, France) were passed through standard mesh sieves to obtain a size fraction

between 355 and 400 μm in diameter. The glass beads were cleaned by acid washing with HCl/chromic acid as described by *Litton and Olson* [1993] and wet packed into glass chromatography columns with 2.4-cm inner diameter and 32-cm length. The packing porosity, determined from NO_3^- breakthrough experiments, was 0.39, and the column Peclet number was $\sim 10^3$.

The columns were preequilibrated with solutions containing varying concentrations of NaCl and NaHCO_3 , giving different ionic strengths and $p\text{H}$ 9.5 in equilibrium with atmospheric CO_2 . The actual ionic strength of the solutions was calculated from the weighted sum of all ionic species in solution [*Stumm and Morgan*, 1996].

Transport experiments were conducted with negatively charged, fluorescent, monodisperse polystyrene latex microspheres with sulfate surface functional groups (sulfate latex batch 1-FY-200,1; Interfacial Dynamics Corporation, Portland, Oregon). The average diameter of the latex colloids was 0.20 μm . Pulses (0.1 mL; 30 mg L^{-1} latex) or continuous step inputs (0.5 mg L^{-1} latex) of suspensions were introduced into the column under saturated flow conditions at a constant flow rate of 2.8 mL min^{-1} . This corresponds to a pore water velocity of 95 cm h^{-1} . All short-pulse experiments were conducted on the same column, whereas for each step experiment a fresh column was prepared. The concentration of colloids in the effluent was measured on-line using a flow-through fluorescence spectrophotometer (Jasco model 821-FP, Jasco Limited, Hachioji City, Japan) with a cell volume of 16 μL . The excitation and emission wavelengths were 490 and 515 nm, respectively.

System 2: Soil/Latex Colloids

In a second set of experiments we measured the deposition rates of negatively charged latex colloids during saturated flow through packed soil columns at various ionic strengths using both step and short-pulse experiments. Samples were collected from the EB horizon of a sandy alluvial soil (Winzlerboden, Psammentic Hapludalf) in northern Switzerland. The soil material consisted of about 90% sand, 5% silt, and 5% clay, had $p\text{H}$ 4.1 (in 0.01 M CaCl_2), and contained approximately 1.5 g kg^{-1} total carbon. Several kilograms of moist soil were thoroughly mixed to produce a homogeneous batch, sieved to pass a 2-mm screen, air dried, and stored. To achieve uniform and reproducible column packings, an aggregate size fraction between 0.20 and 0.63 mm was separated by dry sieving. This material was packed into glass chromatography columns with 1.0-cm inner diameter and lengths between 6 and 45 cm. The columns containing the dry soil were purged with CO_2 gas and were then water-saturated by slowly pumping a 0.5 M CaCl_2 solution through a degasser and then through the column in the upward direction. In order to conduct experiments with carefully controlled solution chemistry, the soil columns were saturated with Ca^{2+} by leaching them with at least 50 pore volumes of 0.5 M CaCl_2 solution. The ionic strength was then reduced to 10 mM CaCl_2 for tracer pulse experiments and further adjusted for colloid transport experiments. The effluent solutions of the preequilibrated soil columns had $p\text{H}$ values between 5.6 and 5.8. The column porosity determined from NO_3^- tracer experiments was approximately 0.50, and the column Peclet numbers were between 107 and 517.

Transport experiments were conducted with negatively charged, fluorescent, monodisperse polystyrene latex microspheres with carboxyl surface functional groups (carboxylate modified latex (CML) batch 2-FY-100,1; Interfacial Dynamics

Corporation, Portland, Oregon). The latex colloids had an average diameter of 0.11 μm . Short pulses (0.1 mL; 6.30 mg L^{-1} latex) or continuous step inputs (0.63 mg L^{-1} latex) of suspensions were introduced into the columns at a constant flow rate of 1.0 mL min^{-1} , and the effluent colloid concentrations were measured on-line using a flow-through fluorescence spectrophotometer as described for system 1. The resulting pore water velocity in these experiments was approximately 153 cm h^{-1} .

System 3: Calcareous Aquifer/Latex Colloids

In a third set of experiments the effect of flow velocity on the deposition rate of negatively charged latex colloids moving through calcareous aquifer material was studied. The aquifer material was collected from a coarse-grained, calcareous aquifer in northern Switzerland. Several kilograms of moist material were thoroughly mixed to produce a homogeneous batch, sieved to pass a 2-mm screen, air dried, and stored. The calcareous aquifer material had $p\text{H}$ 8.0 and coarse sandy texture. For column experiments the same size fractionation, column packing, and preequilibration procedures were used as described for system 2. The resulting packing porosity of the aquifer material was approximately 0.46. The experiments were conducted using two different column dimensions: one column with 1-cm inner diameter and 45-cm length ($Pe = 393$) and the other with 2.5-cm inner diameter and 10-cm length ($Pe = 161$).

After preequilibrating the aquifer columns with 0.5 M CaCl_2 , the ionic strength was reduced by flushing with several pore volumes of deionized water which had previously been equilibrated for several days with CaCO_3 (Fluka Chemie, Buchs, Switzerland). The column influent and effluent solutions had Ca concentrations of 0.17 ± 0.02 mM and $p\text{H}$ 8.4. Colloid transport experiments were conducted at flow rates between 0.05 and 0.98 mL min^{-1} using the same carboxyl latex colloids as described above for system 2. The pore water velocities in this experiment were between 1.3 and 163 cm h^{-1} .

System 4: Soil/Iron Oxide Colloids

In a fourth set of experiments we used the short-pulse technique to study the deposition kinetics of humic-coated iron oxide colloids in soil columns as a function of flow velocity. Soil columns were prepared and preconditioned as described for system 2, but the column dimensions were the same as in system 3. The column Peclet numbers were 547 for the long column and 159 for the short column.

Hematite colloids were synthesized by aging a completely neutralized, condensed ferric Fe hydroxide gel for 65 hours at 100°C [*Sugimoto and Sakata*, 1992]. Excess salt was removed by washing and dialysis for 12 days. The resulting hematite was well-crystalline, and no impurities could be detected by X ray diffraction analysis and transmission electron microscopy (TEM). The number average diameter of the hematite colloids as determined from TEM micrographs was 122 nm, with 29 nm standard deviation.

Soil humic acid was extracted and purified from an acidic surface soil using standard procedures [*Schnitzer*, 1982; *Kretzschmar et al.*, 1997]. For colloid transport experiments, suspensions of humic-coated hematite were prepared by equilibrating 30 mg L^{-1} hematite with 1 mg L^{-1} organic carbon as soil humic acid for 24 hours at $p\text{H}$ 5.8 in 0.1 M CaCl_2 . The electrophoretic mobility of the humic-coated hematite colloids was $-2.3 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ at $p\text{H}$ 5.8, indicating negative net

particle surface charge. For comparison, the hematite colloids without humic acid were positively charged and had an electrophoretic mobility of $+3.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ at pH 5.8.

Short pulses (0.1 mL; 30 mg L^{-1} hematite) of suspension were injected into the columns at constant flow rates between 0.05 and 1.0 mL min^{-1} . All experiments were conducted in 0.1 mM CaCl_2 electrolyte solution with pH 5.8. The colloid concentration in the effluent was monitored using a flow-through UV-VIS spectrophotometer (Linear model 204, Linear, Reno, Nevada) at a wavelength of 430 nm.

Results and Discussion

Influence of Electrolyte Concentration

In the first two sets of experiments (systems 1 and 2), colloid deposition rates were determined using both step and short-pulse breakthrough experiments. In each of the two systems the electrolyte concentration was varied over almost 2 orders of magnitude. System 1 was a simple model system (latex/glass beads/NaCl electrolyte) which has frequently been used in colloid filtration studies [Fitzpatrick and Spielman, 1973; Elimlech and O'Melia, 1990]. System 2 represented a more complex system, i.e., transport of latex colloids through soil columns in the presence of Ca^{2+} . Such experiments could be of interest in field-related studies in which fluorescent latex particles are injected as model colloids [Harvey et al., 1989; Higgs et al., 1993]. Such systems could also be used to study the effects of a complex and heterogeneous matrix (rough surfaces, complex pore geometry, microporosity, charge heterogeneity, etc.) on colloid transport and deposition without confounding the effects with polydispersity effects of the colloids themselves.

Typical breakthrough curves obtained for the model system (system 1) are presented in Figure 2. Colloid breakthrough occurred after approximately 1 pore volume, and the breakthrough curves resulting from step-inputs reached a stable plateau after approximately 1.3 pore volumes (Figure 2a). The final C/C_0 value at the plateau strongly decreased with increasing electrolyte concentration. Similarly, the area of breakthrough peaks resulting from short-pulse inputs decreased with increasing electrolyte concentration (Figure 2b). The short-pulse breakthrough curves exhibited little tailing, indicating that the release of colloids was very small. The first-order kinetic deposition rate coefficients determined from such experiments are summarized in Figure 2c.

The breakthrough experiments for latex colloids through Ca^{2+} saturated soil yielded similar results (Figure 3). In the soil columns, however, colloids traveled considerably faster than the conservative tracer, resulting in colloid breakthrough after approximately 0.84 pore volumes (Figures 3a and 3b). This is due to a size exclusion effect, in which colloidal particles are excluded from small pores and hence from part of the total pore space. Similar size exclusion effects have previously been observed in studies on colloid transport through natural porous media [Higgs et al., 1993; Kretzschmar et al., 1995]. Like in the simple model system, colloid breakthrough curves resulting from step-inputs leveled off and formed a plateau (Figure 3a). However, at the lowest ionic strength (0.15 mM CaCl_2), the colloid concentration in the effluent continued to increase slightly, possibly due to blocking effects [Liu et al., 1995]. The initial colloid deposition rate coefficient, calculated from the normalized effluent concentration after 1.3 pore volumes, may have been slightly underestimated in this experiment. The colloid deposition rate coefficients determined from the step and

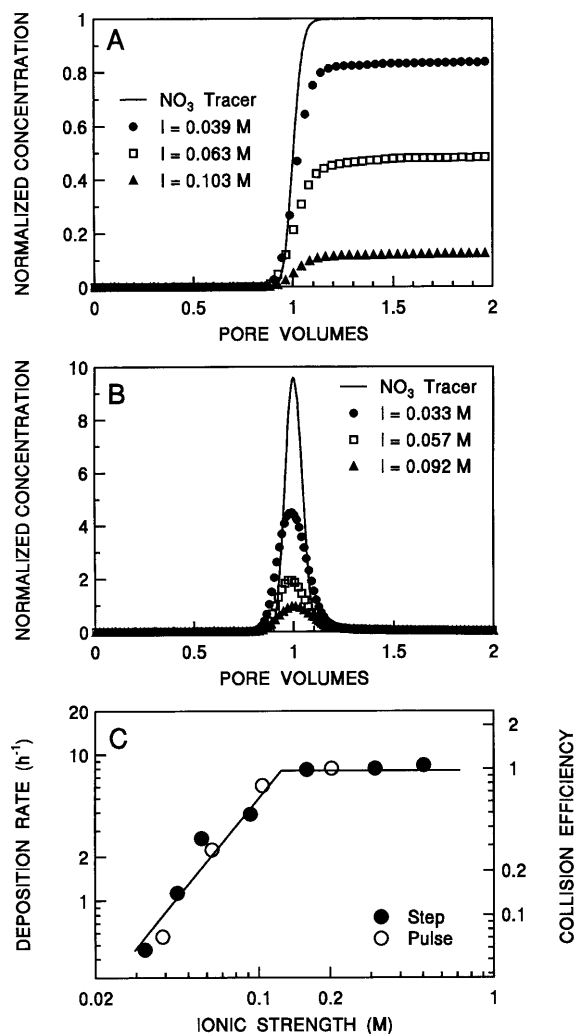


Figure 2. Influence of electrolyte concentration (NaCl) on transport and deposition kinetics of sulfate latex colloids in columns packed with soda-lime glass beads (pH 9.5; system 1). (a) Breakthrough curves resulting from step experiments. (b) Breakthrough curves resulting from short-pulse experiments. (c) Deposition rate coefficients and experimental collision efficiencies determined from step and short-pulse experiments.

short-pulse breakthrough experiments are summarized in Figure 3c.

Figures 2c and 3c represent typical “stability plots” for colloid deposition. Both are characterized by two distinct regions: (1) At low ionic strength the colloid deposition rate strongly increases with increasing electrolyte concentration. In this region, electrostatic repulsive forces between colloids and matrix surfaces significantly reduce the collision efficiency ($\alpha < 1$; slow deposition). (2) At higher ionic strength the deposition rate is independent of electrolyte concentration. In this region, the surface charge is well screened so that electrostatic repulsive forces are insignificant. As a result, every collision results in attachment and the deposition rate is only limited by the frequency of colloid-matrix collisions ($\alpha = 1$; fast deposition).

The transitions from the slow to the fast deposition regimes occurred approximately at 0.120 M NaCl for system 1 and at 0.001 M CaCl_2 for system 2. Thus, in the Ca^{2+} system, this transition occurred at approximately 120 times lower concen-

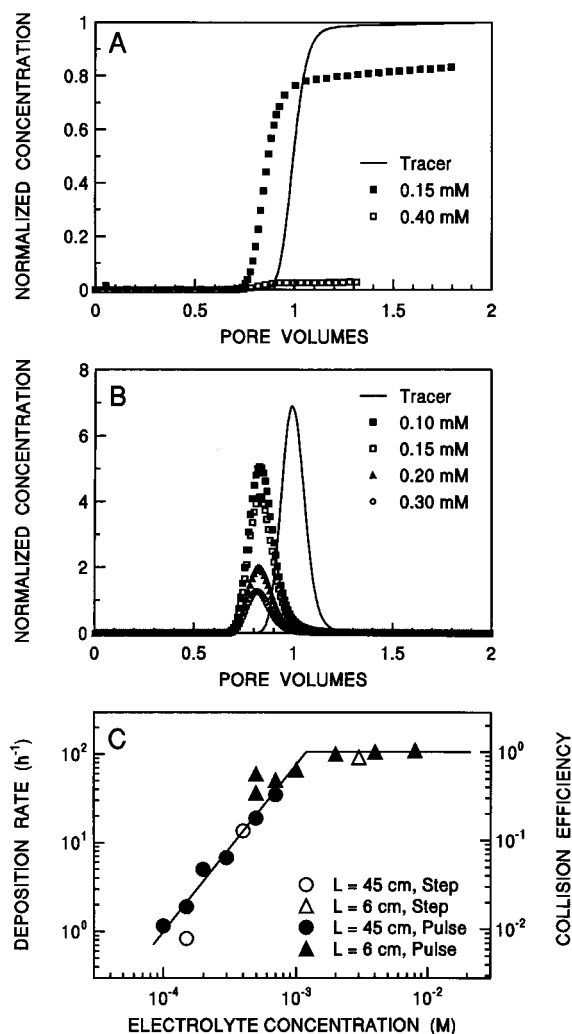


Figure 3. Influence of electrolyte concentration (CaCl_2) on transport and deposition kinetics of carboxyl latex colloids in columns packed with sandy soil material (pH 5.8; system 2). (a) Typical breakthrough curves resulting from step experiments; column length, 45 cm. (b) Typical breakthrough curves resulting from short-pulse experiments; column length, 45 cm. (c) Deposition rate coefficients and experimental collision efficiencies determined from step-input and short-pulse experiments; column length, 6 or 45 cm.

trations compared with the Na^+ system. Even though the two systems are not directly comparable, most of this difference is a result of the different valencies of the two cations Na^+ and Ca^{2+} and can be explained by the classical DLVO theory [Hiemenz, 1986]. Similar concentrations of Na^+ and Ca^{2+} have recently been reported to induce rapid attachment of montmorillonite colloids to mineral surfaces [Degueldre et al., 1996].

For simple and well-characterized model systems, fast deposition rates can be estimated theoretically [McDowell-Boyer et al., 1986; Elimelech et al., 1995]. However, for heterogeneous natural porous media, this is currently not possible. Only if the fast deposition rate can be determined experimentally can the data be expressed in terms of collision efficiencies α . The collision efficiency for colloid deposition reflects the chemical interactions between colloids and matrix surfaces and is, as a first approximation, independent of physical parameters such

as column packing, grain size, or bulk density. This allows comparisons of results obtained for different experimental systems, for example, columns packed with different soil or aquifer materials. The collision efficiencies are indicated by the right y axes of Figures 2c and 3c. To our knowledge, such complete stability plots including regions of slow and fast deposition have not previously been published for colloid deposition in heterogeneous soil or aquifer materials. This may partly be due to the difficulty of determining fast deposition rates in natural porous media, where the colloid removal rates are often very high under favorable deposition conditions.

Influence of Flow Velocity

In the third and fourth sets of experiments (systems 3 and 4), the short-pulse technique was applied to study the influence of flow velocity on deposition rates of latex colloids in calcareous aquifer material (system 3) and of humic-coated Fe oxide colloids in sandy soil material (system 4). Adsorption of humic acid to Fe oxides results in reversal of surface charge from positive to negative (at pH 5.8). This, in turn, can result in increased colloidal stability and enhanced transport through natural porous media [Kretzschmar et al., 1995]. Humic-coated oxide colloids can, for example, originate from dispersible surface soil horizons [Kaplan et al., 1993].

Both experimental systems gave similar results (Figures 4 and 5). The breakthrough curves for colloids and the conservative tracer are depicted in Figures 4a and 5a. In both porous media, colloid breakthrough occurred considerably earlier than breakthrough of the tracer, which is due to the exclusion of colloids from small pores. The colloid concentrations detected in the column effluents generally decreased with decreasing flow rate. The fractions of colloids recovered in the effluents (i.e., the integrated peak areas) of columns with different dimensions are plotted in Figures 4b and 5b. At a given pore water velocity the fractions of colloids recovered from the short columns (10 cm) were much larger than those recovered from the longer columns (45 cm).

The colloid deposition rate coefficients as a function of pore water velocity for systems 3 and 4 are depicted in Figures 4c and 5c, respectively. In both experimental systems the colloid deposition rate coefficients increased with increasing pore water velocity. The slopes of the log-log relationships were 0.31 and 0.18 for systems 3 and 4, respectively. This is consistent with a recent theoretical analysis of colloid deposition rates, which predicts that at low to moderate flow velocities the deposition rate increases with flow velocity by a power of zero to one third [Song and Elimelech, 1993b].

Importance of Column Dimensions

In systems 2–4, columns of variable length (6–45 cm) and diameter (1.0–2.5 cm) were used. The results clearly demonstrate that the colloid deposition rate coefficients determined from short-pulse breakthrough experiments are independent of column dimensions (Figures 3c, 4c, and 5c). This strongly supports the assumption underlying equations (1)–(5), that colloid removal from suspension during flow through natural porous media follows a first-order kinetic rate law. It also shows that colloid breakthrough data should, wherever possible, be evaluated in terms of the kinetics of colloid deposition (and release, if it is significant). In many studies on colloid transport through natural porous media, this has not been attempted, even though different flow rates and column dimen-

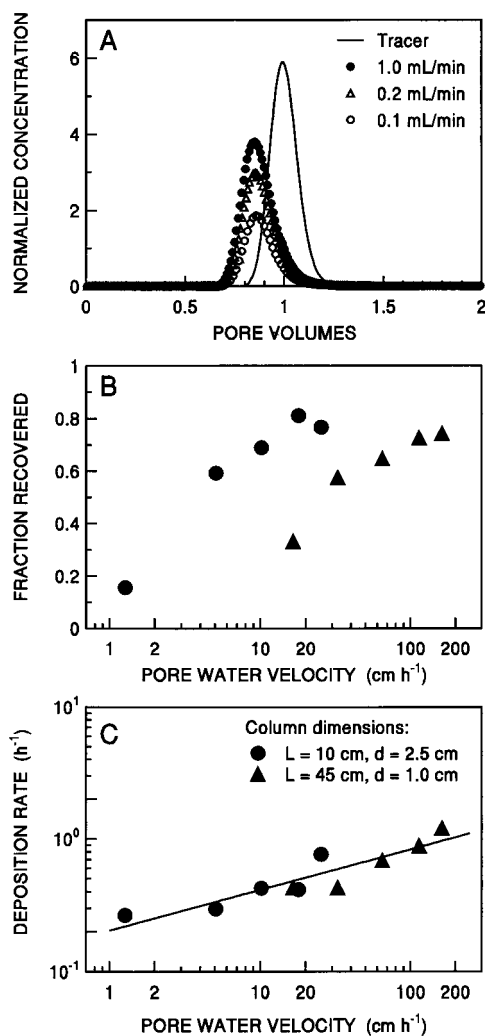


Figure 4. Influence of flow velocity on transport and deposition kinetics of carboxyl latex colloids in columns packed with calcareous aquifer material (pH 8.4; system 3). (a) Typical breakthrough curves for a NO_3^- tracer and colloids resulting from short-pulse inputs. (b) Fractions of colloids recovered in the column effluents (i.e., integrated peak areas) as a function of pore water velocity for two columns with different dimensions (see Figure 4c for legend). (c) Deposition rate coefficients as a function of pore water velocity determined with different column dimensions.

sions were used [Lahav and Tropp, 1980; Vinten and Nye, 1985; Puls and Powell, 1992; Puls et al., 1993].

Because column dimension does not influence the kinetic results obtained, we can (and should) systematically vary the dimensions in order to increase the measurable experimental windows. For example, when studying the effect of electrolyte concentration on colloid deposition kinetics (system 2), the length of the columns had to be varied between 6 and 45 cm. The fast deposition rate was only measurable using a short column (6 cm), because from a longer column, not enough colloids were recovered in the effluent for accurate measurements. Vice versa, the slowest deposition rates could only be measured using a longer column (45 cm), because not enough colloids were retained in a short column. Another example is the study of flow velocity effects on colloid deposition kinetics

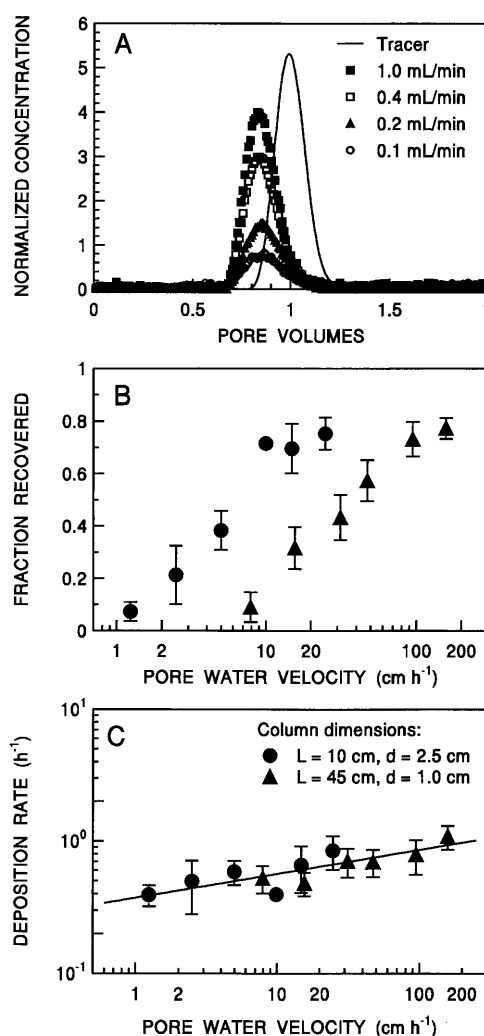


Figure 5. Influence of flow velocity on transport and deposition kinetics of humic-coated hematite colloids in columns packed with sandy soil material (pH 5.8; system 4). (a) Typical breakthrough curves for a NO_3^- tracer and colloids resulting from short-pulse inputs. (b) Fractions of colloids recovered in the column effluents (i.e., integrated peak areas) as a function of pore water velocity for two columns with different dimensions; means and standard deviations of four experiments (see Figure 5c for legend). (c) Deposition rate coefficients as a function of pore water velocity determined with different column dimensions.

(systems 3 and 4). For small pore water velocities, a short column is necessary to recover measurable colloid concentrations in the effluent. Vice versa, the deposition rates at high pore water velocities can better be measured using a longer column. In addition, varying the column diameter expands the range of pore water velocities that can be controlled by a given type of pump delivering a limited range of volumetric flow rates (Figures 4b and 5b).

Step Versus Short-Pulse Experiment

It was shown that the colloid deposition rate coefficients determined from short-pulse breakthrough curves are in excellent agreement with those obtained from the more traditionally used step-input experiments (Figures 2c and 3c). Com-

pared with step-input experiments, the short-pulse method offers several practical advantages:

1. Much smaller amounts of colloids are introduced into the column in each breakthrough experiment. Blocking or filter ripening effects due to deposited colloids are thereby minimized. As a result, replicated experiments or even complete sets of experiments can be run on a single column. For example, all data shown in Figure 5 for a given column geometry were obtained from a single column. The points and error bars in Figures 5a and 5b represent the means and standard deviations of four replicated experiments. The replications were blocked, each block consisting of six experiments at different flow rates in randomized order. No trends were observed that would indicate significant blocking or filter ripening effects due to loading of matrix surfaces with deposited colloids. This greatly facilitates the systematic study of the influence of chemical or physical parameters on the kinetics of colloid deposition. This is especially true in studies on colloid deposition in natural porous media, where uniform column packing and preconditioning are more difficult and tedious than with sieved glass beads or quartz sand.

2. The amounts of colloids needed for a short-pulse experiment are smaller compared with a step experiment. This may turn out to be a great advantage in studies where only small amounts of colloids are available, for example, experiments with natural colloids.

3. When on-line detection systems such as UV-VIS or fluorescence spectrophotometers are used to monitor colloid concentrations in the column effluent, a short-pulse method allows better baseline correction because the baseline is obtained on both sides of the breakthrough peak.

Conclusions

The results of this study demonstrate that the short-pulse method allows fast and accurate determination of colloid deposition rate coefficients during saturated flow through natural soil or aquifer materials. The results were in excellent agreement with those obtained from step-input breakthrough experiments. The kinetic rate coefficients were shown to be independent of column dimensions, confirming the assumption of first-order colloid deposition kinetics. Thus the length and diameter of the columns can be systematically varied in order to expand the measurable range of colloid deposition rates. Furthermore, the short-pulse method offers several practical advantages over the more traditionally used step-input breakthrough experiment, which greatly facilitate the systematic study of colloid deposition kinetics in natural porous media.

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