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Journal of Hydrology 163 (1994) 271–288

Journal of Hydrology

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Colloidal silica transport through structured, heterogeneous porous media

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Received 8 November 1993; revision accepted 24 May 1994

Abstract

In order to better understand factors controlling the migration of inorganic colloids through heterogeneous porous media, the transport of colloidal silica through columns containing a single preferred flow path was investigated. The preferred flow path, which consisted of a tubule of coarse-grained sand, was embedded in a matrix of fine-grained sand. The relative importance of advection, dispersion, deposition (removal of particles from suspension), entrainment (resuspension of deposited particles), and mass exchange between the two pore water regions was evaluated by comparing experimental data to calculations of a two-dimensional advection-dispersion model. Results of this comparison indicate that silica movement could be understood in terms of advective-dispersive transport in the preferred flow path and surrounding matrix with small interaction between the adjacent regions. Deposition of silica was found to follow a first-order kinetic process and was at least partially reversible.

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1. Introduction

The movement of both inorganic and organic contaminants through subsurface environments may be influenced by the presence of colloidal particles which exist suspended in groundwater (McCarthy and Zachara, 1989; Penrose et al., 1990; Torok et al., 1990). Some colloids, such as viruses and bacteria, may represent a source of pollution themselves (McDowell-Boyer et al., 1986). These issues have stimulated research into factors controlling the fate and transport of colloids in porous media. The effects of advection, dispersion, deposition (removal of particles from suspension), and entrainment (resuspension of previously deposited particles)

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SSDI 0022-1694(94)02543-K

on the migration of colloidal particles has been investigated using laboratory columns packed homogeneously with sand or glass beads (Elimelech and O'Melia, 1990a; Hornberger et al., 1992; McDowell-Boyer, 1992; Puls and Powell, 1992). A complete description of colloid transport in geologic systems, however, will require that the impact of these processes be considered in the presence of physical heterogeneities.

Structured heterogeneities, such as macropores or fractures, are ubiquitous features in subsurface environments. These preferred flow paths are capable of transmitting a disproportionately large volume of flow through the subsurface (Duguid and Lee, 1977; Beven and Germann, 1982); thus, they may exert a dominating influence on colloidal mobility. While the literature is replete with studies of solute movement through macroporous or fractured medium (e.g. Hoogmoed and Bouma, 1980; van Genuchten et al., 1984), only a few studies are available which deal with colloidal transport through heterogeneous systems, and in these cases, bacteria is used almost exclusively as the colloidal particle (Allen and Morrison, 1973; Fontes et al., 1991; Toran and Palumbo, 1992). Perhaps due to the limited availability of experimental data, even fewer attempts have been made to develop and test colloidal transport models which may be suitable for heterogeneous media (e.g. Bonano and Beyeler, 1985). This task is necessary in order to elucidate processes which contribute to particle migration as well as to begin development of a predictive theory of colloidal movement in the natural subsurface.

We focus our attention on the transport of colloidal silica (SiO_2) through laboratory columns containing a single structured heterogeneity. This structured heterogeneity was fabricated from a tubule of coarse-grained sand and embedded in a matrix of fine-grained sand. In order to evaluate the key processes affecting silica transport in these columns, experimental breakthrough curves were compared with those calculated from a two-dimensional advection-dispersion model. For our experimental system, which employs environmentally realistic colloids in combination with a porous medium composed of a natural aquifer material, there are no adequate theoretical or experimental techniques for independently estimating the full compliment of model parameters. Consequently, some of the parameters were determined on the basis of a best fit of the advection-dispersion model to the experimental data. While this approach does not ensure a mechanistic understanding of the processes involved, it does provide a means of quantifying the contributions of advection, dispersion, deposition, and entrainment to the fate and transport of colloidal particles in a structured, heterogeneous porous medium. We view this as an important step in gaining empirical evidence that will be needed in applying predictive models to the migration of colloids through geologic systems.

2. Methods

2.1. Laboratory procedures

Colloidal suspensions of amorphous silica (SiO_2) were prepared from a concentrated sol (PQ Corporation, Ashland, MA). The sol (50% by weight) was diluted to a concentration of 1000 mg L^{-1} with a 10^{-3} M NaCl solution which had been adjusted to pH 8.5 by addition of 0.1 M NaOH. Suspensions then were placed in an ultrasonic bath for one hour in order to disperse the colloidal particles. Upon removal from the bath, the colloidal mixtures were allowed to stand for approximately 36 h at room temperature. Following this equilibration period, the pH was readjusted to 8.5, and the suspensions were sonicated for another 15 min period before introduction into the columns.

Admittedly, the concentration of colloids used in these experiments (1000 mg L^{-1}) is much greater than colloidal concentrations commonly observed in natural environments. This high input concentration was used because of the limited sensitivity of the technique used to measure colloidal concentrations. That is, quantification of particle concentration by measuring the extinction of light with a spectrophotometer provided a lower limit of detection of about 10 mg L^{-1}; therefore, it was necessary to use an input concentration of 1000 mg L^{-1} to obtain adequate resolution between influent and baseline concentrations.

The mean diameter and standard deviation of colloidal silica, as determined by photon correlation spectroscopy (N4MD Sub-Micron Particle Sizer, Coulter Electronics, Amherst, MA), was 91 ± 31 nm. The average zeta potential of the silica particles, in a 10^{-3} M NaCl solution at pH 8.5, was −64.2 mV. This value was estimated from the electrophoretic mobility which, in turn, was measured by microelectrophoresis (Coulter Electronics). Converting electrophoretic mobility to zeta potential involved using particle mobility in coordination with the tabulated numerical calculations of Ottewill and Shaw (1972). These calculations consider corrections for both retardation and relaxation effects.

The columns used were glass chromatography columns (Kontes, Vineland, NJ) with an internal diameter of 4.8 cm. These columns were oriented vertically and sealed at the top and bottom with teflon end-fittings (Kontes, Vineland, NJ). The teflon end-fitting at the base of the column contained a nylon mesh with a nominal pore diameter of 80 μm. This mesh permitted the flow of water and colloids while retaining the sand within the column.

Columns were packed with well rounded quartz sand (Unimin Corporation, New Canaan, UT). Heavy minerals such as magnetite and garnet which are often associated with quartz sand were absent from these samples. A small fraction of the sand, however, possessed an orange-reddish color which is a sign of an iron-oxide coating. The sand was repeatedly rinsed with deionized water (DIW) until the rinse water was free of quartz dust and other suspended impurities. It then was washed in a 10% HNO_3 solution for approximately 1 h, rinsed thoroughly with DIW, and dried at 105°C. The electrophoretic mobility of the quartz sand grains was not determined; however, we assumed that the sand grains possessed a net negative surface charge at pH 8.5 as the isoelectric point of quartz is approximately 2.0 (Parks, 1965).

Displacement experiments were performed in both homogeneously- and heterogeneously-packed laboratory columns. Homogeneous columns were constructed by pouring 440 g of fine sand or 450 g of coarse sand into 250 mL of water standing in the chromatography columns. As used in this paper, 'fine' sand was that which passed through a 0.420 mm sieve but not a 0.297 sieve; 'coarse' sand was that which passed through a 1.00 mm sieve but not a 0.740 mm sieve. The sand beds measured 14.25 cm and 14.5 cm in length for the fine and coarse media respectively. The average pore volume of the coarse-grained columns was 110 mL while the average pore volume of the fine-grained columns was 100 mL (Table 1).

The structured, heterogeneous columns also were fabricated by wet packing. A thin-walled glass tube (1.6 cm i.d.) was first inserted into the center of the column containing 250 mL of water, and the fine sand (390 g) was added carefully to the column so that it evenly surrounded the glass tube. Once this was accomplished, the coarse sand (60 g) was poured gently into the tube, and the tube was slowly withdrawn from the column. Measurements of the total pore volume and length of the sand pack were similar to those of the homogeneous columns (Table 1).

All column experiments were performed in duplicate. Prior to injection of the silica suspension, a particle-free solution of 10^{-3} M NaCl, which had been adjusted to pH 8.5, was introduced to the top of the columns. At least 25 pore volumes of this solution was applied in order to thoroughly flush the columns of particles suspended from the quartz sand as well as stabilize the pH of the system. The downward flow of the salt solution was controlled by a variable-flow peristaltic pump located beyond the column outlet. Following equilibration of the columns, application of the particle-free solution was terminated, and the colloidal suspension was injected into the columns at a constant rate (Table 1). Samples of effluent were collected at the base of the columns at 0.1 pore volume increments in Pyrex test tubes by use of a fraction collector and analyzed for colloidal concentrations by light scattering. The extinction of light was measured at a wavelength of 400 nm with a Model 1001 Plus spectrophotometer (Milton Roy, Rochester, NY). The duration of the colloidal injection for the three media treatments depended on the time required for relative concentrations to reach $C/C_0 = 0.95$ (Table 1). After this concentration was achieved, injection of the colloids was terminated, and the particle-free solution was reapplied until colloid concentrations in the effluent returned to baseline levels.

In order to characterize the hydraulic properties of the homogeneous and heterogeneous columns, additional displacement experiments were performed using

Table 1

Measured parameters for the fine homogeneous (FINE), coarse homogeneous (COARSE), and structured heterogeneous (SHE) column experiments conducted with chloride and colloidal silica

	Chloride			Silica		
	FINE	COARSE	SHE	FINE	COARSE	SHE
Column height (cm)	14.25	14.5	15.0	14.25	14.5	14.5
Pore volume (cm^3)	100	110	112	100	109	109
Porosity ($cm^3 cm^3$)	0.38	0.39	–	0.38	0.39	–
Discharge rate ($cm^3 h^{-1}$)	102	104	106	106	108	108
Darcian velocity ($cm h^{-1}$)	5.7	5.7	26.7, 2.5[a]	5.9	6.0	27.1, 2.5[a]
Pulse duration (h)	1.27	1.89	3.26	1.83	2.42	3.40

[a] These values were calculated from Eqs. (3) and (4). The first value is the Darcian velocity within the preferred flow path (q_A) and the second value is the Darcian velocity within the fine-grained matrix (q_B).

chloride as a conservative tracer. These tests, which also were performed in duplicate, involved displacing a 10^{-3} M $NaNO_3$ solution with an equimolar solution of NaCl. The flow rates used in these column runs were similar to those of the colloid experiments (Table 1).

2.2. A two-dimensional advection-dispersion model

For the columns with a structured heterogeneity, the transport in a system with radial symmetry can be described by a two-dimensional advection-dispersion equation:

$$\frac{\delta C}{\delta t} = \frac{q}{n}\alpha_{\mathrm{L}}\frac{\delta^2 C}{\delta z^2} + \frac{q}{n}\alpha_{\mathrm{T}}\frac{\delta^2 C}{\delta r^2} + \frac{q}{n}\frac{\alpha_{\mathrm{T}}}{r}\frac{\delta C}{\delta r} - \frac{q}{n}\frac{\delta C}{\delta z} - k_c C + k_y S \tag{1}$$

where C is the concentration of colloidal particles in suspension (mg cm^{-3}), t is the time (h), z is the coordinate parallel to flow (cm), r is the radial coordinate normal to flow (cm), q is the Darcian velocity (cm h^{-1}), n is the porosity (cm^3 cm^{-3}), α_{L} is the is the longitudinal dispersivity (cm), α_{T} is the transverse dispersivity (cm), S is the concentration of colloidal particles on the solid phase but expressed per volume of pore water (mg mL^{-1}), k_{c} is the deposition coefficient (h^{-1}), and k_{y} is the entrainment coefficient (h^{-1}).

The equation for transport is coupled with the equation for rate-limited deposition and entrainment:

$$\frac{\delta S}{\delta t} = k_{\mathrm{c}} C - k_{\mathrm{y}} S \tag{2}$$

Eqs. (1) and (2) must be solved simultaneously to determine the colloid concentrations in the aqueous and attached phases. Eq. (1) describes the time rate of change of suspended particles due to advection, dispersion, deposition, and entrainment, while Eq. (2) expresses the change in deposited colloidal concentration as the difference between the deposition and entrainment rates.

The computer program of Voss (1984), as modified to account for rate-limited adsorption (Haggerty, 1992), was used to solve the equations subject to the appropriate initial and boundary conditions. The finite element method used in SUTRA (Voss, 1984), involves division of the porous medium into subregions, which for the radially symmetric geometry of this experimental system are a series of wedge-shaped elements. The values of the system parameters are constant within an element but can vary between elements. In this case, the elements can be separated into two distinct groups – elements composing the preferred flow path and elements composing the fine-grained matrix. Discretization of the porous medium in this fashion allows each mobile water domain to be characterized by its own set of transport parameters.

2.3. Parameter estimation

The parameters required to run the two-dimensional model are the longitudinal dispersivity, lateral dispersivity, hydraulic conductivity, porosity, deposition coefficient, and the entrainment coefficient. Estimates of the lateral dispersivity and hydraulic conductivity were obtained by fitting solutions of Eqs. 1 and 2 (by eye) to experimental data on chloride transport through the structured, heterogeneous columns. The porosities of the homogeneously-packed sand columns, which were calculated from measurements of the pore volume, mass of the sand pack, and the density of quartz sand (2.65 g cm^{-3}), were used as the porosities for each domain of the heterogeneous columns. Using the estimates of hydraulic conductivity and porosity, the average linear pore water velocity within each mobile water zone could then be determined by

$$V_A = q_A/n_A = K_A{}^*\Delta H/\Delta L \tag{3}$$

$$V_B = q_B/n_B = K_B{}^*\Delta H/\Delta L \tag{4}$$

where A and B refer to the preferred flow path and fine-grained matrix respectively, K is the hydraulic conductivity, H is the hydraulic head, and L is the column length. We assume that size and charge exclusion effects were small so that the colloidal particles moved at the same rate as the average linear pore water velocity. Such as assumption seems reasonable given that, in our experiments the colloids traveled only a small distance, and the pore size distribution within each mobile water domain was relatively uniform.

Values of k_c were originally calculated using a mathematical expression developed from filtration theory (see, for example, Kim and Rajagopolan, 1982); however, the resulting predictions greatly underestimated observed deposition rates. More precise estimates of k_c were obtained by assuming that the kinetics of particle attachment within each region of the heterogeneous columns could be understood in terms of deposition within homogeneous mixtures of the fine or coarse sand. Estimates of k_c, as well as k_y, were obtained by applying the one-dimensional form of the advection-dispersion equation to breakthrough curves produced from silica transport through columns packed homogeneously with either the fine or coarse sand. The equations describing this one-dimensional transport are

$$\frac{\delta C}{\delta t} = \frac{q}{n}\alpha_L \frac{\delta^2 C}{\delta z^2} - \frac{q}{n}\frac{\delta C}{\delta z} - k_c C + k_y S \tag{5}$$

$$\frac{\delta S}{\delta t} = k_c C - k_y S \tag{6}$$

Values of the longitudinal dispersivity were similarly determined by fitting solutions of the advection-dispersion equation to experimental data on chloride transport through the fine or coarse sand beds. Chloride travels conservatively through quartz sand, so the kinetic coefficients were set to zero leaving only the dispersivity to be optimized.

The parameters required for the one-dimensional simulations (α_L, k_c, and k_y) were estimated using the nonlinear least-squares curve fitting routine of Van Genuchten (1981) with a constant-flux lower boundary condition. This algorithm calculates three dimensionless groups that correspond to the non-dimensional form of the advection-dispersion equation. These dimensionless groups are the Peclet number (Pe), an equilibrium partition coefficient (R), and a dimensionless mass transfer coefficient (w) which, in turn, are related to the parameters of concern by: $\alpha_l = L/\text{Pe}$; $k_c = w(q/n_L)$ and $k_y = k_c/(1 - R)$.

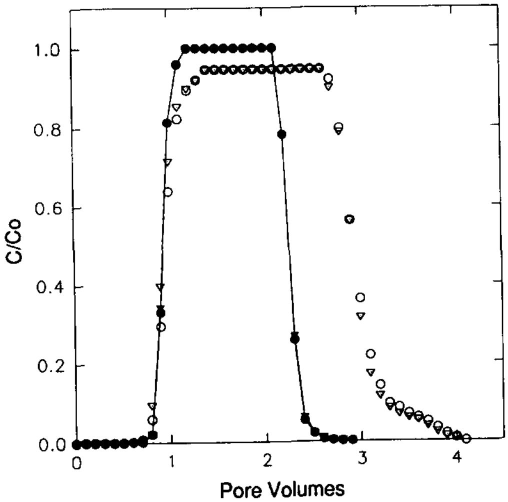

Fig. 1. Duplicate breakthrough curves of chloride (solid symbols with lines) and colloidal silica (hollow symbols) for columns packed homogeneously with fine-grained sand.

3. Results

3.1. Modeling transport in homogeneous media

Relative to the breakthrough curves of chloride, those of silica could be characterized by a slow approach to $C/C_0 = 1.0$ as well as elution-front tailing (Figs. 1 and 2). This deviation from the ideal behavior of a conservative tracer results primarily from rate-limited interactions between the colloidal particles and the quartz collectors (i.e.

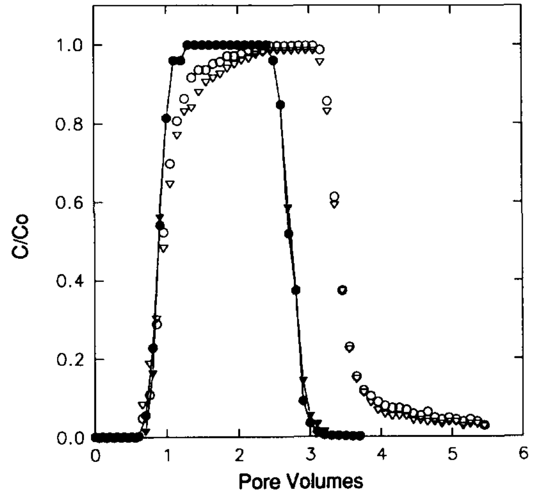

Fig. 2. Duplicate breakthrough curves of chloride (solid symbols with lines) and colloidal silica (hollow symbols) for columns packed homogeneously with coarse-grained sand.

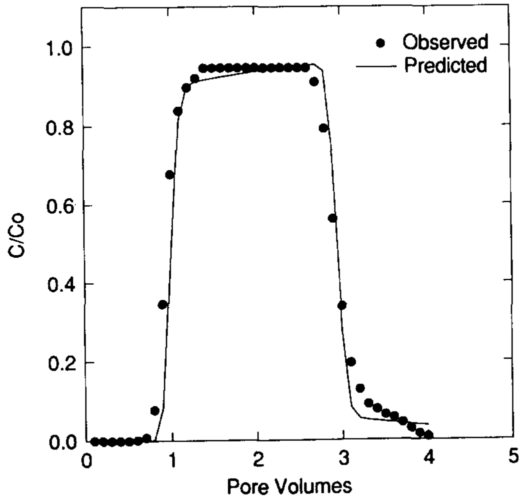

Fig. 3. Concentrations as predicted by the first order advection-dispersion model and those measured experimentally for silica transport through fine-grained, homogeneous media. Solid circles represent averaged concentrations from duplicate experiments.

sand grains). The one-dimensional advection-dispersion equation, modified for first-order deposition and entrainment, was capable of reproducing the features of the silica breakthrough curves quite well using small values for the deposition coefficient (Figs. 3 and 4). Optimal values of k_c were slightly smaller for the fine relative to coarse-grained experiments, and for both cases, time scales for attachment (k_c^{-1}) were on the order of hours (Table 2). Silica deposition was at least partially reversible

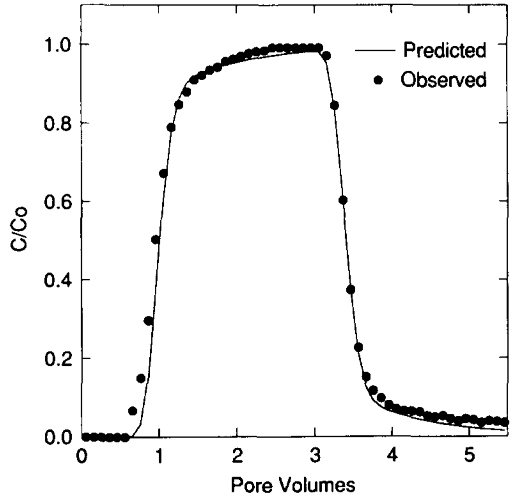

Fig. 4. Concentrations as predicted by the first order advection-dispersion model and those measured experimentally for silica transport through coarse-grained, homogeneous media. Solid circles represent averaged concentrations from duplicate experiments.

Table 2
Fitted parameters describing silica transport through fine- and coarse-grained homogeneous media. The Peclet Numbers were estimated from the chloride data. Standard errors are in parenthesis

Parameter	Fine sand	Coarse sand
Pe	339.3 (30.2)	91.8 (12.8)
w	0.105 (0.027)	0.123 (0.024)
R	1.22 (0.115)	1.12 (0.024)
α_L (cm)	0.042	0.158
k_c (h^{-1})	0.114	0.130
k_y (h^{-1})	0.518	1.082

as best exhibited by the significant tailing of the breakthrough curves. Similarly to k_c, estimates of k_y were marginally greater in the coarse- relative to fine-grained column experiments (Table 2).

The close agreement between modeled and experimental concentrations was achieved by using estimates of dispersivity obtained from chloride displacement experiments. The dispersivity of the coarse sand pack was roughly three times greater than that of the fine sand bed (Table 2). This result is in qualitative agreement with past studies that have demonstrated a direct relationship between the magnitude of dispersivity and the size of the mineral grains (Harleman et al., 1963; Klotz and Moser, 1974).

3.2. Migration of chloride and colloidal silica through structured, heterogeneous media

The multiple inflections in the chloride breakthrough curve are indicative of advective-dispersive transport along pathways of differing velocity (Fig. 5). Initial breakthrough occurred at 0.2 pore volumes as the chloride tracer was quickly

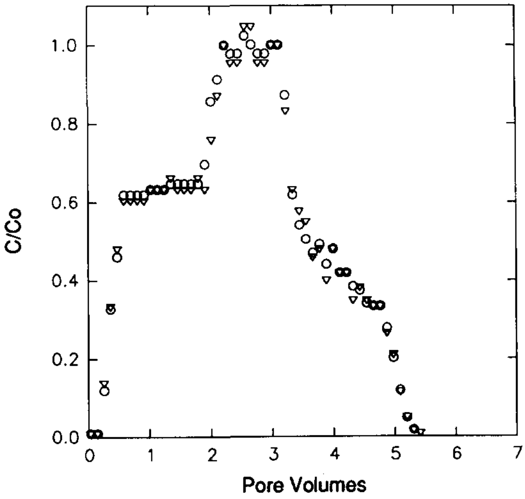

Fig. 5. Duplicate breakthrough curves of chloride for columns containing a structured heterogeneity.

transported through the preferred flow path. Effluent concentrations rapidly increased until approximately 0.6 pore volumes and then leveled off at a concentration of $C/C_0 = 0.6$ signalling that all of the chloride-free water within the preferred flow path had been displaced by the salt tracer. At 2 pore volumes, the concentrations again began to increase towards $C/C_0 = 1.0$ resulting from tracer delivery through the fine-grained matrix. After the input pulse was terminated and the chloride-free water was reapplied (at 3.1 pore volumes), the output concentrations rapidly declined as the preferred flow path was flushed of chloride. The decline in concentration beginning at roughly 3.5 pore volumes and lasting until the conclusion of the experiment represents the elution of chloride from the fine-grained matrix.

The breakthrough curve of silica is similar in appearance to that of chloride indicating that, within this heterogeneous system, solute and colloids were governed by the same advective-dispersive transport processes (Fig. 6). Unlike chloride, silica migration was influenced by rate-limited reactions with the quartz sand which prevented effluent concentrations from reaching unity ($C/C_0 = 1.0$) during the course of the experiment. Deposition of silica seemed to be partially reversible – the breakthrough curves exhibit a substantial tail and nearly all (> 99%) of the colloidal input mass was recovered from the base of the columns.

3.3. Two-dimensional modeling

3.3.1. Sensitivity analyses

Initial simulations with the two-dimensional model involved examining the effect of changes in transverse dispersivity on colloidal transport behavior. Results of these simulations show that as this parameter is increased, the inflections in the breakthrough curves become less pronounced and the curves approach a shape similar to that for a homogeneous column (Fig. 7). This behavior suggests that an increase

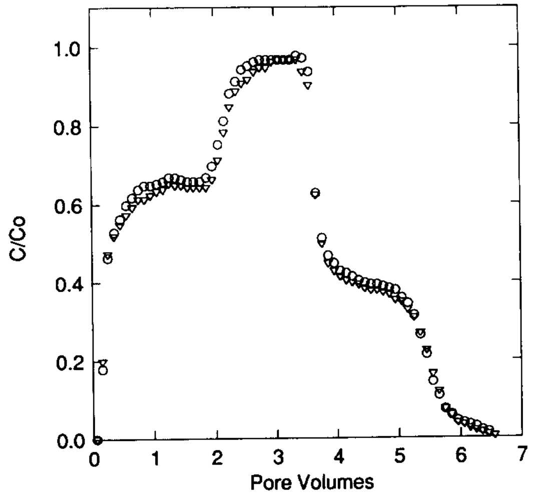

Fig. 6. Duplicate breakthrough curves of colloidal silica for columns containing a structured heterogeneity.

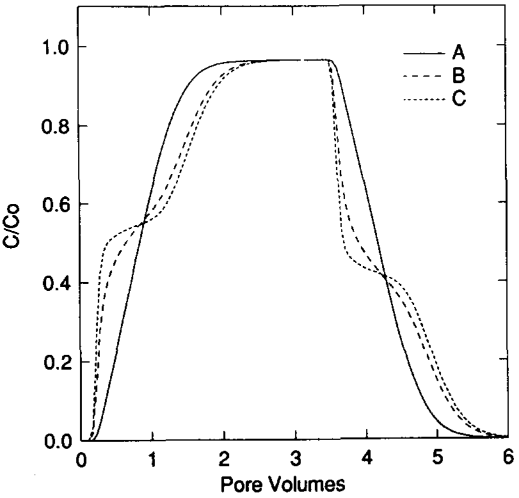

Fig. 7. Sensitivity of effluent concentrations to transverse dispersivity. Transverse dispersivities were set at (A) 1, (B) 1/10, and (C) 1/100 the values of the longitudinal dispersivity.

in transverse dispersion causes a proportionate increase in mass exchange between the two mobile water regions which, in turn, is reflected by a more complete mixing of colloidal particles between the adjacent domains. It is expected that if the transverse dispersivity were made great enough, the colloidal particles would experience a transport described by a one-dimensional model with some 'effective' longitudinal dispersion.

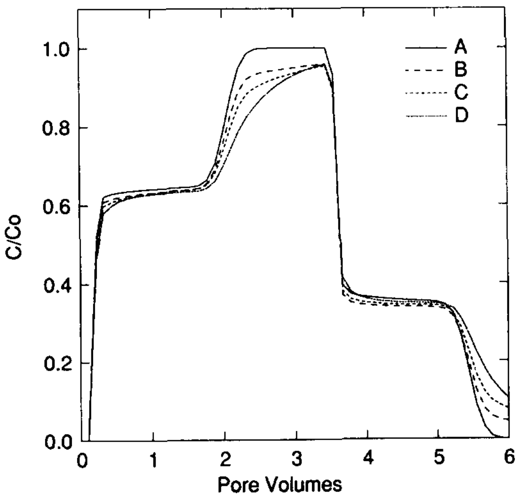

Fig. 8. Sensitivity of colloidal concentrations to the deposition coefficient (k_c) and entrainment coefficient (k_y). (A) no deposition or entrainment, (B) $k_{c\text{-path}} = 0.130\text{h}^{-1}$, $k_{y\text{-path}} = 1.082\text{h}^{-1}$, $k_{c\text{-matrix}} = 0.114\text{h}^{-1}$, $k_{y\text{-matrix}} = 0.518\text{h}^{-1}$, (C) $k_{c\text{-path}} = 0.260\text{h}^{-1}$, $k_{y\text{-path}} = 2.164\text{h}^{-1}$, $k_{c\text{-matrix}} = 0.228\text{h}^{-1}$, $k_{y\text{-matrix}} = 1.036\text{h}^{-1}$, (D) $k_{c\text{-path}} = 0.650\text{h}^{-1}$, $k_{y\text{-path}} = 5.410\text{h}^{-1}$, $k_{c\text{-matrix}} = 0.570\text{h}^{-1}$, $k_{y\text{-matrix}} = 2.590\text{h}^{-1}$.

Table 3
Parameters used in the two-dimensional model

Parameter	Chloride		Silica	
	Path	Matrix	Path	Matrix
α_L (cm)	0.158	0.042	0.158	0.042
α_T (cm)	0.00158	0.00042	0.00158	0.00042
K (cm h^{-1})	3888.0	360.0	3888.0	360.0
k_c (h^{-1})	0.0	0.0	0.130	0.114
k_y (h^{-1})	0.0	0.0	1.082	0.518

An additional sensitivity analysis was performed with the two-dimensional model in order to evaluate the effects of deposition and entrainment on the appearance of the breakthrough curves. These simulations demonstrate that as the magnitude of the kinetic coefficients increase, peak concentrations diminish while elution-front tailing becomes more prominent (Fig. 8).

3.3.2. Modeling the migration of chloride and colloidal silica in structured, heterogeneous media

The purpose of modeling chloride transport was to provide independent estimates of the lateral dispersivity and hydraulic conductivity required for the simulations of silica migration. Agreement between calculated and observed concentrations was found to be the closest when the lateral dispersivity of each pore water domain was set at 1/100 the value of the longitudinal dispersivity (Table 3). Such small values of

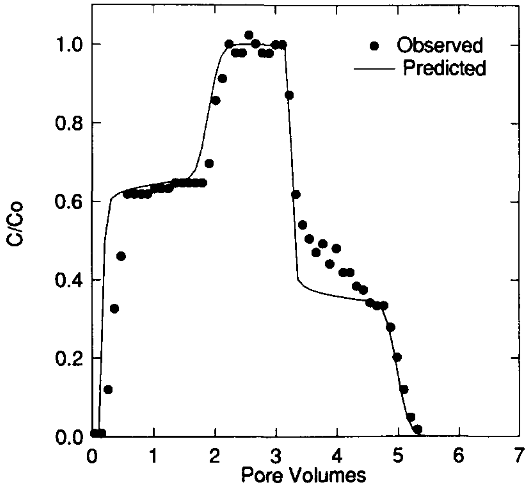

Fig. 9. Concentrations as predicted by the two-dimensional model and those measured experimentally for chloride transport through structured, heterogeneous media. The simulated curve was generated using the parameters shown in Table 3. Solid circles represent averaged concentrations from duplicate experiments.

the lateral dispersivity indicate that mass exchange between the preferred flow path and surrounding matrix was limited in the experiments with chloride.

We based our initial guesses of the hydraulic conductivity of each pore water zone on information gathered from falling head permeameter tests conducted in homogeneous mixtures of the fine and coarse sand. Results of these tests suggested that the coarse sand was 6.4 times more permeable than the fine sand. The best fit to the chloride data, however, was obtained by reducing the permeability of the fine sand so that the ratio in hydraulic conductivity between the two regions was approximately 11 (Fig. 9). The inability to precisely determine the hydraulic conductivity of the matrix material from the permeameter test performed on the fine-grained homogeneous columns is not apparent but may have resulted from slight procedural differences in the manner in which the homogeneous and heterogenous columns were packed.

The parameter set for the silica simulation was similar to the one used for chloride except that rate-limited reactions between the colloids and quartz sand grains were included (Table 3). In general, the two-dimensional model described the data from the silica experiments very well (Fig. 10). The ascending portion of the breakthrough curve was closely reproduced suggesting that the advective-dispersive transport of silica was well represented by the two-dimensional model. Accurate prediction of peak concentrations and the total colloidal mass released over 6 pore volumes indicates that extrapolation of the kinetic parameters from the homogeneous simulations was successful. Experimental concentrations were slightly underpredicted over the interval from 4 to 5 pore volumes. One explanation for this discrepancy is that the nature of mass transfer between the mobile water regions was not depicted well by the two-dimensional model.

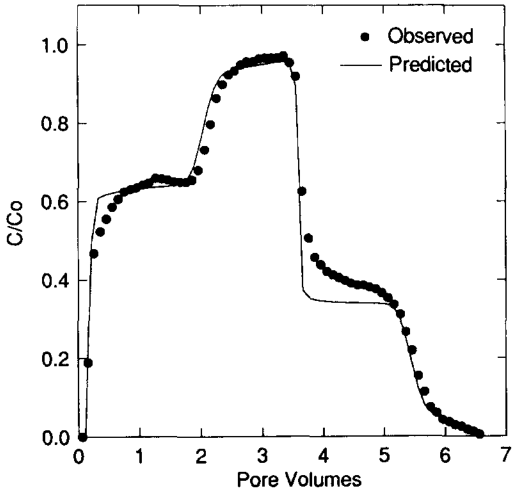

Fig. 10. Concentration as predicted by the two-dimensional model and those measured experimentally for colloidal silica transport through structured, heterogeneous media. Solid circles represent averaged concentrations from duplicate experiments.

4. Discussion

The transport of colloidal silica through columns containing a structured heterogeneity could be closely predicted by a two-dimensional advection-dispersion model modified to account for first-order deposition and entrainment. Although the parameters for deposition and entrainment could not be determined on a theoretical basis, they could be extrapolated successfully from results of the homogeneous columns experiments. In all cases, deposition rates were slow due to electrostatic repulsion arising between the negatively charged surfaces of the silica colloids and quartz sand grains. Under these conditions, some of the attached colloids may have been associated with 'patches' of positive charge present on the quartz sand. The existence of such localized areas of attractive minima has been used to explain deposition of both Brownian and non-Brownian particles in the presence of repulsive electrical double-layer forces (Tobiason, 1989; Elimelech and O'Melia, 1990b).

The effects of grain size on silica deposition in the structured, heterogeneous columns can be elucidated by examination of the results from the homogeneous column experiments. Within the homogeneous columns, we expected attachment rates to be roughly 80% less for the coarse relative to fine media as the value of k_c has been theoretically determined to vary inversely with the 5/3 power of the collector diameter (Tien et al., 1979). Comparison of the fitted values of k_c, however, shows the opposite trend – estimates of k_c were 0.02 h^{-1} greater for the coarse relative to fine media. The discrepancy between theory and observation remains large even when taking into account the standard errors of the parameter estimates (see Table 2 for standard errors) as well as the small variability in deposition rates between duplicate experiments. This anomalous behavior may be attributable to slight differences in the surface composition of the fine and coarse sand, despite efforts to fabricate columns which were chemically identical. According to the supplier, the quartz sand contains trace amounts of metals including iron, aluminum, and titanium which, if distributed unequally between the fine and coarse sand, could cause the unsuspected depositional behavior of silica. The importance of surface contamination has recently been documented by Litton and Olson (1993) who found that impurities remaining on quartz sand following mechanical sieving and certain cleaning procedures strongly affected the attachment efficiencies of latex microspheres. This apparent sensitivity of colloidal deposition to the presence of trace constituents suggests that it may be necessary to consider heterogeneities in the surface composition of the collectors, in addition to collector diameter, if the fate of colloids in geologic materials is to be predicted accurately.

In order to mimic the details of the silica breakthrough curves, it was necessary to retain the term for particle entrainment within the models. This reversible nature of silica attachment is substantiated by mass balance calculations which show that nearly 100% of the input mass was recovered from the homogeneous as well as heterogeneous column experiments. As alluded to above, at least some of the attached silica particles may have been associated with patches of positive charge distributed about the surface of the sand grains. Detachment from these areas of deep energy minima, however, would not be likely as long as the chemical conditions remained unchanged (Bowen and Epstien, 1979; Kolakowski and Matijevic', 1979). Particles may also be removed from the bulk fluid flow by diffusion into dead-end pores or stagnation films that surround the mineral grains (Hunter and Alexander, 1963; Wollum and Cassel, 1978). This removal process would be completely reversible as particles could easily diffuse away from these regions if the local concentration gradients were altered. Such a diffusional mechanism has been incorporated into mathematical models used to describe solute transport through aggregated porous media (e.g. DeSmedt and Wierenga, 1979; Nkeddi-Kizza et al., 1983). In these models, the rate of diffusional exchange is expressed as the difference in concentration between the mobile pore water and the immobile water immediately surrounding the mineral grains.

The ability to extrapolate the parameters describing deposition and entrainment from the homogeneous to heterogeneous system indicates that these processes are relatively insensitive to pore water velocity. By Eqs. (3) and (4), it can be shown that the Darcian velocity within the preferred flow path was more than 350% greater than that measured in the coarse-grained homogeneous experiments, while the Darcian velocity in the fine sand annulus was roughly 60% less than that measured in the fine-grained homogeneous experiments (Table 1). According to the formulations of Tien (1979), the deposition rate for Brownian particles is only weakly dependent on flow rate varying with the 1/3 power of the Darcian velocity. If corrections are made for fluid velocities, deposition rates should be only 0.6 times greater in the preferred flow path relative to the coarse homogeneous columns and 0.2 times less in the fine-grained matrix compared to the fine homogeneous columns. The impact of these changes were assessed by running a two-dimensional simulation with the corrected values of the deposition coefficients. These modifications did not alter the appearance of the breakthrough curve.

While advective-dispersive transport and rate-limited interactions between the particles and sand grains contributed greatly to the breakthrough behavior of colloidal silica, mass transfer between the two domains seemed to play a secondary role. The best fit to the silica breakthrough curve was accomplished by using values for the transverse dispersivity that were two orders of magnitude smaller than the values of the longitudinal dispersivity (Table 3). This small degree of dispersive exchange may reflect the geometry of our experimental system. The extent of interaction is, in part, dependent on the available surface area between the two domains – as the interfacial surface area increases, it is expected that mass transfer processes should proportionately increase. The surface area at the interface of a single, cylindrical channel, used in this study, is small in comparison to other geometries such as a series of spherically- shaped lenses of high permeability. Also, our experiments were designed to have vertical flow in both regions, i.e. to not have advective flow between regions. Consequently, mass exchange between the two domains should be limited.

Although the two-dimensional formulation captured most details of the silica breakthrough curve successfully, experimental concentrations were slightly underestimated over the interval between 4 and 5 pore volumes (see Fig. 10). An order of magnitude increase in the transverse dispersivity improves this discrepancy, but depiction of the ascending limb of the breakthrough curve is made worse. The inability to improve the overall fit suggests that our conceptual model of the flow field is somewhat over-simplified. That is, flow within the heterogeneous columns must occur at more than two discrete pore water velocities. Near the interface between the preferred flow path and fine-grained matrix, a transitional zone must exist where the magnitude of the pore water velocity is intermediate between those velocities measured far away from the interface. Transport of colloidal particles within such a transitional zone will effectively increase colloidal dispersion which would be reflected in the slow decline of experimental concentrations between 4 and 5 pore volumes of the silica breakthrough curve. Although particles are transported at more than two discrete rates through the structured media, such a complication need not be incorporated into the two-dimensional model as the disparities between predicted and experimental concentrations presently observed are small.

5. Summary and conclusions

In this study, we examined the transport of colloidal silica in heterogeneously-packed columns which were constructed by centering a thin vein of coarse sand within a matrix of fine sand. Analysis of the experimental data with respect to a two-dimensional advection-dispersion model indicated that both zones contributed to the transport of silica with over 60% of the total colloidal mass being transmitted through the preferred flow path. While mass exchange between the two mobile water domains was found to be small, rate-limited interactions between the colloids and sand grains contributed significantly to the fate of colloidal silica. Due to the presence of repulsive energy barriers, deposition rates within each pore water region were slow corresponding to time scales for equilibration (k_c^{-1}) on the order of tens of hours. Deposition seemed to be at least partly reversible, as the process of particle entrainment had to be retained within the two-dimensional model in order to mimic the tailing region of the silica breakthrough curves. The reversible nature of deposition is consistent with other column studies in which silica was used as the colloidal particle (e.g. Tipping et al., 1993).

Our results, then, demonstrate that colloidal migration through structured heterogeneous media can be understood and even closely predicted in a well-defined laboratory system. Unfortunately, this task will be much more difficult at the field scale where extreme spatiotemporal variability in the physical properties of the porous media is known to exist. Modeling colloidal movement in the natural subsurface will require extensive measurements of properties that affect colloidal transport.

Acknowledgments

The work reported here was supported jointly by the Environmental Restoration and Waste Management Fellowship program administered by Oak Ridge Associated

Universities and the Subsurface Science Program of the U.S. Department of Energy through Grant Number DE-FG05-89ER0842. We wish to thank Janet Herman, Aaron Mills, and Patricia Wiberg for their constructive comments on an earlier draft of this manuscript. We are also grateful to Liyuan Liang, Phil Jardine, and John McCarthy for their assistance in development of the experimental methods.

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