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Silica-Coated Titania and Zirconia Colloids for Subsurface Transport Field Experiments

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Silica-coated titania (TiO₂) and zirconia (ZrO₂) colloids were synthesized in two sizes to provide easily traced mineral colloids for subsurface transport experiments. Electrophoretic mobility measurements showed that coating with silica imparted surface properties similar to pure silica to the titania and zirconia colloids. Measurements of steady electrophoretic mobility and size (by dynamic light scattering) over a 90-day period showed that the silica-coated colloids were stable to aggregation and loss of coating. A natural gradient field experiment conducted in an iron oxide-coated sand and gravel aquifer also showed that the surface properties of the silica-coated colloids were similar. Colloid transport was traced at $\mu\text{g L}^{-1}$ concentrations by inductively coupled plasma-atomic emission spectroscopy measurement of Ti and Zr in acidified samples.

Introduction

Ever since McCarthy and Zachara (1) emphasized the importance of colloid-facilitated transport of contaminants, researchers have strived to understand colloid transport in porous media in laboratory and field experiments (2, 3). In most of the field experiments conducted to date, "organic" colloids (e.g., latex microspheres, viruses, bacteria, protozoa) have been used to study colloid transport (4–10) because these organic colloids can be distinguished from naturally present colloids at detection limits of 10^{-6} or better of the injected concentrations (11). Unfortunately, organic colloids are not particularly good surrogates for the clay mineral, oxide, carbonate, and quartz colloids responsible for the facilitated transport of radionuclides and metals (12–17). The surface properties and densities of organic colloids are quite different from those of mineral colloids. To directly test mineral colloid transport, the ideal mineral colloid would be (1) readily distinguished from natural colloids, (2) easily measured at very low concentrations, (3) variable in size, density, and surface properties, (4) available in narrow (monodisperse) size distributions, (5) stable, both colloiddally

and compositionally, for the duration of the experiments, and (6) environmentally benign.

To date, only two field studies of mineral colloid subsurface transport have been conducted, both with silica (6, 18). Higgs et al. (6) injected 25 nm silica colloids in a glacial sand aquifer and traced their forced-gradient transport over a 3.4 m distance with static light scattering (to measure concentration) and dynamic light scattering (to identify the colloids by size). Ryan et al. (18) injected 107 nm silica colloids into an iron oxide-coated glacial outwash aquifer and monitored their natural-gradient transport over a 1.8 m distance by turbidity, a form of static light scattering. The detection limit for these silica colloids was only about 3% of the injected concentration because the naturally present colloids also scattered light. Of course, the range of detectable concentrations could have been improved by injecting higher concentrations, but silica was already being added at the upper end of colloid concentrations considered environmentally relevant (17).

For surface water studies, researchers have labeled mineral particles with fluorescent compounds (19), DNA (20), lanthanide ions (21), and gold and silver (22). These labeled particles are readily distinguished from natural particles and detectable at low concentrations, but problems may be anticipated for subsurface experiments. First, the labels may alter the surface chemistry of the particles. Particle transport in porous media is much more sensitive to surface-chemical interactions than transport in surface water. Second, the labels may desorb over the longer times needed to conduct colloid transport experiments in porous media. Third, the labels must be applied to mineral particle suspensions that may not be monodisperse or variable in size, density, and surface properties.

To overcome these difficulties, we developed two new mineral colloids for field experiments: silica-coated titania (TiO₂) and zirconia (ZrO₂). Synthesized titania colloids and commercial zirconia colloids were coated with silica following established procedures. The ability of the silica to mask the surface properties of the underlying colloids was tested by microelectrophoresis and field experiments in an iron oxide-coated sand and gravel aquifer on Cape Cod, MA. The ability to distinguish the silica-coated colloids from natural colloids and each other and to detect the silica-coated colloids at low concentrations was also tested in the Cape Cod aquifer.

Materials and Methods

Titania and Zirconia Colloids. Titania (TiO₂) colloids were synthesized by hydrolysis of titanium(IV) ethoxide (1.0 mL, Ti ~ 20%; Aldrich Chemical Co.) in ethanol (100 mL, reagent grade), high-purity water (1 mL, > 18 M Ω resistivity), and hydroxypropyl cellulose (7.0–70 mg; 80 000 average molecular weight, Aldrich Chemical Co.) at 2 and 23 °C (23, 24). Mean colloid size increased from 370 to 1170 nm as the temperature was lowered from 23 to 2 °C with an ice bath and hydroxypropyl cellulose mass was reduced from 70 to 7.0 mg. Hydroxypropyl cellulose was removed by centrifugation in polyethylene bottles (20 min, 8 050 g) and sequential resuspension in 100 mL of methanol, pH 10.75 solution, and high-purity water with the aid of an ultrasonic water bath (10 min, 80 W). For the field experiments, the synthesis procedure producing the largest colloids was scaled up by a factor of 10 (1000 L of ethanol, 10 mL of water, 70 mg of hydroxypropyl cellulose, and 10 mL of titanium(IV) ethoxide at 2 °C) and repeated 10 times, yielding about 5 g of colloids for each batch.

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Spherical zirconia (ZrO_2) colloids of about 0.1 μm diameter were obtained from Alfa Aesar (20% ZrO_2 colloidal dispersion, nitric acid solution, pH 3). Zirconia colloids are synthesized by hydrolysis of Zr(IV) solutions (25, 26). The stock zirconia colloid suspensions were subjected to the same centrifugation and resuspension procedures used for the titania.

Silica Coating. The titania and zirconia colloids were coated with silica by hydrolysis of tetramethyl orthosilicate (99+%, Aldrich Chemical Co.) in an ethanol/ammonium hydroxide aqueous solution (27–29), similar to techniques that have been used to coat silica on iron oxide, iron, silver, and gold colloids (30–36). Portions of the aqueous colloid suspensions were centrifuged, dried, and weighed (50 ± 1 g titania, 10.0 ± 0.2 g zirconia). The colloids were resuspended in ethanol (100 mL) and ammonium hydroxide aqueous solution (2%, 1 mL) in polyethylene bottles. Three 0.6 mL additions of tetramethyl orthosilicate (as silica, a total of 0.97 g) were made at 15 min intervals during constant stirring at room temperature. The suspensions were stirred for 12 h and purified by three repetitions of centrifugation and resuspension in 10^{-4} M KCl solution to produce suspensions containing about $15\text{--}20$ g L^{-1} colloids.

Colloid and Silica Coating Characterization. Colloid size was measured by dynamic light scattering (Particle Sizing Systems, NICOMP 370) at a 90° scattering angle. Colloid morphology and elemental composition was examined by scanning electron microscopy (SEM; International Scientific Instruments SX-30, 30 kV accelerating voltage) and energy-dispersive X-ray (EDX; Tracor-Northern) analysis. Colloid suspensions were filtered through 0.1 μm polycarbonate filters, dried at room temperature, mounted on aluminum stubs, and coated with carbon prior to SEM/EDX analysis. Electrophoretic mobilities were measured by laser Doppler velocimetry/microelectrophoresis (Brookhaven Instruments Corp., Zeta-Plus) in 10^{-4} M KCl and Cape Cod groundwater solutions as a function of pH. Sodium hydroxide and nitric acid were used to adjust pH. The natural groundwater was amended with sodium bromide (1.0 mM) and sodium dodecylbenzenesulfonate (72 μM) to mimic the conditions of the field experiments.

Colloidal and coating stability were examined over 90 d by biweekly measurements of colloid size and electrophoretic mobility in 10^{-4} M potassium chloride and Cape Cod groundwater samples. Single- and dual-colloid suspensions of about 100 mg L^{-1} were prepared in both potassium chloride and groundwater in polyethylene containers. The groundwater suspensions were amended with 1 mM sodium bromide and 72 μM NaDBS.

Natural Gradient Transport Experiment. Field tests were conducted during August, 1997, in the surficial aquifer at the U.S. Geological Survey's Cape Cod Toxic Waste Research Site near the Massachusetts Military Reservation on Cape Cod, MA (37). Detailed characteristics of the groundwater and aquifer sediment are reported in previous field studies (9, 18, 38). Uncontaminated groundwater (100 L) was pumped at a rate of 0.5 L min^{-1} from the injection multilevel sampler (MLS; designated 4–15) at 6.4 and 6.7 m depths into a 114 L polyethylene tank. The groundwater was amended with 1 L suspensions of both silica-coated colloids, a 1 L solution of 100 mM sodium bromide, and a 1 L solution of 7.2 mM sodium dodecylbenzene sulfonate (NaDBS; Table 1) and mixed by rolling the tank for 10 min. Sodium bromide was added as a conservative tracer. Sodium dodecylbenzene sulfonate was added to increase colloid breakthrough and transport distance in hopes of better testing the enhanced detection limits for the silica-coated colloids. The amended groundwater was pumped at a rate of 1.0 L min^{-1} back into the injection MLS at a depth of 6.4 m. Colloid transport was monitored at a down-gradient distance of 1.0 m in a second

TABLE 1. Injection Constituents for Natural Gradient Silica-Coated Colloid Transport Experiment on Cape Cod, MA^a

constituent	concn in injectate	concn immediately after injection (C_0)	background concn before injection
SiO_2 -coated TiO_2	93 mg L^{-1} Ti	41 mg L^{-1} Ti	0.6 μg L^{-1} Ti
SiO_2 -coated ZrO_2	61 mg L^{-1} Zr	63 mg L^{-1} Zr	1.8 μg L^{-1} Zr
NaDBS	72 μM	72 μM	bdl
NaBr	1.0 mM	0.99 mM	bdl

^a Injection volume was 100 ± 3 L. Sodium dodecylbenzene sulfonate (NaDBS) and sodium bromide background concentrations were below the detection limits (bdl) of the analytical techniques.

MLS (designated 4A-15) at 6.1, 6.4, and 6.7 m depths. Breakthrough curve data was reported only for the 6.4 m depth, where at least 50% of the injected bromide, colloid, and surfactant was detected. After the injections, groundwater samples were taken twice daily. In both the injection and monitoring MLS, three depths were sampled immediately before and after the injections to measure the background and initial concentrations (C_0) for each constituent. Groundwater was purged (200 mL) and collected (100 mL) by peristaltic pumps at a rate of 200 mL min^{-1} through polyethylene and Norprene tubing.

Field Experiment Analyses. Field measurements included pH (combination electrode, Fisher Accumet 20 meter), specific conductance (Orion 122 meter), turbidity (Hach Ratio X/R meter), dissolved oxygen (colorimetric test kits, CHEMetrics, Inc.), bromide (specific ion electrode, Orion 250A meter), and dodecylbenzene sulfonate (methylene blue active substances (MBAS) test kit, CHEMetrics, Inc.). Bromide replicate sample error was less than 5% with a 5×10^{-6} M detection limit. MBAS replicate sample error was less than 25% with a 0.72 μM detection limit.

Titanium and zirconium were measured in acidified samples (1 mL concentrated HNO_3 /10 mL sample) by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Varian Liberty Series II). The silica-coated colloids were dissolved prior to ICP-AES analysis by the acidification. Ti and Zr standards ($10\,000$ mg L^{-1} in 5% HNO_3 and 2% HF) were used to prepare linear standard curves from 0.1 to 100 μg L^{-1} (800 V photomultiplier tube voltage) and $100\text{--}10\,000$ μg L^{-1} (500 V photomultiplier tube voltage) concentrations. Samples at Ti and Zr concentrations greater than $10\,000$ μg L^{-1} were diluted with high-purity water for analysis. Ti and Zr replicate sample errors varied by less than 5% with detection limits for Ti and Zr of 0.6 and 1.5 μg L^{-1} , respectively.

Calculation of Colloid Transport Parameters. The relative breakthrough of the colloids was calculated as the ratio of the time-integrated mass of the colloid relative to that of the conservative bromide tracer (39). Bromide, Ti, and Zr concentrations were corrected for background concentrations measured before injection. Collision efficiencies (α) were calculated for pulse inputs accounting for longitudinal dispersion (39). Single collector efficiencies (η) were calculated using the correlation equation of Rajagopalan and Tien (40) using a temperature of 288 K, an average grain diameter of 0.6 mm, a porosity of 0.39, colloid diameters of 1080 nm for silica-coated titania and 130 nm for silica-coated zirconia, and colloid densities estimated by maximum silica precipitation (Table 2).

Results

Silica-Coated Colloid Characterization and Stability. Titania synthesis produced roughly spherical and monodisperse suspensions with standard deviations averaging about 20%

TABLE 2. Coating Thickness and Density of Silica-Coated Titania and Zirconia Colloids^d

colloid	dynamic light scattering results					maximum precipitation results ^c		
	uncoated diameter ^a (nm)	silica-coated diameter ^a (nm)	silica volume (%)	coating thickness ^b (nm)	silica-coated colloid density (g cm ⁻³)	silica volume (%)	coating thickness (nm)	silica-coated colloid density (g cm ⁻³)
titania	1030 ± 440	1080 ± 480	13	25	3.4	3.4	6	3.8
zirconia	110 ± 34	130 ± 49	39	10	4.4	21	5	5.1

^a Dynamic light scattering colloid size reported as the mean diameter ± 1 SD. ^b Coating thickness estimated as one-half the difference between the mean diameters of the uncoated and coated hydrodynamic diameters. ^c Coating thicknesses are maximum values based on the complete precipitation of added silica. ^d Results based on dynamic light scattering hydrodynamic diameter before and after silica coating and maximum amount of silica precipitated on colloids surfaces. The densities estimated by maximum silica precipitation were used in the analysis of transport parameters.

of the mean colloid sizes. The size distribution of the combined silica-coated titania suspension (1080 ± 480 nm, Table 2) widened owing to variations in the titania colloid diameter from batch to batch. The mean diameters of individual batches ranged from 840 to 1220 nm with standard deviations of about 20% of the means. The silica-coated zirconia colloids were roughly spherical and monodisperse. Coating with silica slightly increased the width of the zirconia size distribution (Table 2), possibly because the thickness of the silica coating varied from batch to batch. The sizes selected for the silica-coated titania and zirconia colloids allowed us to compare the transport of colloids for which collisions are dominated by different mechanisms. For the larger titania colloids, sedimentation causes the majority of the colloid-grain collisions. For the smaller zirconia colloids, Brownian diffusion causes nearly all of the collisions.

For the zirconia colloids, a silica coating thickness of 10 nm was estimated with dynamic light scattering results (Table 2). Using specific gravities of 5.9 for zirconia and 2.2 for silica (41), the estimated density of the silica-coated zirconia is 4.4 g cm⁻³. Because colloid sizes measured by dynamic light scattering have high uncertainties (mostly due to the real width of the size distribution), these estimates of coating thickness and density are also uncertain. A maximum coating thickness was also estimated by assuming that the entire 0.97 g of silica added during coating precipitated on the surfaces of 10 g L⁻¹ of zirconia colloids with a coated diameter of 130 nm. In this case, the coating thickness is 5 nm, and the colloid density is 5.1 g cm⁻³. Similar estimates were made for the titania colloids based on a specific gravity of 3.9 for titania (23).

EDX analysis revealed Si/Ti ratios of 0.066 ± 0.034 and Si/Zr ratios of 0.35 ± 0.09 for 40 spot analyses on each colloid sample. The EDX spot size is about 1 μm², so each analysis includes about one silica-coated titania colloid and 60 silica-coated zirconia colloids. Using the silica volumes of each colloid assuming maximum silica precipitation (Table 2), the Si/Ti molar ratio is 0.027 and the Si/Zr molar ratio is 0.20. Even though EDX analysis is not very surface-sensitive (penetration depths of about 0.5 to 1 μm), the EDX-measured ratios of Si/Ti and Si/Zr are about twice those estimated for the total colloid composition.

Coating with silica reduced the 10⁻⁴ M KCl isoelectric point (pH_{iep}) of both the titania and zirconia colloids to the 2.5–3.5 range from about 4.1 for titania and 8.1 for zirconia (Figure 1). The expected point of zero charge values for titania and zirconia are 4.7–6.7 and 6.7, respectively (42). In the groundwaters amended with 1.0 mM NaBr, the pH_{iep} values of the silica-coated zirconia colloids were below the lowest observed pH of 3.0 (Figure 2). The electrophoretic mobilities of the silica-coated colloids are less negative in the groundwater than in the 10⁻⁴ M KCl solution. This difference can be attributed to the groundwater ionic strength, which is about 5 × 10⁻⁴ M, and the presence of multivalent cations (18, 38). In the groundwater, the electrophoretic mobility of

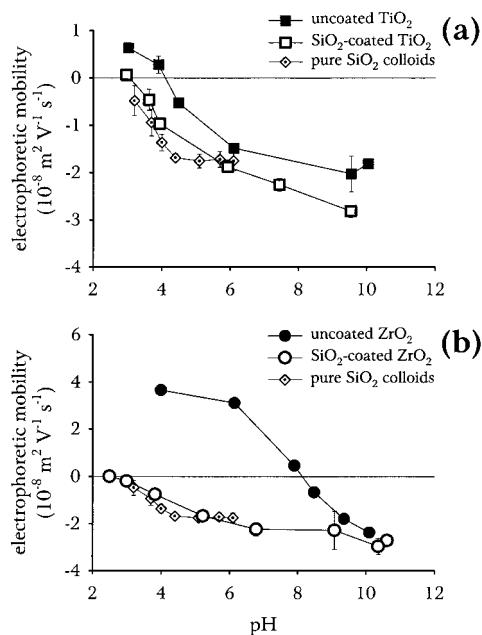


FIGURE 1. Electrophoretic mobilities of uncoated and silica-coated (a) titania and (b) zirconia in 10⁻⁴ M potassium chloride solution as a function of pH. Electrophoretic mobilities of pure silica colloids of 107 nm diameter (18) shown for comparison. Error bars show 1 SD for three replicate measurements.

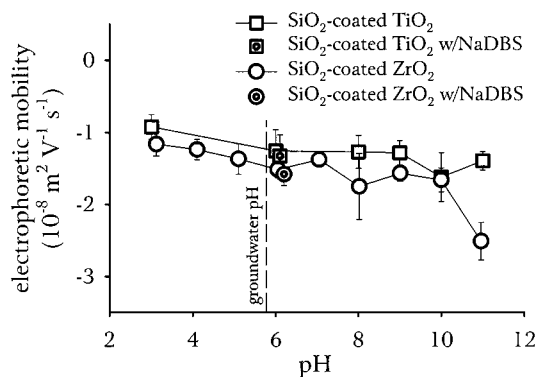


FIGURE 2. Electrophoretic mobilities of silica-coated titania and silica-coated zirconia in uncontaminated Cape Cod groundwater as a function of pH. Each sample contains 1 mM sodium bromide. Two samples were amended with 72 μM sodium dodecylbenzene sulfonate (NaDBS). Ambient groundwater pH indicated by the dashed vertical line. Error bars show 1 SD for three replicate measurements.

the silica-coated zirconia colloids was not significantly changed by the addition of dodecylbenzene sulfonate.

Over 90 days, the size of the silica-coated titania and zirconia colloids varied by less than 15% in 10⁻⁴ M KCl

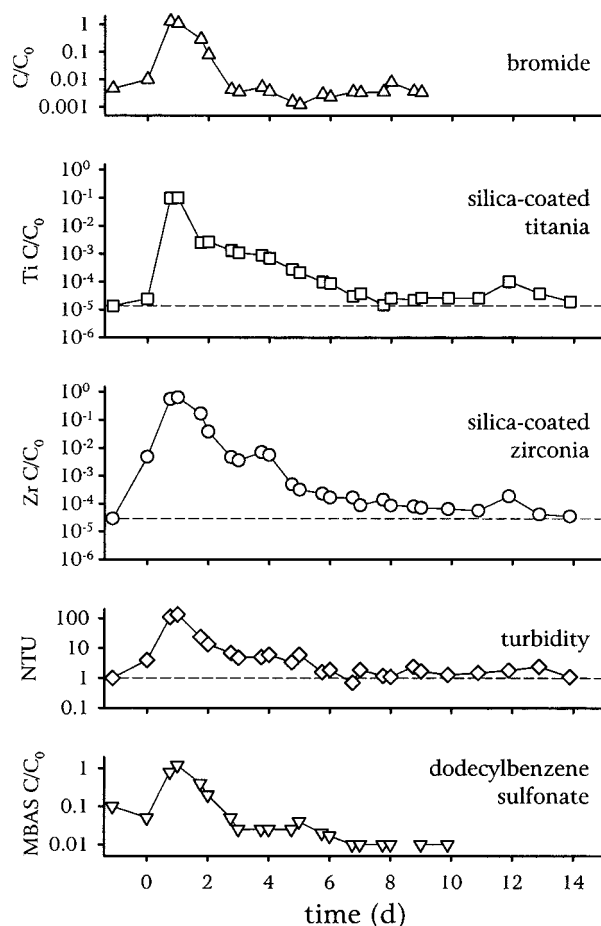


FIGURE 3. Natural gradient experiment breakthrough curves at 1.0 m transport distance for bromide, silica-coated titania and zirconia colloids, turbidity, and dodecylbenzenesulfonate (measured as MBAS). Colloid and turbidity ambient concentrations shown as dashed horizontal lines. The concentrations of these parameters are normalized by the concentration measured immediately after injection (C/C_0) of the 100 L pulse injectate.

solution in both the single- and dual-colloid suspensions. In the single-colloid amended groundwater suspensions, the size of the silica-coated colloids varied by less than 15%. In the dual-colloid amended groundwater suspensions, dynamic light scattering was unable to resolve the two colloids consistently. In all of the single-colloid suspensions, the electrophoretic mobility of the silica-coated colloids varied by less than 10% during the 90 d.

Natural Gradient Transport Experiment. The initial breakthrough of the silica-coated colloids coincided with the breakthrough of bromide, turbidity, and dodecylbenzene sulfonate over a 1 m transport distance (Figure 3; Table 3). The bromide and dodecylbenzene sulfonate peaks returned to background levels after 3 days, while substantial colloid concentrations were measured as Ti, Zr, and turbidity to the sixth day. After the sixth day, colloid concentrations hovered

slightly above background for Ti and Zr and essentially at the background level for turbidity (Table 3).

Discussion

Silica Coating Thickness, Uniformity, and Stability. The estimates of silica coating thickness ranged from 5 to 25 nm. Maximum coating thicknesses (5–6 nm) estimated by complete precipitation of added silica were considered more reliable than those estimated by dynamic light scattering. A comparison of the electrophoretic mobilities of the silica-coated colloids with those of pure silica in 10^{-4} M KCl solution clearly indicates that the silica coating masked the underlying surface properties of the titania and zirconia colloids (Figure 1). Other colloid characterizations indicated that all of the titanium and zirconium colloids received uniform amounts of silica coating. For example, if some colloids received less silica coating than others, they would be less negatively charged and more prone to aggregation. If colloids aggregate, we would see an increase in colloid size over time; however, we did not see any significant change in colloid size over 90 d. Furthermore, the Si/Ti and Si/Zr ratios measured by EDX analysis were fairly consistent for all colloids examined. Although we did not investigate the uniformity of silica coating on individual colloids, previous studies have shown with transmission electron microscopy that silica coatings applied by the controlled hydrolysis of tetramethyl orthosilicate are quite uniform even on individual colloids (36).

Natural Gradient Transport Experiment. We highlight three results: (1) the silica coating of the titania and zirconia colloids allowed monitoring of the transport of two mineral colloids of different size and density in the same transport experiment, (2) the collision efficiencies of the silica-coated titania and zirconia colloids were similar, and (3) the silica-coated colloids were measurable at $\mu\text{g L}^{-1}$ concentrations nearly 5 orders of magnitude below the injection concentrations (Figure 2, Table 3).

The silica-coated colloids were easily distinguished from naturally present colloids by virtue of their titania and zirconia cores and the low Ti and Zr content of the Cape Cod groundwater. Obviously, turbidity and other light scattering measurements could not distinguish between the two colloids and any colloids naturally present because all colloids scatter light. Dynamic light scattering distinguished the two silica-coated colloids in dual-colloid suspensions without natural colloids (the size of the two silica-coated colloids were sufficiently different), but the presence of natural colloids obscured distinction of the silica-coated colloids by size. Presumably, dynamic light scattering would not have been useful in distinguishing these colloids from the natural colloids in the manner that Higgo et al. (6) tracked 25 nm silica colloids. Because dynamic light scattering uses inverse solution techniques to fit the scattering intensity autocorrelation function (an exponential decay curve) with a minimum number of discrete colloid sizes, wide size distributions of natural colloids cannot be reliably characterized (43, 44).

The collision efficiencies of the silica-coated titania and zirconia colloids vary by a factor of about 2 (Table 3). Given

TABLE 3. Natural Gradient Transport Parameters for the Silica-Coated Titania and Zirconia Colloids in the Cape Cod Aquifer in the Presence of 1.0 mM Sodium Bromide and 72 μM Sodium Dodecylbenzene Sulfonate at 1.0 m Transport Distances

colloid	approach velocity ^a (m d ⁻¹)	colloid longitudinal dispersivity (m)	relative breakthrough (%)	single collector eff ^b η_{tot}	collision eff ^a α
silica-coated TiO ₂	0.78	0.11	7.2	0.19	0.011
silica-coated ZrO ₂	0.78	0.11	49	0.093	0.0054

^a Approach velocity determined using the time and distance (1.0 m) of the colloid breakthrough. ^b Single collector efficiency determined using the correlation equation of Rajagopalan and Tien (40).

the frequency of sampling (only twice daily) and the lack of mass balance in this experiment as well as the uncertainty in calculating single collector efficiencies using the Rajagopalan and Tien (40) approximations (45), the collision efficiencies of the silica-coated titania and zirconia colloids are probably not significantly different. The similarity in collision efficiency indicates that the silica coatings imparted the same surface characteristics to the two core colloids. The similar surface characteristics resulted in colloid transport that was not significantly dependent on colloid size. Elimelech and O'Melia (46) showed that colloid size did not affect collision efficiency in much more controlled experiments examining the transport of polystyrene latex colloids through glass beads.

The ambient Ti and Zr concentrations measured at the start of the natural gradient experiment (Ti, $0.6 \mu\text{g L}^{-1}$; Zr, $1.8 \mu\text{g L}^{-1}$) are at or near the Ti and Zr detection limits, resulting in C/C_0 detection limits of 1.4×10^{-5} for Ti and 2.9×10^{-5} for Zr. In contrast, the ambient turbidity for the natural gradient experiment was 1.0 NTU, giving a C/C_0 detection limit of about 0.01. The span of measurable C/C_0 values for the silica-coated colloids could be even wider if higher concentrations of silica-coated colloids were injected; however, the concentrations of colloids injected in this natural gradient experiment were already at the upper end of natural colloid concentrations (17). With detection limits for the silica colloids approaching C/C_0 of 10^{-5} , the silica-coated colloids rival the practical detection limits of viruses, bacteria, and other organic colloids.

For the silica-coated zirconia colloids, the low Zr detection limits revealed tailing not evident in the turbidity breakthrough. Most likely, the tailing is caused by the slow release of attached colloids after the passing of the injected pulse of colloids. Similar tailing may have occurred for the silica-coated titania colloids, but the Ti concentrations at times greater than 5 d are too close to the background Ti concentration to be certain that significant release occurred. Previously, such tailing had been observed only for viruses and bacteria in field experiments, resulting in the incorporation of reversible attachment and release kinetics in biocolloid transport models (41, 47–49). We attributed tailing of virus breakthroughs to release of viruses from aquifer grain surfaces not coated by iron oxyhydroxides (38), and we suggest that the same phenomenon may be responsible for the slow release of the silica-coated zirconia colloids in this experiment.

Environmental Usefulness. Owing to low background concentrations of Ti and Zr, these mineral colloids are readily distinguishable from natural colloids and detectable at low concentrations in most porous media. Their analysis by acidification and ICP-AES analysis is relatively simple. Using established synthesis procedures, monodisperse mineral colloid suspensions of variable size, density, and surface properties can be produced. The low relatively low solubility of these minerals and the presence of relatively high concentrations of silica in most groundwaters ensure the compositional stability of these colloids. The ability to impart similar surface properties by silica coating ensures colloidal stability. These colloids are environmentally benign; thus, obtaining permission to inject these colloids at field sites is not a problem. The ability to control the size, density, and surface properties of these readily traceable colloids will allow better assessment of mechanisms of colloid deposition processes and reversibility.

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Literature Cited

- (1) McCarthy, J. F.; Zachara, J. M. *Environ. Sci. Technol.* **1989**, *23*, 496–502.
- (2) Ryan, J. N.; Elimelech, M. *Colloids Surf. A* **1996**, *107*, 1–51.
- (3) Kretzschmar, R.; Borkovec, M.; Grolimund, D.; Elimelech, M. *Adv. Agron.* **1999**, *66*, 121–193.
- (4) Wood, W. W.; Ehrlich, G. G. *Ground Water* **1978**, *16*, 398–403.
- (5) Harvey, R. W.; George, L. H.; Smith, R. L.; LeBlanc, D. R. *Environ. Sci. Technol.* **1989**, *23*, 51–56.
- (6) Higgo, J. W. W.; Williams, G. M.; Harrison, I.; Warwick, P.; Gardiner, M. P. *Colloids Surf. A* **1993**, *73*, 179–200.
- (7) McKay, L. D.; Cherry, J. A.; Bales, R. C.; Yahya, M. T.; Gerba, C. P. *Environ. Sci. Technol.* **1993**, *27*, 1075–1079.
- (8) Rossi, P.; De Carvalho-Dill, A.; Müller, I.; Aragno, M. *Eng. Geol.* **1994**, *23*, 192–200.
- (9) Bales, R. C.; Li, S.; Maguire, K. M.; Yahya, M. T.; Gerba, C. P.; Harvey, R. W. *Ground Water* **1995**, *33*, 653–661.
- (10) Cumbie, D. H.; McKay, L. D. *J. Contam. Hydrol.* **1999**, *37*, 139–157.
- (11) Harvey, R. W. In *Manual of Environmental Microbiology*; Hurst, C. J., Ed.; ASM Press: Washington, DC, 1996; pp 586–599.
- (12) Nyhan, J. W.; Drennon, B. J.; Abeele, W. V.; Wheeler, M. L.; Purtymun, W. D.; Trujillo, G.; Herrera, W. J.; Booth, J. W. *J. Environ. Qual.* **1985**, *14*, 501–509.
- (13) Buddemeier, R. W.; Hunt, J. R. *Appl. Geochem.* **1988**, *3*, 535–548.
- (14) Magaritz, M.; Amiel, A. J.; Ronen, D.; Wells, M. C. *J. Contam. Hydrol.* **1990**, *5*, 333–347.
- (15) Amrhein, C.; Mosher, P. A.; Strong, J. E. *Soil Sci. Soc. Am. J.* **1993**, *57*, 1212–1217.
- (16) Vilks, P.; Cramer, J. J.; Bachinski, D. B.; Doern, D. C.; Miller, H. G. *Appl. Geochem.* **1993**, *8*, 605–616.
- (17) McCarthy, J. F.; Degueudre, C. In *Environmental Particles, Volume I*; Buffle, J., van Leeuwen, H. P., Eds.; Lewis Publishers: Boca Raton, FL, 1993; pp 247–315.
- (18) Ryan, J. N.; Elimelech, M.; Ard, R. A.; Harvey, R. W.; Johnson, P. R. *Environ. Sci. Technol.* **1999**, *33*, 63–73.
- (19) Carey, D. A. *Limnol. Oceanogr.* **1989**, *34*, 630–635.
- (20) Mahler, B. J.; Winkler, M.; Bennett, P.; Hillis, D. M. *Geology* **1998**, *26*, 831–834.
- (21) Mahler, B. J.; Bennett, P. C.; Zimmerman, M. *Ground Water* **1998**, *36*, 835–843.
- (22) Olmez, I.; Pink, F. X.; Wheatcroft, R. A. *Environ. Sci. Technol.* **1994**, *28*, 1487–1490.
- (23) Jean, J. H.; Ring, T. A. *Colloids Surf.* **1988**, *29*, 273–291.
- (24) Look, J. L.; Zukoski, C. F. *J. Colloid Interface Sci.* **1992**, *153*, 461–482.
- (25) Kumazawa, H.; Hori, Y.; Sada, E. *Chem. Eng. J. Biochem. Eng.* **1993**, *51*, 129–133.
- (26) Hu, M. Z. C.; Harris, M. T.; Byers, C. H. *J. Colloid Interface Sci.* **1998**, *198*, 87–99.
- (27) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.
- (28) Osseo-Asare, K.; Arriagada, F. J. *Colloids Surf.* **1990**, *50*, 321–339.
- (29) van Blaaderen, A.; Vrij, A. *J. Colloid Interface Sci.* **1993**, *156*, 1–18.
- (30) Ohmori, M.; Matijević, E. *J. Colloid Interface Sci.* **1992**, *150*, 594–598.
- (31) Ohmori, M.; Matijević, E. *J. Colloid Interface Sci.* **1993**, *160*, 288–292.
- (32) Philipse, A. P.; van Bruggen, M. P. B.; Pathmanathan, C. *Langmuir* **1994**, *10*, 92–99.
- (33) Liz-Marsán, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, *12*, 4329–4335.
- (34) Ung, T.; Liz-Marsán, L. M.; Mulvaney, P. *Langmuir* **1998**, *14*, 3740–3748.
- (35) Liu, Q. X.; Xu, Z. H.; Finch, J. A.; Egerton, R. *Chem. Mater.* **1998**, *10*, 3936–3940.

- (36) Hardikar, V. V.; Matijević, E. *J. Colloid Interface Sci.* **2000**, *221*, 133–136.
- (37) LeBlanc, D. R. Water Supply Paper 2218, U.S. Geological Survey, Washington, DC, 1984; 28 pp
- (38) Pieper, A. P.; Ryan, J. N.; Harvey, R. W.; Amy, G. L.; Illangasekare, T. H.; Metge, D. W. *Environ. Sci. Technol.* **1997**, *31*, 1163–1170.
- (39) Harvey, R. W.; Garabedian, S. P. *Environ. Sci. Technol.* **1991**, *25*, 178–185.
- (40) Rajagopalan, R.; Tien, C. *AIChE J.* **1976**, *22*, 523–533.
- (41) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1983.
- (42) Parks, G. A. *Chem. Rev.* **1965**, *65*, 177–198.
- (43) Rees, T. F. *J. Contam. Hydrol.* **1987**, *1*, 425–439.
- (44) Schurtenberger, P.; Newman, M. E. In *Environmental Particles, Volume 2*; Buffle, J., van Leeuwen, H. P., Eds.; Lewis Publishers: Boca Raton, FL, 1993; pp 37–115.
- (45) Elimelech, M.; Gregory, J.; Jia, X.; Williams, R. *Particle Aggregation and Deposition*; Butterworth-Heinemann: Oxford, 1995.
- (46) Elimelech, M.; O'Melia, C. R. *Environ. Sci. Technol.* **1990**, *24*, 1528–1536.
- (47) Bales, R. C.; Hinkle, S. R.; Kroeger, T. W.; Stocking, K.; Gerba, C. P. *Environ. Sci. Technol.* **1991**, *25*, 2088–2095.
- (48) Hornberger, G. M.; Mills, A. L.; Herman, J. S. *Water Resour. Res.* **1992**, *28*, 915–938.
- (49) Schijven, J. F.; Hoogenboezem, W.; Hassanizadeh, S. M.; Peters, J. H. *Water Resour. Res.* **1999**, *35*, 1101–1111.

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