Transport and Retention Mechanisms of Colloids in Partially Saturated Porous Media

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ABSTRACT

The transport, retention, and release of hydrophobic and hydrophilic polystyrene latex microparticle colloids were examined in 0.5-cm-thick, 26-cm-long slab chambers filled with either regular (hydrophilic) or weakly water-repellent sand. The water-repellent sand consisted of a mixture of 0.4% strongly water-repellent grains with unmodified regular sand for the remainder. The concentration of colloids in the outflow water was measured at the same time as the pore-scale distribution of colloids was recorded in still and video images. Although the type of sand affected the flow pattern in the top of the chamber, it did not affect the breakthrough for the same type of colloids. More hydrophilic colloids were eluted in the drainage water than hydrophobic colloids. Images showed that there was a greater retention of the hydrophobic colloids due to strongly attractive hydrophobic interaction forces between colloids and subsequent filtering of colloidal aggregates in the narrow passages between grains. Once filtered, these aggregates then served as preferred sites for attachment of other hydrophobic colloids. The hydrophilic colloids were retained primarily in a thin film of water at the edge of the meniscus, the air–water–solid (AWS) interface. Centrifugal motion within the pendular rings observed in the videos contributed to movement of the colloids toward the AWS interface, where colloids were retained due to both low laminar flow velocities near the grain surface and straining in the thin water film at the edge of the meniscus. Except near the solid interface, sorption at the air–water (AW) interface was not observed and appeared unimportant to the retention of colloids. The findings form an essential link between colloid retention and transport processes at the interfacial, pore, and Darcy scales.

MOBILE SUBSURFACE COLLOIDS have received considerable attention in recent years because of their important role in the translocation of particle-reactive contaminants in soils (Wan and Tokunaga, 1997; Kretzschmar et al., 1999). Colloids are defined as suspended particulate matter with diameters <10 μm (Stumm, 1977). Colloidal sized materials may form stable complexes with various pollutants previously considered to have very limited mobility in the subsurface (McCarthy and Zachara, 1989; Ryan and Elimelech, 1996), including metals (Grolimund et al., 1996; Jordan et al., 1997; Karathanasis, 1999), pesticides (de Jonge et al., 1998; Sprague et al., 2000; Williams et al., 2000), and radionuclides (McCarthy et al., 1998; Kersting et al., 1999; Flury et al., 2002). These complexes can significantly enhance the movement of contaminants in both saturated and unsaturated porous media in a process termed colloid-facilitated (or colloid-mediated) transport. Though our understanding of colloid mobilization and deposition has improved in the past 10 yr, scientific reviews emphasize the need for more research on the mechanisms controlling transport in the unsaturated zone (Ouyang et al., 1996; Kretzschmar et al., 1999).

In a review of colloid transport in the vadose zone, Lenhart and Saiers (2002) described the transport and distribution of colloids in the vadose zone as advection and dispersion, together with a sink–source term. The advection–dispersion is relatively well understood and could be modified to include the effects of preferential flow (Steenhuis et al., 2001). Difficulties arise from size exclusion that limits the accessibility of colloids to portions of the pore space. Determining the sink–source term is even more uncertain and currently an area of active research. As shown below, one of the major limitations in understanding and modeling this term is the difficulty of visualizing the processes in a medium where the location and extent of the AW interface is a function of other hydrophobic colloids. Images showed that there was a greater retention of the hydrophobic colloids due to strongly attractive hydrophobic interaction forces between colloids and subsequent filtering of colloidal aggregates in the narrow passages between grains. Once filtered, these aggregates then served as preferred sites for attachment of other hydrophobic colloids. The hydrophilic colloids were retained primarily in a thin film of water at the edge of the meniscus, the air–water–solid (AWS) interface. Centrifugal motion within the pendular rings observed in the videos contributed to movement of the colloids toward the AWS interface, where colloids were retained due to both low laminar flow velocities near the grain surface and straining in the thin water film at the edge of the meniscus. Except near the solid interface, sorption at the air–water (AW) interface was not observed and appeared unimportant to the retention of colloids. The findings form an essential link between colloid retention and transport processes at the interfacial, pore, and Darcy scales.


Abbreviations: AW, air–water; AWS, air–water–solid; BTC, breakthrough curve; DLVO, Derjaguin–Landau–Verwey–Overbeek forces; PV, pore volume; SW, soil–water; 2D, distilled-deionized.
moisture content, colloids are retained because the thickness of the water film connecting one pendular ring to the next falls below the diameter of the colloid (Fig. 1 in Wan and Tokunaga, 1997). However, calculations of film thicknesses for a range of matric potentials from −10 to 30 cm (Iwamatsu and Horii, 1996; Lenhart and Saiers, 2002) demonstrated that the thicknesses of the films are tens of nanometers under equilibrium conditions. Thus, such thin films can simply be interpreted as discontinuities in pendular rings between individual grains (Lenhart and Saiers, 2002; Crist et al., 2004).

The goal of our study is to extend understanding of colloid retention mechanisms at the AWS interface suggested by visual observations of Crist et al. (2004) for microspheres and implied earlier by Thompson et al. (1998), Thompson and Yates (1999), and Chu et al. (2001, 2003) for virus transport. Specific objectives include comparison of the behavior of negatively charged hydrophilic and hydrophobic colloids in water-repellent (hydrophobic) and unmodified hydrophilic coarse sands.

Results will include colloid breakthrough curves (BTCs), CaCl2, pH 5.6) was delivered through the sampling port at an inlet flow rate of 2 mL min

\[ \approx 1 \]

by measuring the top layer of sand. One pore volume of colloidal suspension was delivered at a flow rate of 2 mL min

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The infiltration chamber was constructed from 0.5-cm-thick, clear acrylic sheets. Interior dimensions of the chamber were 26.0 cm high, 4.8 cm wide, and 0.5 cm deep. The front plate interfered with the image analysis and was mounted with bolts and wing nuts for disassembly after the sand was added. The infiltration chamber was supported on a mounting assembly as a function of the separation distance, \( x \):

**MATERIALS AND METHODS**

**Apparatus and Experimental Design**

A similar experimental setup as Crist et al. (2004) was used and includes an infiltration chamber, light source, electro-optical equipment (lens, camera, and computer system), and imaging software (Fig. 1). The electro-optical equipment included a Zoom 6000 II lens assembly with 1X adaptor (Navitar, Inc., Rochester, NY) and color charged-coupled device camera (Cohu, Inc., Poway, CA). An IBM-compatible computer, monitor, frame grabber card (Scion Corp., Frederick, MD), and Scion Image software were used for image processing and display. Image resolution for the complete system was 212,000 square pixels mm

\[ ^{-2} \]

In addition to capturing still digital images with Scion Image, a videocassette recorder and monitor were used to gather continuous real-time images for subsequent review and analysis. Several sets of colloid breakthrough experiments (described below) were performed with this visualization system. The viewing area was illuminated from underneath using a variable intensity, 150-W tungsten-halogen lamp with fiber optics cable (D.O. Industries, Inc.).

Twelve colloid breakthrough experiments were completed (six with unmodified hydrophilic sand and six with water-repellent sand), producing six sets of replicate experiments with hydrophilic colloids, hydrophobic colloids, and no colloids. Nonfluorescent, blue-dyed polystyrene latex microspheres (Magsphere, Inc., Pasadena, CA) comparable in size to *Cryptosporidium parvum* oocysts were used in the experiments. The surfaces of the colloids were either negatively charged, hydrophilic 4.8-µm carboxylated microspheres or hydrophobic 5.2-µm undervatized microspheres. Hydrophilic sand consisted of translucent quartz sand (Unimin Corp., New Canaan, CT) with grain diameters equivalent to 0.85 to 1.70 mm, and was washed and rinsed 10 times in distilled water to remove loose surface impurities. The procedure of Bauters et al. (1998) was used to modify the surfaces of sand grains to make them hydrophobic and water-repellent, with a negative matric entry value. The hydrophobic water-repellent sands used in these experiments consisted of a mixture of 0.4% of the modified water-repellent grains with unmodified sand for the remainder.

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The infiltration chamber was prepared by filling it with sand; then one pore volume (PV, ~26 mL) of water (0.1 mM CaCl2, pH 5.6) was delivered through the sampling port at an inlet flow rate of 2 mL min

\[ ^{-1} \]

The pore volume was determined in initial experiments at a flow rate of 2 mL min

\[ ^{-1} \]

by measuring the volume required to obtain 50% of the initial Cl− concentration in the leachate. With the sand completely wetted, the chamber was placed on the inclined mounting assembly and left to drain undisturbed for 30 min. The front plate was removed, and using a peristaltic pump, a suspension of either hydrophilic or hydrophobic microspheres at a concentration of approximately 3 × 10⁷ particles mL

\[ ^{-1} \]

in a slow-speed agitator. The released colloids were quantified using the spectrophotometer. The sand was oven-dried at 105°C, and the retained colloids were suspended by mixing with 7 mL of distilled–deionized (2D) water for 30 min in a slow-speed agitator. The released colloids were quantified using the spectrophotometer. The sand was oven-dried at 105°C a second time and reexamined with the electro-optical equipment. The efficiency of colloid recovery in the effluent and mean arrival time of the colloids were evaluated using moments analysis of the observed BTCs for each replicate.

**Interfacial Potential Energies**

The interactions of colloids approaching each other or the AW or SW interfaces were evaluated as the sum of Derjaguin–Landau–Verwey–Overbeek (DLVO) forces, including van der Waals and double layer potential energies. Additionally, hydrophobic forces were considered, although these interactions were important only for interactions of colloids with the AW interface and of hydrophobic colloids with each other. The total potential energy, \( \Phi \), to these interactions was evaluated as a function of the separation distance, \( x \):

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The van der Waals potential, \( \Phi^{vdw} \), was estimated using Eq. [2]. Interactions of a colloid with another colloid or a grain surface were formulated as an unretarded sphere–sphere interaction, assuming pair-wise additivity of the interatomic potentials (Eq. [2a]; Hamaker, 1937). Colloid interactions with a macroscopically flat surface (the AW interface) were approximated using Eq. [2b] (Norde and Lyklema, 1989).

\[
\Phi^{vdw} = -\frac{A_{12}}{12} \left( \frac{y}{r^2 + ry + r} + \frac{y}{r^2 + ry + r + y} \right) + 2 \ln \left( \frac{r^2 + ry + r}{r^2 + ry + r + y} \right) \tag{2a}
\]

\[
\phi^{vdw} = -\frac{A_{12}}{6} \left[ 2a_c(x^2 + a_c^2) - \ln \left( \frac{x + 2a_c}{x} \right) \right] \tag{2b}
\]

where \( y = a_c/a_g \), \( r = x/a_c \), \( a_c \) and \( a_g \) are the colloid and grain radii, respectively; \( x \) is the separation distance; and \( A_{12} \) is the complex Hamaker constant for solids 1 and 2 in medium 3.

\[
A_{12} = \left( \sqrt{A_{11}} - \sqrt{A_{22}} \right) \left( \sqrt{A_{22}} - \sqrt{A_{33}} \right) \tag{3}
\]

where \( A_{11} \), \( A_{22} \), and \( A_{33} \) are the Hamaker constants for each component. The value of \( A_{12} \) was calculated to be \( 4.8 \times 10^{-21} \) J for the polystyrene–water–quartz system, \( 5.2 \times 10^{-21} \) J for the polystyrene–water–polystyrene system, and \( -1.2 \times 10^{-20} \) J for the air–water–polystyrene system (Israelachvili, 1992).

For the interaction of the colloids with each other, the double layer potential, \( \Phi^{dl} \), was calculated for sphere–sphere interaction for the constant potential case (Hogg et al., 1966):

\[
\Phi^{dl} = \frac{1}{2} \varepsilon \left[ \psi_a \frac{2a_c \ln \left( 1 + \exp(-\kappa x) \right)}{a_c + a_g} + \int \ln \left( 1 - \exp(-2\kappa x) \right) \right] \tag{4}
\]

where \( \varepsilon \) is the dielectric constant of water (dimensionless), \( \varepsilon_0 \) is the permittivity of free space, \( \psi_a \) is the surface potential of the colloid, and \( \kappa \) is the reciprocal double layer thickness calculated from the valence and ionic strength of the electrolyte solution. The surface potentials, \( \psi_a \), were calculated based on the \( \zeta \)-potential. For small potentials, the potential decays exponentially in the diffuse double layer, and the surface potential is related to the \( \zeta \)-potential by

\[
\psi_a = \zeta \left( 1 + \frac{z}{a_c} \right) \exp(-\kappa z) \tag{5}
\]

where \( z \) is the distance between the surface of the charged particle and the slipping plane (van Oss et al., 1990). That distance, \( z \), is a theoretical construct, but is usually taken to be \( 5 \zeta \). However, the calculated interaction energy profile did not change substantially over a several-fold range of values of \( z \). The \( \zeta \)-potential of the colloids in the electrolyte solution used in the experiments was measured using a Zetasizer (Malvern Instruments, Southbough, MA) and found to be \(-18.6\) and \(-23.4\) mV for the hydrophilic and hydrophobic colloids, respectively. The \( \zeta \)-potential of the quartz sand was taken to be \(-60\) mV (Elimelech, 1985; Elimelech et al., 2000).

For the interaction of colloids with the sand grains or with the AW interface, the double layer potential for a sphere and flat surface was approximated (Norde and Lyklema, 1989):

\[
\Phi^{dl} = \frac{1}{2} \varepsilon \left[ \psi_a \frac{2a_c \psi_a}{\psi_a + \psi_b} \ln \left( 1 + \exp(-\kappa x) \right) \right] + \ln \left( 1 - \exp(-2\kappa x) \right) \tag{6}
\]
where $\Psi_0$ is the surface potential of the flat surface; the $\xi$-potential of the AW interface was taken to be $-60$ mV (Schäfer et al., 1998b).

In addition to the DLVO interactions, hydrophobic forces act between particles and AW interfaces. Asymmetrical hydrophobic interactions between two surfaces can be calculated based on the respective water contact angles (Yoon et al., 1997; Schäfer et al., 1998b). The hydrophobic interaction energy between small particles and a flat surface thus can be described by (Schäfer et al., 1998b)

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The force constant, $K_{123}$, for asymmetric interactions between macroscopic bodies 1 and 2 in medium 3 can be described as (Yoon et al., 1997; Schäfer et al., 1998b)

$$\log K_{123} = a \left( \frac{\cos \Theta_1 + \cos \Theta_2}{2} \right) + b$$

where $\Theta_1$ and $\Theta_2$ are the water contact angles for the AW interface (180°; Schäfer et al., 1998b) and water–colloid interface (10°) for the hydrophilic and hydrophobic latex microsphere, respectively; Wan and Wilson, 1994a, 1994b; Butt et al., 2002). The terms $a$ and $b$ are system-specific constants. For a system of silica surfaces with different contact angles, $a = -7$ and $b = -18$ (Schäfer et al., 1998b). We adjusted $a$ and $b$ until the $\phi_{\text{hyd}}$ approached zero at large separation distances, which yielded $a = -6$ and $b = -22$.

**RESULTS AND DISCUSSION**

**Total Potential Energies of Interaction**

Figure 2 plots the total interaction energies for the hydrophilic colloids (left panel) and hydrophobic colloids (right panel) as a function of the separation distance. The interaction of the colloid and sand (Fig. 2; dot-dash line) has a substantial repulsive energy barrier that would act to prevent attachment of either the hydrophobic or hydrophilic colloids. Interactions of the hydrophilic colloids with the AW interface are also strongly repulsive. However, attractive hydrophobic forces moderate the net repulsive energy barrier of the hydrophobic colloids with the AW interface, and the interaction energy becomes attractive at smaller separation distances. No repulsive energy barrier exists at any separation distance for the interactions of the hydrophobic colloids with each other, and there is a strong attractive potential at closer approach distances. These results would predict that the hydrophilic colloids should be efficiently transported through the porous media, while the hydrophobic colloids should experience greater retention, primarily due to aggregation of the colloids with each other. However, for both the hydrophobic and hydrophilic colloids, a substantial repulsive energy barrier at larger separation distances hinder colloid attachment at the AW interface.
Breakthrough Experiments and Colloid Retention Measurements

Moisture contents and bulk densities were determined after 30 min of drainage. Water contents ranged from 0 at the top layer to saturation at the lowest depth directly after the infiltration period. Bulk densities ranged between 1.66 and 1.74 g cm$^{-3}$. Three zones can be delineated: 0 to about 0.08 cm$^3$ cm$^{-3}$ for the 0- to 14-cm depth, approximately 0.08 to 0.29 cm$^3$ cm$^{-3}$ for the 14- to 19-cm depth, and approximately 0.29 to 14-cm depth. Standard deviations in moisture contents were greatest in the intermediate and lower zones. Moisture contents during the colloid experiments were greater, increasing shortly after water was added initially and then remaining essentially constant since the visualization showed that menisci were stationary. After the water flux was stopped, drainage stopped within a few minutes. The exact moisture contents during the experiments could not be measured because the soils drained much faster than the samples could be taken.

As expected from the results of Bauters et al. (2000), the presence of a few water-repellent grains affected the water flow pattern. Infiltration in the unmodified hydrophilic sand produced one fingered flow path for colloid and water movement, measuring approximately 2 cm wide in the upper packed sand layers and increasing to the width of the chamber below the 11- to 13-cm depth (Fig. 3). In contrast, for infiltration in the weakly water-repellent sand, flow across the whole width of the chamber was established within 2 to 4 cm below the point of application. The type of colloid did not affect the infiltration pattern, although, as will be discussed, differences in the flow pattern may have had an effect on the extent of colloid retention.

At the Darcy scale, the colloid BTCs were significantly different for the hydrophilic and hydrophobic colloids while the type of sand had a much smaller effect (Fig. 4). Breakthrough of hydrophilic colloids was first detected at 0.3 PV (Fig. 4a), and effluent concentrations increased steadily to a peak value at 1.2 PV. Hydrophobic colloids first appeared at 0.15 PV, reached a plateau of approximately 0.03 $C/C_0$, increased again at 0.4 PV, and then reached the peak concentration at 1.2 PV, similar to the hydrophilic colloids (Fig. 4b). For both types of sand, the retention of the hydrophobic colloids was almost twice that of the hydrophilic colloids.

The type of sand had no effect on either the shape of the BTC or the extent of the hydrophilic colloid retention ($p > 0.27$). Approximately one-half (49.6 ± 1.8%) of the hydrophilic colloid mass was recovered in the effluent for the replicate columns of the two types of sand (Fig. 4). There was a small but significant difference in hydrophobic colloid retention between the two sands, with less retention ($p < 0.05$) of the hydrophobic colloids on the water-repellent sand (30.1 ± 1.3% of the colloid mass was recovered in the effluent, or ≈70% retained in the columns), compared with the hydrophilic sand (25.6 ± 0.5% recovery in the effluent) (Fig. 4). It is unlikely that the differences in the flow pattern between the two types of sand played a role in the extent of the retention of hydrophobic colloids because the hydrophilic colloids should have been affected in a similar way. Thus, the difference may be related to greater attraction between the hydrophobic colloids and the strongly water-repellent grains despite that these grains constituted only 0.4% of the porous media. We did not

Fig. 3. Image of the sand layers after application of hydrophobic colloids and water, showing the distribution of the blue-dyed colloids within the preferential (fingered) flow path.
Fig. 4. Colloid breakthrough curves, the solid line represents the mean $C/C_0$ values for regular (hydrophilic) sand, and the dashed line represents the slightly water-repellent sand. (a) Hydrophilic colloids, (b) hydrophobic colloids.

attempt to estimate the potential energy of interaction of the colloids with the water-repellent grains.

The depth distribution of the colloids retained in the porous media but capable of being detached by extraction with 2D water was determined for the unmodified hydrophilic sand (Fig. 5). No measurements were made for the water-repellent sand. For the unmodified hydrophilic sand the relative greatest amount of colloids retained was around the 14-cm depth, where the capillary fringe begins. Besides this similarity, the trends of retention with depth varied with colloid type. The retention of hydrophobic colloids did not show a clear trend with depth in the first 10 cm, where the moisture contents are the smallest, and then decreased farther down (open and solid circles in Fig. 5). The concentration hydrophilic colloids retained on the sand increased first and then became approximately constant below the 15-cm depth (open and solid squares in Fig. 5). Although the trend was correct, the absolute concentrations are underestimated for the hydrophilic colloids because when the amount of colloids in the effluent water and that retained in the soil were summed, the mass balance could only account for 73 and 75% of the total amount of colloids for the replicate columns. The mass balance for the hydrophobic colloids was 95 and 116%. That is, after drying and resuspension in 2D water, all the hydrophobic colloids could be released, but only one-half of the hydrophilic colloids retained on the unmodified sand grains could be removed by the same procedure.

Visualization of Colloid Retention in Video and Still Images

Visualization of the colloids provided unique and valuable information that is critical in understanding the
Retention of Hydrophilic Colloids

The processes affecting the retention of hydrophilic colloids are well illustrated in the photograph, taken at the 10-cm depth in the regular hydrophilic sand 30 min after the hydrophilic colloid suspension was added (Fig. 7). In the figure, grains are clearly visible. Most of the pore spaces contain water, except in the right-hand corner where one of the pore spaces between four grains is filled.

Fig. 6. Four isolated menisci (or a pendular ring of water) between four sand grains associated with static air–water and air–water–solid interfaces. These are the same sand grains that are shown in Videos 1 and 2.
with air. Partial pendular rings can be observed bordering this pore space. In the remainder of the photograph (Fig. 7), the grains stick out above the water as pebbles. The most distinct feature and the main mechanism of retention are the blue bands of colloids at the fringes of the menisci, associated with the AWS interface (Fig. 7). Although the details of the menisci are difficult to discern, it was clear from direct observations that the dark band of blue hydrophilic colloids was located near the grain surfaces at the edge of the meniscus where the thickness of the water film is smallest. Preferential attachment at the AWS interface is also apparent in Figs. 8a and 5 at locations labeled B and C. Crist et al. (2004) also found the attachment at or near the AWS interface to be the primary retention mechanism for 1-μm colloids. In addition, although of less importance, Fig. 7 shows the retention of colloids as a result of filtration in the small pore spaces where the grains come together. This is evidenced by the dark blue band at the location where the grains touch (Fig. 7). Another form of retention that has not often been mentioned in the literature is coagulation of the hydrophilic colloids, the formation of a “bridge” between grains. In Fig. 7, the pendular rings bordering the air space at the lower right side contains a dark blue concentrated “patch” of colloids extending across the meniscus between two grains. We do not think that this represents attachment at the AW interface between the grains, but rather an accumulation of coagulated colloids that bridge from one AWS interface to another. Hydrophilic colloid aggregation is counter to the DLVO theory presented in Fig. 2, since it shows a strong repulsive force at distances >1 nm between colloids. However, at distances <1 nm there is an attractive force. The velocity of the moving colloid could provide sufficient momentum to break through the repulsive barrier during the collision with the stationary colloid resulting in coagulation. This could be aided by certain functional groups of the carboxylated microspheres that attach to each other. The “v-shaped strings” of colloids visible in a close-up image of the bridge in Fig. 9 would support this assumption. Finally, of minor importance are some colloids at the SW interface, which we have attributed to gravitational settling.

Since the negatively charged, hydrophilic colloids are repelled by both the AW and SW interfaces (Fig. 2), the colloids are also repelled by the AWS interface. Despite this hydrophilic colloids are retained at the AWS interface. Thus an additional mechanism is needed to counteract the repellent force of the AWS interface. This mechanism can best be deduced from the movement of colloids in the pendular ring labeled B in Video 1. In this video, single colloids can be seen moving through the pendular rings as small black dots and a few as larger colloidal aggregates. Although most of these colloids move through the middle of the pore, a few of these colloids veer off the path, bringing them close to the edge of the meniscus. This veering off perhaps is caused by the force imparted by the centrifugal motion of the circular flow through the pendular ring. The larger colloidal aggregates suddenly become trapped at the AWS interface, and single colloids are caught by the colloids already present at the interface. There is no regularity in the interval between “catches,” and we are not sure why the colloids are caught; it is likely related to the small thickness of the meniscus at the AWS interface.

In addition, Video 1 shows that colloids are unlikely to be retained at the AW interface as proposed originally by Wan and Wilson (1994a). The water in the AW interface, except close to the edges near the solid interface, is in motion, and any colloid at the AW interface will
move with the water in the main flow direction. The water in the pendular ring labeled D is stationary and, at the same time, is unconnected during infiltration and drainage. Therefore, colloids were not present at any time, and the pendular ring cannot retain any colloids.

Finally, in Video 2 another mechanism of colloid retention can be observed that was not visible in the still images. In the images of Video 2, which is at the location depicted in Fig. 6 and appears later in the flow experiment, aggregated particles are seen accumulated in the lowest part of the pendular ring labeled A. This is likely due to gravitational settling of the aggregates near the meniscus even though it is apparent that the water is flowing upward at this time. It is interesting to see that sometimes the water movement stops and even moves backward. This has a large effect on the stability of the accumulated colloids. It is not clear if a blockage upstream or the pump caused the change in flow condi-

Fig. 9. Coagulated hydrophilic colloids forming “bridges” between sand grains at the 13-cm depth 98 min after adding colloid suspension.
tions. In this video, filtering of colloids can also be seen in pendular rings labeled B and C in Fig. 6. It is a dynamic process where colloids sometimes move slowly and sometimes quickly, almost similar to rocks as bedload in a fast flowing river.

Retention of Hydrophobic Colloids

For the hydrophobic colloids (Fig. 8b), retention at the AWS interface was present but minor compared with the hydrophilic colloids. The major deposition mechanisms are due to the strong attachment force that exists between hydrophobic colloids, resulting in the formation of larger colloid aggregates that can be more easily filtered by the relatively narrow pore spacing close to where the grains are touching. Also, the colloidal aggregates can attach to those colloids already present at the grain surface. The dynamic nature of this process was not captured on video, but it is well illustrated in still images (Fig. 8b). Even though the injection solution contained colloids of a uniform size, it is apparent from visual observations during the experimental run that the mobile colloids occur in a range of sizes, suggesting that the colloids have aggregated during transport.

The images of colloid retention are in agreement with the BTCs. The presence of fewer hydrophobic than hydrophilic colloids in the drainage water is consistent with rapid aggregation of the hydrophobic colloids and retention of the aggregates by straining at pore throats as postulated by Bradford et al. (2002, 2003). Although some aggregate formation was observed for the hydrophilic colloids, the images suggest that aggregation was far less extensive than for the hydrophobic colloids, which is consistent with the existence of a relatively small repulsive energy barrier for hydrophilic colloid–colloid interactions.

Absence of Film Straining

The resolution of the visualization equipment made it difficult to prove the absence or presence of film straining, because water films thinner than approximately 1 μm could not be observed. Despite that, we did not find any microspheres on the grains itself away from the AWS interface. Thus, the relatively large 5-μm microspheres were not strained by the films where water moves from one pendular ring to the next via film flow. Further, we would expect that, as water covering the grain thins to films during drainage and films approach the diameter of the colloids, capillary pressure would push the colloids toward the bulk solution, as shown in Sur and Pak (2001) for suspended films.

Mobilization of Colloids Deposited at the Air–Water–Solid Interface

During a trial run, the water flow was increased, and the accompanying video (Video 3) demonstrates colloid behavior consistent with the proposed mechanism of Saiers and Lenhart (2003a) that immobilization of the hydrophilic colloids at the AWS interface was easily reversible. In this video, coagulated colloids are deposited at the AWS interface, but as soon as the water surface expands due to an increase in flow rate, the deposited colloids are swept away. Moreover, the video images show an air bubble trapped in the pore space. While a few colloids are trapped within the ring, the majority of the colloids pass by the bubble.

Mechanisms of Colloid Retention and Transport

On the basis of the results of the Darcy-scale BTCs and the video and still images at the pore scale, we can identify the mechanisms of colloid transport in our partially saturated porous media.

The observed retention of a greater amount of hydrophobic than hydrophilic colloids is consistent with the calculated balance of attractive and repulsive electrostatic forces. Repulsive energy barriers limit attachment between the colloids and the hydrophilic surfaces of the unmodified sand grains, as well as with the AWS interface (Fig. 2). The absence of an energy barrier between hydrophobic colloids and attractive interactions at shorter separation distances favors aggregation of the hydrophobic colloids. Rapid aggregation would be expected in the absence of energy barriers, resulting in formation of the extended structures seen in Fig. 8b. Kim and Berg (2000) also observed that as the aggregate grew, new particles were more likely to contact and immediately attach to the periphery of existing aggregates. This is presumably the most significant mechanism of hydrophobic colloid retention.

The retention of hydrophilic colloids in the very thin film of water at the edge of the meniscus is probably the result of hydrodynamic processes. Saiers and Lenhart (2003b) also reasoned that silica colloids were trapped in the narrow wedges near the three-phase contact of pore-corner menisci and at the termini of discontinuous corner water, whereas colloid retention did not occur at water films. The centrifugal motion within the pendular rings observed in the videos would tend to force colloids toward the AWS interface, and then any deviation from the primary direction of flow could move the particle toward the AWS interface, as shown in Video 1. Under laminar flow, the particle velocity approaches zero near the grain surface and increases at distances away from the surface. Thus, colloids propelled toward the edge of the meniscus would encounter the very slow moving water near the AWS interface and become immobilized. Alternately, or in addition, the retention in the thinnest portion of the SW interface at the edge of the meniscus may represent a form of film straining, with colloids becoming immobilized in films as the film thickness approaches that of the colloid diameter. Assuming a contact angle for water and quartz sand of 30° (Freitas and Sharma, 1999), the meniscus thickness will equal that of the colloid diameter (5 μm) at a distance of only 5 to 7 μm from the edge of the AWS interface. However, when the immobilized colloids are aggregated, we find that for an aggregate 10-fold larger than the primary particle, the theoretical distance from the AWS interface (=50 μm) is in better agreement with the observed distances (e.g., Fig. 8A).
Lenhart and Saiers (2002) found that colloid transport in unsaturated porous media depended principally on the degree of pendular ring discontinuity, pore water velocity, and the retention capacity of the AW interface. Since we worked with relatively large colloid sizes (≥5 μm), our interpretation of the transport processes in the vadose zone is not inconsistent with this description, but requires the following modifications. Retention occurs at the AWS interface, and depends on the retention capacity of this triple-point interface. Second, particle motion within the curved pendular rings may be important in attachment at the AWS interface, as shown in the video images. Furthermore, the mechanisms for colloid retention at the AWS interface are not clear, but may be related to factors such as pore water motion with the pendular rings, low laminar flow velocities near the grain surface, and/or retention of colloids or colloidial aggregates in the thin water films near the AWS interface. The latter is affected by changes in flow regime (Video 3). More studies are needed to examine the importance of these processes.

APPENDIX

The following videos are available as supplemental material. Use of high speed internet connection is recommended since each video is around 30 MB.

Video 1. Retention of hydrophilic colloids at AWS interface.


Video 3. Instability of colloid retention at AWS interface with changing flow rate.

REFERENCES


Atrazine adsorption and colloid-facilitated transport through the unsaturated zone. J. Environ. Qual. 29:1632–1641.


