Pore-Scale Visualization of Colloid Transport and Retention in Partly Saturated Porous Media

John T. Crist, John F. McCarthy, Yuniati Zevi, Philippe Baveye, James A. Throop, and Tammo S. Steenhuis*

ABSTRACT

In unsaturated porous media, sorption of colloids at the air–water (AW) interface is accepted as a mechanism for controlling colloid retention and mobilization. However, limited actual pore-scale observations of colloid attachment to the AW interface have been made. To further investigate these processes, a real-time pore-scale visualization method was developed. The method builds on the light transmission technique for fingered flow studies in packed-sand infiltration chambers and combines it with high-resolution, electro-optical hardware and public domain imaging software. Infiltration and drainage of suspensions of hydrophilic negatively charged carboxylated latex microspheres provides compelling visual evidence that colloid retention in sandy porous media occurs via trapping in the thin film of water where the AW interface and the solid interface meet, the air–water–solid (AWS) interface. With this modified theory of trapped colloids at the AWS interface, we are able to explain the apparent discrepancy between previous experimental evidence of hydrophilic colloids seemingly partitioning to the AW interface and more recent findings that suggest this type of colloid does not adsorb at the AW interface.

Typically defined as suspended particulate matter with diameters <10 μm (Stumm, 1977), colloids exist as organic and inorganic materials such as microorganisms, humic substances, clay minerals, and metal oxides (McCarthy and Zachara, 1989). Scientific reviews emphasize the need for more research on the mechanisms controlling transport and retention of colloids in the unsaturated zone (Ouyang et al., 1996; Kretzschmar et al., 1999; McCarthy, 2003). While colloid transport in saturated porous media is dominated by colloid interactions at water–solid interfaces, the presence of a third phase, air, introduces additional retention mechanisms for colloid transport in partially saturated porous media. Based on the pioneering work of Wan and Wilson (1994a), the interaction of colloids with the AW interface has been invoked as a dominant process in colloid retention. Wan and Tokunaga (1997) also introduced an additional mode of colloid retention. Invoking a concept of film straining, they proposed that transport of suspended colloids could be retarded due to physical restrictions imposed when the thickness of water films fell below the diameter of the colloids.

Other than the pioneering visualization studies of Wan and Wilson (1994a), colloid transport experiments with porous media have been based on mass balance of breakthrough colloid concentrations in packed-sand columns (Wan and Wilson, 1994b; Schafer et al., 1998; Jewett et al., 1999; Jin et al., 2000; Lenhart and Saiers, 2002). On the basis of analyses of outflow concentrations of colloid particles, these authors found that more particles were retained in the column at lower water contents (or under conditions where there were higher percentages of trapped air). Retention, measured as reduced colloid concentrations in the column outflow, was attributed to sorption at the AW interface and film straining. In one case retention of bacteriophages in a batch system was ascribed to the presence of a dynamic AWS interface (Thompson et al., 1998; Thompson and Yates, 1999). New data suggest, however, that conceptual models of colloid transport in unsaturated media need to be reexamined. It has been generally assumed, based on visualization studies using etched-glass micromodels (Wan and Wilson, 1994a), that retention at the AW interface was relevant to a wide variety of colloids, including hydrophilic and hydrophobic latex microspheres, clay particles, and bacteria. In contrast, Wan and Tokunaga (2002) demonstrated in bubble column experiments that only positively charged particles attached to the negatively charged AW interface, suggesting that immobilization at the AWS interface would be limited to a smaller subset of environmental colloids. Wan and Tokunaga (1997) conceptualized film straining as a colloid retention process within thin films of water flowing from one pendular ring to the next. However, Lenhart and Saiers (2002), noting that calculated water film thicknesses were 20-fold smaller than their 0.4-μm colloids, concluded that the relevant immobilization process was the degree of pendular ring discontinuity, rather than immobilization in thin water film.

Therefore, it is appropriate to consider alternate explanations for the observed retention of colloids in unsaturated transport studies. In this paper, we describe a novel pore-scale visualization technique. In contrast to two-dimensional micromodel visualization studies, this new method is adapted to the three-dimensional, sandy soil matrix with flowing water through a complete infiltration and drainage cycle (Wan and Wilson, 1994a, 1994b; Wan et al., 1994). The results help to reconcile some inconsistencies among earlier studies.

MATERIAL AND METHODS

The principal components of the experimental setup were the infiltration chamber, mounting assembly, light source, electro-optical equipment (lens, camera, and computer sys-
The infiltration chamber was supported on a mounting assembly at an incline of 35° from horizontal and perpendicular to the focus of the camera. The viewing area was adjusted across the camera by sliding the chamber along rails on the mounting assembly. Alignment slots on the rails, separated at 1-cm intervals, allowed for consistent placement to record images at each height of the chamber. The viewing area was illuminated using a variable intensity, 150-W tungsten-halogen lamp with a fiber optics cable (D.O. Industries, Inc., Rochester, NY). The electro-optical equipment included a Zoom 6000 II lens assembly with 1X adaptor (D.O. Industries, Inc.) and a 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. Maximum 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.

The infiltration experiments depended on detection of micrometer- and submicrometer-sized particles on silica sand grains and on the menisci connecting sand grains. Fluorescent and nonfluorescent dyed polystyrene latex microspheres (Magsphere Inc., Pasadena, CA) of different sizes and surface characteristics were evaluated as surrogates for natural colloids. In trial studies, analysis of spectral output or transmitted light using a fiber optic spectrophotometer (Ocean Optics, Inc., Dunedin, FL) revealed no significant wavelength peaks for characterizing fluorescent colloid distribution in packed sand. More encouraging results were found with the nonfluorescent dyed particles in various colors such as red, bright green, and blue. Through visual inspection, it was determined that microspheres dyed blue provided excellent color contrast against the yellowish-white and grayish-white (acid-washed) sand grains.

Quartz sand (Unimin Corp., NJ), with grain diameters between 0.43 and 0.60 mm, was chosen as the porous media because of its semitranslucent quality, well-established characterization (Schroth et al., 1996), and successful application in light transmission studies (Darnault et al., 1998). Inorganic and organic impurities on the sand surface were removed using concentrated hydrochloric and chromic acids, following procedures outlined by Litton and Olson (1993). The chamber was assembled, placed in a vertical position, and filled with sand to a height of 20 cm. Bulk densities were between 1.66 and 1.70 g cm$^{-3}$, and porosities ranged from 0.36 to 0.37 cm$^3$ cm$^{-3}$.

The chamber was laid flat after packing with dry sand, and the front panel was removed to avoid light reflections that obscured the view and, thus, exposed one side of the packed-sand column to air. One pore volume (PV, ~18 mL) of distilled, deionized water was delivered through the drainage channels at an inlet flow rate of 2 mL min$^{-1}$ at the flat position. The one-PV injection completely saturated the pore space in the packed-sand column. The infiltration chamber was then placed at a 35° incline to maximize gravitational effects on flow while preventing erosion of the packed-sand layers during infiltration and drainage. Images of water distribution in the packed-sand column were captured at 1-cm intervals from depths of 1 to 18 cm. Image recordings were continued every hour for the next 6 h as the wetted sand was allowed to drain. A gradient in water content developed during the 6-h drainage period, simulating various saturation values, from unsaturated near the surface of the soil to completely saturated at the bottom of the chamber. Six hours after prewetting the packed-sand layers, microspheres dispersed in a low ionic strength solution (0.1 mM CaCl$_2$ and pH 5.6) were applied as a point source over the top layer (0-cm depth) of the packed sand using a peristaltic pump. One PV of colloidal suspension was delivered at a flow rate of 1.3 mL min$^{-1}$, after which the column was allowed to drain.

Digital still images were captured before and immediately following application of the colloidal suspension, and every hour thereafter for the next 2 h. Images were recorded at 1-cm intervals from depths of 1 to 18 cm, yielding over 160 still images at the end of each experiment. The chamber was laid flat after the additional 2-h drainage period and was sectioned at 1-cm intervals for oven drying and gravimetric water content determination.

Several experiments were completed to demonstrate the practicability of the new visualization method and to examine the distribution of colloids on silica sand. We will report on three of these experiments conducted with negatively charged hydrophilic (carboxylated) microspheres. Variations in microsphere diameters and concentrations were evaluated in these experiments. Microspheres (Magsphere Inc., Pasadena,
CA) were chosen with mean diameters of 0.3 and 0.8 \( \mu \text{m} \), and prepared in two different concentrations of approximately 3 \( \times \) 10\(^7\) and 6 \( \times \) 10\(^7\) particles mL\(^{-1}\), respectively. These experiments were performed in duplicate, and consistent results were obtained between replicates. Picture clarity between the experimental results was variable and only the best visualizations are shown.

**RESULTS**

Regardless of the colloid concentrations, the size of the colloids had a large effect on our ability to visually detect the particles. The 0.8-\( \mu \text{m} \) hydrophilic colloids were easily visible from the background environment with this experimental setup. However, the 0.3-\( \mu \text{m} \) hydrophilic colloids were only faintly visible. Consequently, experimental results relating to colloids in this size range are not presented.

After 2 h of drainage, moisture contents in the chamber ranged from 0.37 cm\(^3\) cm\(^{-3}\) saturation at the bottom to 0.16 cm\(^3\) cm\(^{-3}\) near the top (Fig. 2). The moisture content did not vary significantly thereafter, as the drainage from the bottom of the column was minimal to undetectable. A similar gradient of moisture distribution was present before and after application of the colloidal suspension, thus providing uniform initial conditions for all experiments. Recorded images (Fig. 3) clearly show the presence of menisci or AW interfaces connecting sand grains.

Direct observations of microspheres during infiltration convincingly showed the dynamic nature of colloid transport. Even though it is impossible to completely convey this dynamic behavior through still photographs, captured images indicate that not all pore spaces carry the same amount of flow during infiltration and that distinct paths are followed. In the example depicted in Fig. 4, the pores with the menisci or AW interfaces connecting wetted sand grains before inputs of the colloidal suspension (Fig. 4a) were filled with water after the infiltration front of the colloidal suspension advanced past a depth of 9 cm (Fig. 4b). It should be noted that the blue rings on the surface of the grains resulted from removal of the front panel of the chamber, creating an additional interface with the air. These rings form at the edges of the menisci at locations where the sand grains stick out of the water. We fully recognize that these rings may not occur in infiltration experiments using vertical sand columns. Nevertheless, our experimental setup provided ample opportunities to investigate our area of interest—the interface region centered about the meniscus—over a broader range.

In Fig. 5, photographs of the 0.8-\( \mu \text{m} \) colloids are shown at depths of 2 to 18 cm below the top of the column immediately after the application of colloids was stopped and colloids had infiltrated to the bottom of the chamber. We first consider observations on the distribution of water along the column, and will then discuss the distribution of colloids. The sand at the bottom of the column (18 cm below the top) was a fully saturated horizon. Moving up the column along the gradient of water content from 12 to 4 cm below the top of the column, the pores below the upper surface of the sand are filled with water. The presence of nearly saturated pores is in agreement with earlier findings on unstable wetting front flow experiments. Water was found to flow as saturated columns through the sand, and not through films, even at low flow rates (Lu et al., 1994). At a depth of 2 cm from the top of the column, the water had drained sufficiently that isolated pendular rings are observed.

The distribution of the colloids can be observed as blue bands. In the fully saturated horizon (18 cm), the suspended colloids could not be distinguished as anything more than a faint blue cast to the water, and there is no evidence of colloid deposition at the solid–water interface of the grains. Moving up the column, drainage exposes more of the AW interface at the upper surface of the column. At depths from 4 to 12 cm, blue bands form where the grains stick out of the water and are seen as partial rings in the photographs in Fig. 5. Although the AW interface is difficult to capture on the photographic film, computer monitor images clearly show that bands form at positions where the meniscus appears to be
Fig. 4. (a) Menisci or air–water interfaces after 6 h of drainage; (b) colloid–water distribution after application of the colloidal suspension. Rewetting of the sand eliminated the static air–water interfaces.

Fig. 5. Distribution of 0.8-μm hydrophilic colloids (≈3 × 10^7 particles mL^-1) after application of the colloidal suspension. Values shown are depths below the top layer of the sand column.
attaching to the sand grains. We refer to this as the AWS interface or water thin film. Visual inspection and analysis of the timed videotape recordings suggest that the bands formed within 30 to 60 s after passage of the colloid solution. The photographs taken near the bottom of the column at depths of 14 to 18 cm show that when the grains are submerged, the characteristic blue rings do not form. Pendular rings with intense blue bands at the edges of the menisci are visible at 2 cm from the surface (see also Fig. 3).

Figure 5 shows that not all of the colloids are captured at the AWS interface. Some are also deposited at other locations on the sand grains, especially in parts where there are imperfections in the grains (see, e.g., photographs at the 6- and 8-cm depths in Fig. 5). Figure 5 shows again that the colloids flow in preferential paths between the grains. This is well illustrated at the depth of 12 cm, where most of the colloids are flowing in the upper and right half of the photograph, as indicated by the diffuse dark blue color in the fluid-filled pores. The videotape clearly showed that there was little movement of the colloidal suspension in the lower left-hand corner.

With time and continued drainage, the banding patterns widened and darkened to a more intense blue as the meniscus retreated and the circumference of the AWS interface decreased (Fig. 6). Similar distribution patterns developed on the sand grains, including the pendular rings, for all experiments.

**DISCUSSION**

Many experimental studies in the literature use breakthrough curves of colloids and their mathematical simulation to infer the mechanisms of colloid transport in partially saturated porous media. These studies have attributed the decreased concentration of colloids in the outflow water to mechanisms such as deposition on solid surfaces, sorption to stagnant AW interfaces, and film straining at low moisture contents (McDowell-Boyer et al., 1986; Wan and Tokunaga, 1997). The novel experimental setup described here can be used to directly investigate the relative importance of the first two processes. The third process, however, could not be examined because moisture contents throughout the chamber were too high for significant film straining to occur as described by Wan and Tokunaga (1997). In our study, the only thin water film occurred at the edge of the menisci, as is visible in Fig. 7.

The data from experiments with unsaturated colloid transport in both natural soils and model systems (Wan and Wilson, 1994b; Jewett et al., 1999; Jin et al., 2000) clearly demonstrate that retention of colloids does occur, and it occurs to a significant extent in some cases. Nonetheless, the question of what actually controls the fate of colloids in the unsaturated subsurface environment is still largely unanswered. Results of this investigation suggest that more serious consideration should be given to colloid interactions at or near the AWS interface. In all cases in our experiments, colloids were retained near the AWS interface, as demonstrated by the blue banding pattern at the edge of the menisci as soon as colloid suspension drained to create an air interface (Fig. 3, 4, and 5). The intensity of the blue bands increased as the water level subsided from individual grains (Fig. 5 and 6). It appeared that colloids initially collected at the AWS interface when the water first fell below the level of the tops of the grains (e.g., faint blue line in Fig. 5, 12 cm), were “trapped” at the interface as the perimeter of the meniscus decreased with continued drainage (Fig. 6). There is likely an additional capture of colloids as the AWS interface recedes. The end result is a widening and darkening of the blue
Fig. 8. Trapped air bubble between narrowly separated, hydrophilic solid surfaces.

banding patterns or rings on the grains reflecting immobilization of the colloids.

The occurrence of AW interfaces in unsaturated porous media increases with decreasing moisture content, and, correspondingly, the number of AWS interfaces also increases at lower saturation levels. Uncovering the front panel of the infiltration chamber considerably increased the prevalence of AW as well as AWS interfaces, extending the possibilities of capturing colloid retention at these two interfaces. However, there was clearly no retention of the negatively charged colloids with the AW interface, which is consistent with recent studies using a bubble column (Wan and Tokunaga, 2002).

It is not clear from our experiments why the negatively charged colloids move to the AWS interface. Once there, thin films that exist at that location appear to prevent further movement. But, rather than being trapped by receding water films as suggested by film straining (Wan and Tokunaga, 1997), the colloids moved with the contracting AWS interface during drainage. Thus, it appears that the colloids were not attached to either the AW interface or the solid–water interface, but rather were trapped near the edges of the meniscus near the AWS interface. Colloid retention at the AWS interface is also consistent with the batch experiments of Thompson et al. (1998) and Thompson and Yates (1999).

Because of the apparent discrepancy between descriptions of colloid retention at the AW vs. AWS interface, it is worth reexamining Wan and Wilson’s (1994a) micromodel images. In these images, the critical region for attachment at the AW interface is at the outside edge of the darkened ring on the stationary air bubble. In an air bubble trapped between narrowly separated, hydrophilic glass plates, the distinction between the AW and AWS interfaces is difficult to distinguish on the basis of transmission-based images alone (Fig. 8). In other words, it is likely that colloids at the AWS interface were interpreted as being at the AW interface.

But, is the distinction between the AWS and AW interfaces important? After all, the AWS interface is part of the AW interface. However, for unsaturated colloid transport experiments, the distinction between the assumptions may be far from inconsequential. In most cases, water movement in column transport experiments occurs via laminar flow. Under laminar flow theory, for pores that carry flow, the velocity at the surface of a solid is zero, while it is positive anywhere else, including the AW interface away from the solid. For pores that do not participate in the flow process, the AW interface would have a zero velocity, but these AWS interfaces are not likely to contain any colloids because they are not connected to the flow paths with colloids. Our observations are, therefore, a refinement on the results of Lenhart and Saiers (2002) who attributed colloid retention to the formation of pendular rings. However, our results suggest that these pendular rings are part of the flow network and not disconnected.

In summary, the laminar flow theory would not explain very well the retention of colloids at the AW interface unless we conceptualize that the medium has a significant number of stationary bubbles. Our visualizations did not reveal many such bubbles. Therefore, the retention of colloids in the thin film of water located at the triple point where the AW and solid–water interfaces meet is much more straightforward to explain colloid retention, and is in agreement with our experimental observations.

REFERENCES


