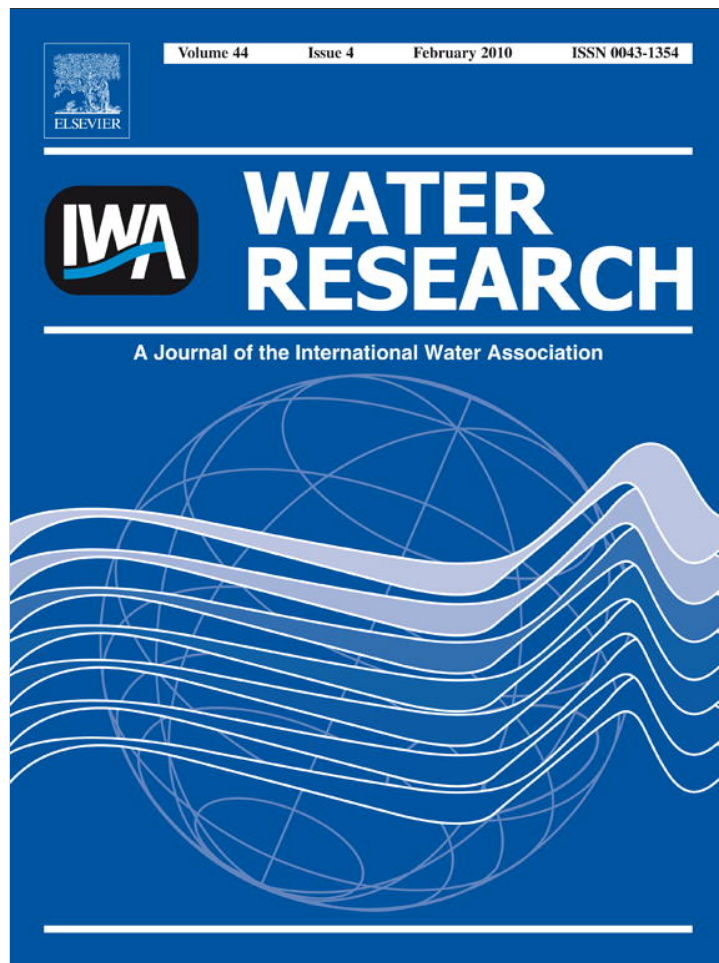


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Direct observations of colloid retention in granular media in the presence of energy barriers, and implications for inferred mechanisms from indirect observations

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ABSTRACT

In this paper we present direct observations of retention of colloids in granular porous media over a large size range (0.21–9.0 μm) and generalize the significance of attachment in grain to grain contacts and attachment on the open surface as a function of colloid:collector ratio. We examine reversibility of attachment via these mechanisms with respect to ionic strength reduction and fluid velocity increase. We relate these direct observations to existing literature, and in some cases offer alternative interpretations of mechanisms of retention drawn from indirect observations (e.g. via column effluent and retained concentrations).

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1. Introduction

Determining the mechanisms of colloid retention in saturated porous media in the presence of energy barriers to attachment is an active area of research that has been shaped significantly by both direct and indirect methods of observation. Direct observation methods are defined here as those that allow the act of retention to be observed. Indirect methods of observation include changes in colloid breakthrough and retained concentrations in porous media columns in response to variations in colloid:collector size ratios, variations in colloid and collector interaction forces (largely via changes in solution ionic strength), and variations in fluid velocity. The major advantage of inferring mechanisms from indirect observations is column-scale integration of pore-scale processes that

influence retention; whereas an important drawback is the fact that multiple mechanisms may often explain an observed change in breakthrough or retention. Neutral consideration of all possible mechanisms to explain a given indirect observation is challenging, and attribution to specific mechanisms is greatly aided by complementary direct observation of deposition. Despite a recent increase in direct observation methodologies, inference from colloid breakthrough-retention behavior remains an important aspect of colloid transport research. [Table 1](#).

The purpose of this paper is to present direct observation results for transport of a range of colloid sizes (0.2–9 μm) through porous media in order to draw generalizations regarding the influence of colloid size on the mechanisms of colloid retention in the presence of energy barriers. The

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Table 1 – Colloid and collector sizes from glass bead experiments.

Colloid diameter (μm)	Collector diameter (μm)	Colloid:collector ratio
0.21	510	0.00041
1.1	750	0.0015
2.0	510	0.0039
4.5	510	0.0088
9.0	510	0.018

experiments and generalizations explored here address a wide range of colloid sizes, fluid velocities, and solution ionic strengths in spherical granular porous media with narrow grain size distributions. The narrow grain size distribution is not representative of all natural aquifer sediment; however, it does represent porous media used in the vast majority of reported colloid transport experiments, allowing observations drawn here to be related to existing research. A major challenge for colloid transport research is to develop predictive models based on identified mechanisms of retention, and this paper attempts to draw generalizations as a step toward meeting that challenge.

1.1. “Overcoming” the energy barrier

Repulsive energy barriers prevent colloids from approaching surfaces closer than some small distance; e.g. 10–100 nm for electric double layer repulsion (depending on ionic strength), and typically larger for steric repulsion (e.g. emanating from extracellular polymers on cell surfaces). In the presence of an energy barrier, colloid retention involves both the process of colloid transport “through” the energy barrier, as well as colloid retention on, or near, the surface despite the mobilizing force of fluid drag and Brownian motion. For the purposes of this paper, we will lump transport and retention into the term “retention”; however, it is critical to recognize that, in order to be retained, the colloid must somehow first “overcome” the energy barrier to attachment, where the term in quotes can include the process of finding a region of attraction outside this barrier (e.g. secondary energy minimum association). The mechanisms by which colloids “overcome” the energy barrier have been discussed for the past three decades (e.g. Adamczyk et al., 1983; Elimelech and O’Melia, 1990; Johnson, 2008) and are briefly described below.

1.2. Heterogeneity and roughness

Colloid attachment in the presence of hetero-domains of attractive surface charge, and roughness, are well established as mechanisms of retention in the presence of energy barriers (Elimelech and O’Melia, 1990; Song and Elimelech, 1994; Johnson et al., 1996; Bhattacharjee et al., 1998; Shellenberger and Logan, 2002; Auset and Keller, 2006; Kemps and Bhattacharjee, 2009). Despite the physics of these two mechanisms being distinct, they are often discussed together because both involve relatively random distribution across grain surfaces, the scale of these features can be similar, and their effect (local reduction or elimination of repulsion) is qualitatively equivalent. The significance of these mechanisms to colloid

deposition was recently downplayed (Tong and Johnson, 2006) on the basis that colloid deposition efficiencies were much greater in porous media relative to flat surfaces under ostensibly equivalent conditions (also observed by Redman et al., 2004; Walker et al., 2004; Brow et al., 2005).

1.3. Secondary energy minima

Retention of colloids in secondary energy minima has been inferred from experiments showing colloid elution from sediment in response to decreased ionic strength (Hahn and O’Melia, 2004; Franchi and O’Melia, 2003; Hahn et al., 2004), as well as from experiments where the height of the calculated energy barrier to attachment did not seem to support the observed retention of large colloids (Tufenkji and Elimelech, 2005). Although colloids may associate with surfaces via secondary energy minima, this does not necessarily result in retention, since fluid drag and other forces continue to act on the colloid. Numerical simulations suggest that secondary energy minimum-associated colloids can be retained in zones of low fluid drag (Johnson et al., 2007), and recently there have been claims of direct observation of retention of colloids in secondary energy minima via light microscopy (Kuznar and Elimelech, 2007; Liu et al., 2009). Numerical simulations also suggest that retention may occur in eddy zones with or without secondary energy minimum association (Torkzaban et al., 2008). More recently, numerical simulations have been used to suggest that secondary energy minimum-associated colloids may in fact be immobilized via colloid-surface frictional forces (Torkzaban et al., 2007, 2008). However, these latter simulations rely on colloid-surface frictional parameters that were developed for surfaces in adhesive contact; hence, extension of these parameters to simulations outboard of the energy barrier is being debated (Johnson et al., 2009). If such a mechanism occurs, those colloids that were immobilized via secondary energy minima interactions should also be mobilized by ionic strength reductions.

An alternative interpretation of colloid elution from porous media in response to reduced ionic strength was recently provided by Duffadar and Davis (2007, 2008), who numerically simulated colloid retention in the presence of energy barriers as resulting from interaction with attractive nano-domains on the overall-repulsive collector surface. In these simulations, the colloid-surface interaction zone included both repulsive and attractive domains, such that colloid retention was supported under conditions where net attraction prevents colloid mobilization via fluid drag. In this model, colloids experience surface friction that is inversely proportional to their separation distance from the surface, such that colloid rolling ceases (colloid is immobilized) when the adhesive torque exceeds the fluid drag torque. Retention and release by this mechanism serves as an alternative explanation to the experimental observations of Liu et al. (2009) who claimed that colloids temporarily immobilized on a collector surface were associated with secondary energy minima. In the simulations by Duffadar and Davis (2008), colloids may be re-entrained in response to perturbations such as increased fluid velocity or decreased ionic strength, in which the latter decreases the net attraction across the interaction area, thereby allowing mobilization. Hence, the observation that colloid retention in

the presence of energy barriers can be reversed via reduction of solution ionic strength can potentially be explained by both colloid retention via secondary energy minima and colloid retention via surface heterogeneity.

1.4. Grain to grain contacts

Direct observation experiments demonstrate accumulation of colloids in grain to grain contacts (e.g. Bradford et al., 2005, 2006; Li et al., 2006; Xu et al., 2006; Yoon et al., 2006; Tong et al., 2008), and mechanistic simulations also yield colloid retention in grain to grain contacts, where the colloid is pushed into contact through one of the two bounding energy barriers (Johnson et al., 2007). This latter process was referred to as wedging (Johnson et al., 2007), whereas many researchers informally use the term straining to refer to both the process of colloid retention in grain to grain contacts and colloid entrapment in pore throats too small to pass. Retention of colloids in porous media by straining has been inferred in numerous papers on the basis of greater retention of larger-sized colloids (e.g. Bradford et al., 2002, 2003, 2004, 2005) and retention in spite of large calculated repulsive energy barriers (e.g. Tufenkji et al., 2004; Foppen et al., 2005; Shen et al., 2008; Xu et al., 2008).

Different researchers have made different assumptions about the nature of colloid retention in pore throats too small to pass and in grain to grain contacts. For example, some researchers assume that these forms of retention does not involve actual attachment to surfaces, but rather involves a stasis whereby the colloid is trapped but not forced into contact with the surface, and this is evidenced by these authors reversing fluid flow within their porous media columns, and attributing those colloids that are eluted to those that were retained by “straining” (e.g. Foppen et al., 2007). Alternatively, on the basis of numerical simulations, Johnson et al. (2007) consider colloids immobilized at grain to grain contacts to be genuinely attached, having pushed through one of the two bounding energy barriers in the grain to grain contact. Both assumptions appear valid in their respective contexts; hence, direct observations of colloid behavior in response to fluid flow perturbations are needed to assess these two possible interpretations.

1.5. Rationale for more observations

Surface heterogeneity, secondary energy minima, and grain to grain contacts are noted features in colloid retention in the presence of energy barriers, as described above. Systematic direct observation studies are needed to determine how the prevalence of retention according to the above features varies with colloid size. Our goal was to characterize the mechanisms of colloid retention across a large range of colloid sizes (0.2–9.0 μm) in a system that allows direct observation of colloid retention in real time. The reversibility of retention as a function of ionic strength reduction, fluid velocity increase, and mild disassembly of the pore structure was also examined in order to further understand the mechanisms of retention. In our experiments we attempted to answer the following questions:

- Do we observe significant retention of colloids at grain to grain contacts?
- Do we observe significant retention of colloids on the open surface (presumably by surface charge heterogeneity and roughness)?
- Do we observe significant retention of colloids in secondary energy minima (retention in close proximity to the surface without immobilization, and/or mobilization by ionic strength reduction)?
- Do we observe significant colloid re-entrainment in response to reduced ionic strength, increased fluid velocity, and mild disassembly of the pore structure?

2. Materials and methods

2.1. Microspheres

The microspheres used in the experiments were spherical mono-dispersed fluorescent carboxylate-modified polystyrene latex microspheres. Five sizes were used: 0.21, 1.1, 2.0 μm (505 nm excitation, 515 nm emission wavelengths, Molecular Probes, Inc., Eugene, OR), 4.5 and 9.0 μm (441 nm excitation, 486 nm emission wavelengths, Polysciences, Inc., Warrington, PA). The solids concentration of the stock solutions was in the range of 2–3%. The solutions used for the experiments were prepared by diluting the stocks using a buffered solution at the desired ionic strength. Colloid injection concentration varied among the different sizes due to different light intensities among the different microsphere stocks; i.e. 1E9, 1E7, 1E7, 5E5, 1E5/ml for 0.21, 1.1, 2.0, 4.5, 9.0 μm sizes, respectively. Electrophoretic mobilities of the microspheres were measured using a ZetaPALS Analyzer (Brookhaven Instruments, Holtsville, NY) and were converted to zeta potentials using the von Smoluchowski approach (Li et al., 2004; Tong and Johnson, 2006), yielding zeta potentials of –27, –59, –43, –49, –48 mV for the 0.21, 1.1, 2.0, 4.5, and 9.0 μm sizes, respectively (20 mM ionic strength solution described below), the zeta potentials of crushed glass beads and quartz sand were similar at this ionic strength, approximately –50 mV (Li et al., 2004; Tong and Johnson, 2006).

2.2. Buffered solutions

The solutions used in the experiments were prepared using milli-Q water and NaCl for the required ionic strengths (1 mM and 20 mM NaCl). The solution was buffered using 2.2 mM of MOPS (3-(N-Morpholino)propanesulfonic acid, 4-Morpholinepropanesulfonic acid; Sigma-Aldrich Co.). The pH was adjusted to 6.72 using a solution of KOH 0.1 M. The solutions were degassed using a low vacuum diaphragm pump (~15 mmHg) for 24 h. Although many previous manuscripts examine retention under conditions of pH 10 or higher to guarantee highly unfavorable conditions, we herein consider conditions more typical of groundwater environments.

2.3. Porous media

Glass beads of 510 μm diameter (Cataphote Inc., Jackson, MS) were used for most of the experiments (except those

corresponding to the 9.0- μm microspheres, where 750- μm glass beads were used). The glass beads and the cover slide used in the flow cell were cleaned using the SC-1 cleaning procedure. This procedure involved boiling the substrata in with a 5:1:1 solution of Milli-Q water, 30% H_2O_2 , and 27% NH_4OH at 75–80 °C for 10 min to remove organic materials and metal oxides from the surfaces. Boiling was performed in a Pyrex glass beaker dedicated to this procedure. Following the SC-1 cleaning process, the porous media and the cover slides were thoroughly rinsed with Milli-Q water, the glass beads were dried in an oven overnight at 85 °C, and the cover slide was dried with pure compressed N_2 gas (high purity), and placed in the impinging jet flow cell. Experiments for the 0.21, 1.1, and 9.0 μm microspheres were also conducted in 395- μm diameter Ottawa sand prepared as described above.

2.4. Flow cell

The microsphere suspension was introduced by a syringe pump (Harvard Apparatus, Holliston, MA) into a custom-made polycarbonate radial stagnation point flow (RSPF) cell downward through a 1-mm inner diameter stainless steel capillary tube. The glass substratum (impinging surface) was a distance of 1 mm from the exit of the capillary tube into the RSPF chamber. Fluid removal from the flow cell occurred via four equally spaced capillary outlets (inner diameter 0.5 mm), located 12.5 mm from the inlet capillary tube on the upper surface of the flow cell. This cell was packed by adding small amounts of glass beads and mildly vibrating to eliminate inefficiencies in packing.

2.5. Experimental procedure

Before injecting the microspheres, the flow cell was initially equilibrated (20 min) using solution without microspheres, but with the same characteristics (pH = 6.72, IS = 20 mM) and flow rate to be injected during the experiments. Injection was continued for several hours until sufficient populations of retained colloids were present to allow observation of potential detachment in response perturbations in solution conditions. The flow rate used (0.08 ml/min) was designed to provide near-surface fluid velocities in the range of near-surface fluid velocities in our previous porous media experiments (e.g. Tong and Johnson, 2006). A higher flow rate (0.74 ml/min) was used for the 9- μm microspheres to avoid settling in the syringe pump during injection. The superficial velocities corresponding to these flow rates are (0.32 m/day and 2.97 m/day) as determined by dividing the flow rate by the area of the chamber. The average pore water velocities are approximately a factor of three larger than the superficial velocities. Although the velocities differ between the 9- μm and smaller microspheres by an order of magnitude, they represent low-end velocities under which transport of the microspheres can occur in groundwater.

Reversibility of deposition was examined during three different elution phases in series: (1) microsphere-free solution with no change in other solution conditions or flow rate; (2) reduction to 1 mM NaCl solution with no change in flow

rate; and (3) continuation of 1 mM NaCl solution with sequential increases in flow rate by factors of 4, 16, and 64 for all microsphere sizes except the 9.0- μm size, where flow rate increases of factors of 2, 5, and 10 were examined since the factor of 10 increase above the already elevated flow rate caused disassembly of the pore structure.

2.6. Image acquisition

Bulk epifluorescence microscopy was used to directly observe deposition of microspheres in the porous media. The microscope (Eclipse TE2000-S inverted microscope; Nikon, Japan) uses two kinds of illumination: fluorescent by a mercury lamp (X-Cite™ 120 PC, Photonic Solutions, Inc. Ontario, Canada), and white light from the microscope lamp. White light was used in combination with fluorescent light in cases where attachment of fluorescent microspheres was insufficient to illuminate the glass beads. The system uses a pass-filter for excitation (478–493 nm). Emission was unfiltered for all experiments.

During microsphere injection, images were acquired every 10 s, and the UV lamp was shuttered between acquisitions to avoid bleaching of fluorescence. During elution, shorter time intervals of acquisition were used (0.05, 0.125, 0.2, 0.5 and 1 s) with the larger intervals corresponding to the smaller microspheres, and the smaller intervals corresponding to the larger microspheres.

In order to ensure generality of results to the media, observations were made and recorded in several locations of the porous media during each change in conditions (reduced colloid concentration, reduced ionic strength, increased flow rate). A high-speed camera (Cool Snap HQ, Photometrics Inc., Tucson, AZ) was used to take images and record movies (20 frames per second) during the highest flow rate changes.

2.7. Interaction energy profiles

The electrostatic interaction energy between a sphere and a plate is given by Gregory (1975) based on the linear superposition approximation for constant surface charge:

$$\Delta G^{\text{EL}} = 64\pi\epsilon a_{\text{colloid}} \left(\frac{kT}{z_j e}\right)^2 \gamma_1 \gamma_2 \exp(-\kappa h) \quad (1)$$

$$\gamma_i = \tanh\left(\frac{z_j e \psi_{0,i}}{4kT}\right) \quad (2)$$

$$\kappa = \sqrt{\frac{e^2 \sum n_{j0} z_j^2}{\epsilon kT}} \quad (3)$$

where ϵ is the permittivity of the medium, z_j is the ion valence, e is the electron charge, $\psi_{0,i}$ is the surface potential (colloid or stationary phase surface), n_{j0} is the number concentration of ions in the bulk solution, a_{colloid} is the colloid radius, and h is the colloid-surface separation distance. Surface potentials were approximated by zeta potentials, which were described above.

The van der Waals attraction was calculated according to Gregory (1981), who developed an expression that includes electromagnetic retardation.

$$\Delta G^{\text{VDW}} = -\frac{A \cdot a_{\text{colloid}}}{6 \cdot h} \left[1 - \frac{5.32 \cdot h}{\lambda_0} \ln \left(1 + \frac{\lambda_0}{5.32 \cdot h} \right) \right] \quad (4)$$

where A is the combined Hamaker constant for the microsphere–water–substratum system, 3.84×10^{-21} J (Bergendahl and Grasso, 1999), λ_0 is the “characteristic length” of the interaction, usually taken as 100 nm.

Under the 20 mM ionic strength condition, secondary energy minimum depths ranged from approximately 0.22 kT to 7.5 kT for the 0.21- and 9.0- μm microspheres, respectively, with intermediate-sized microspheres having intermediate secondary energy minimum depths relative to these two extremes (Fig. 1). Energy barrier heights ranged from approximately 100 kT to 12,000 kT for the 0.21- and 9.0- μm microspheres, respectively, with intermediate-sized microspheres having intermediate energy barrier heights relative to these two extremes. These results indicate that large energy barriers existed even under the higher (0.02 M) ionic strength condition used for deposition. The energy profiles indicate that barrier heights are increased and secondary energy minima are eliminated upon reduction of solution ionic strength to 0.001 M, (Fig. 1), indicating that colloids associated with secondary energy minima during loading at the 0.02 M ionic strength condition should be re-entrained via reduction of ionic strength to 0.001 M.

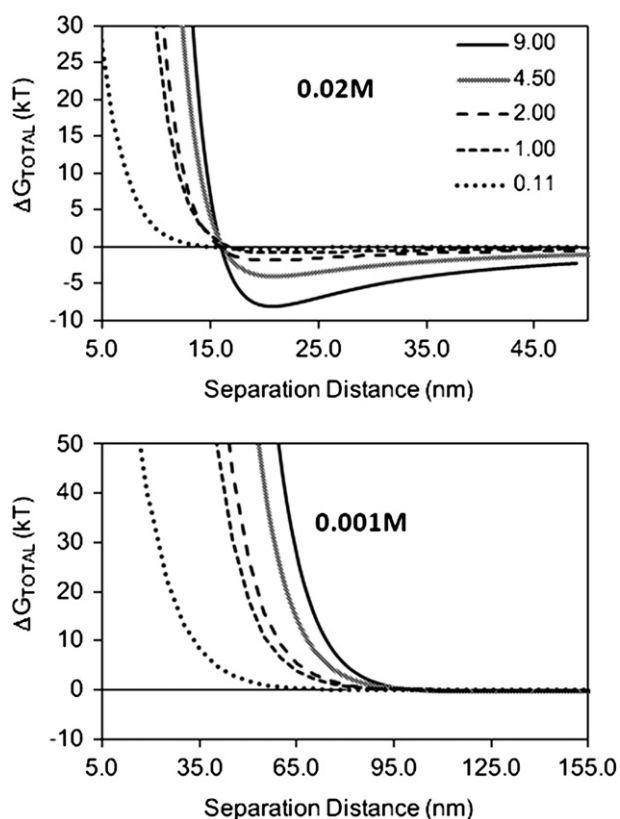


Fig. 1 – Energy profiles for interaction of the various sized microspheres with glass beads under the 0.02 M (top) and 0.001 M (bottom) ionic strength conditions. Values used to develop the energy profiles are given in Section 2.

3. Results

Images from the early and later stages of colloid loading onto the porous media are shown in Figs. 2 and 3, respectively, for the five sizes of microspheres examined. Most apparent from these figures is the small size of the colloids relative to the pore throat sizes (even for the largest colloid). No entrapment in pore throats too small to pass was observed for any of the colloid sizes including the largest, for both initial and later stages of loading (Figs. 2 and 3).

Colloid accumulation at grain to grain contacts was important for larger colloid sizes (Figs. 2 and 3), and this form of retention dominated the observed initial attachment for colloid sizes 2.0 μm and larger (Fig. 2) and remained the dominant observed form of retention for the largest size (9.0 μm) even at later times (Fig. 3). Note that the lower influent concentration for the larger microspheres yields a much lower cumulative delivery of colloids to the surfaces at later times for the larger relative to the smaller colloids. Also note that for a given colloid size, the retention occurred consistently in grain to grain contacts regardless of distance from the exit of the capillary tube into the RSPF chamber, indicating that the deposition mechanism was equivalent across the cell despite decreasing pore water velocity with increasing distance from the cell center.

Attachment on the open surface was important for all sizes; and attachment was evenly distributed (not concentrated in particular zones) except for the fact that attachment was greater on upstream relative to leeward surfaces (e.g. Fig. 3, 0.21 and 1.1 μm). Widespread attachment on the open surface is demonstrated using images at multiple focus planes (Fig. 4) where it is observed that attachment (shown for 0.21 and 9.0 μm colloids) occurred on the entire collector surface and was not restricted to grain to grain contacts. Although distinction of mobile from immobile colloids was not possible in these static images, the time series of images demonstrates that colloids immobilized on the collector surfaces remained immobilized with no discernable motion even over long periods of time (Supporting Information). As was observed for retention in grain to grain contacts, deposition on the open surface for a given colloid size occurred consistently with distance across the flow cell.

Slow-moving colloids associated with surfaces were observed (Supporting Information), and it is possible that these colloids would be effectively retained across the time and spatial scales of column experiments. Rear stagnation zones showed no accumulation of colloids, and the surfaces associated with these zones showed lesser concentration of attached colloids relative to upstream surfaces and forward stagnation zones (Fig. 3, 0.21 μm).

Negligible detachment from the glass beads was observed in response to reduction of colloid concentration, reduction of solution ionic strength (Fig. 5), increase in fluid velocity up to a factor of 64 times or more (Fig. 5), and mild disassembly of the pore structure (Supplementary Information), and this was true for all colloid sizes, although the observation is shown for only two sizes for brevity.

The observations described above also applied to the experiments performed in Ottawa sand, which involved the

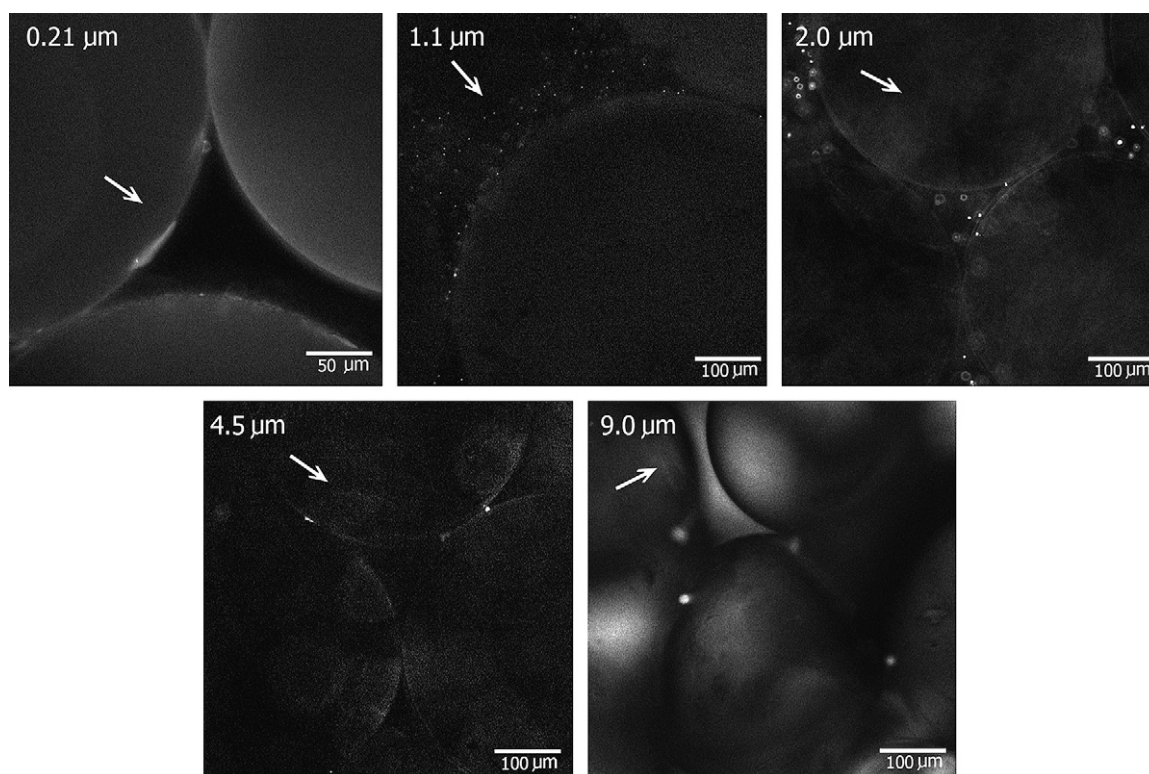


Fig. 2 – Images of initial attachment of microspheres in glass bead porous media using white light combined with fluorescence. Bright spots emanate from microspheres. Light from individual microspheres is observable for sizes greater than 1.1 μm in size, whereas lighter areas indicate accumulation of microspheres of 0.21 μm in size. Focus planes in all panels are at the collector centers (grain to grain contacts). Arrow denotes principal direction of flow, although it should be noted that flow is three-dimensional in the volume represented by the image.

0.21, 1.1, and 9.0 μm microspheres (Supporting Information), demonstrating that the observations were general among the two porous media (smooth spherical and rough angular) for the large range of colloid sizes examined here.

4. Discussion

The lack of observed colloid re-entrainment in response to ionic strength reduction in our experiments indicates that the observed retained colloids were not associated with secondary energy minima, since secondary energy minima were eliminated by ionic strength reduction (Fig. 1). This finding does not refute the possibility of colloid retention in secondary energy minima in general, or even in our experiments. Rather, it may reflect the difficulty of direct observation of retention in, and re-entrainment from, secondary energy minima. Re-entrainment in response to reduced ionic strength is well established, and a survey of existing literature indicates that between 10% and 85% of retained colloids can be recovered via ionic strength reduction (Litton and Olson, 1996; Redman et al., 2004; Franchi and O'Melia, 2003; Tong and Johnson, 2006; Shen et al., 2007; Kim et al., 2009). Kuznar and Elimelech (2007) described direct observation of translation of secondary energy minimum-associated colloids to rear flow stagnation zones in packed glass beads where they were retained despite calculated energy barriers in the range of

1000 kT. The number of colloids retained by this mechanism increased with increasing ionic strength (corresponding to a secondary energy minimum depth range from -5 to -22 kT), which is consistent with the mechanistic simulations of Johnson et al. (2007). Our experiments indicate that direct observation of these weakly-associated colloids is difficult; likely because of the limited focus depths (e.g. <5 μm) within which the residence times of even slow-moving colloids will be highly limited, especially if the trajectory is not parallel to the focus plane, which is of course the dominant case.

Colloid deposition in grain to grain contacts was the dominant form of retention for 2.0- μm -sized colloids and larger. Colloid deposition in the presence of energy barriers has been widely directly observed in grain to grain contacts; e.g. 1.1- and 3.0- μm colloids in 150- μm Ottawa sand (Bradford et al., 2005), *E. coli* O157:H7 in 150- μm Ottawa sand (Bradford et al., 2006), 5.1- μm colloids in 98- μm quartz sand (Xu et al., 2006), 1.0- to 25- μm colloids ($d_{50} = 7$ μm) in smooth 4-mm glass beads (Yoon et al., 2006), 38- μm colloids in 780- μm glass beads (Li et al., 2006), and 2.0- μm colloids in 510- μm glass beads (Tong et al., 2008).

In our experiments, the colloids associated with grain to grain contacts remained in place despite extreme increases in fluid velocity that led to disassembly of the pore structure (Fig. 5), indicating that these colloids were genuinely attached to the surface. The observed increase in retention at grain to grain contacts for colloids equal to and larger than 2 μm

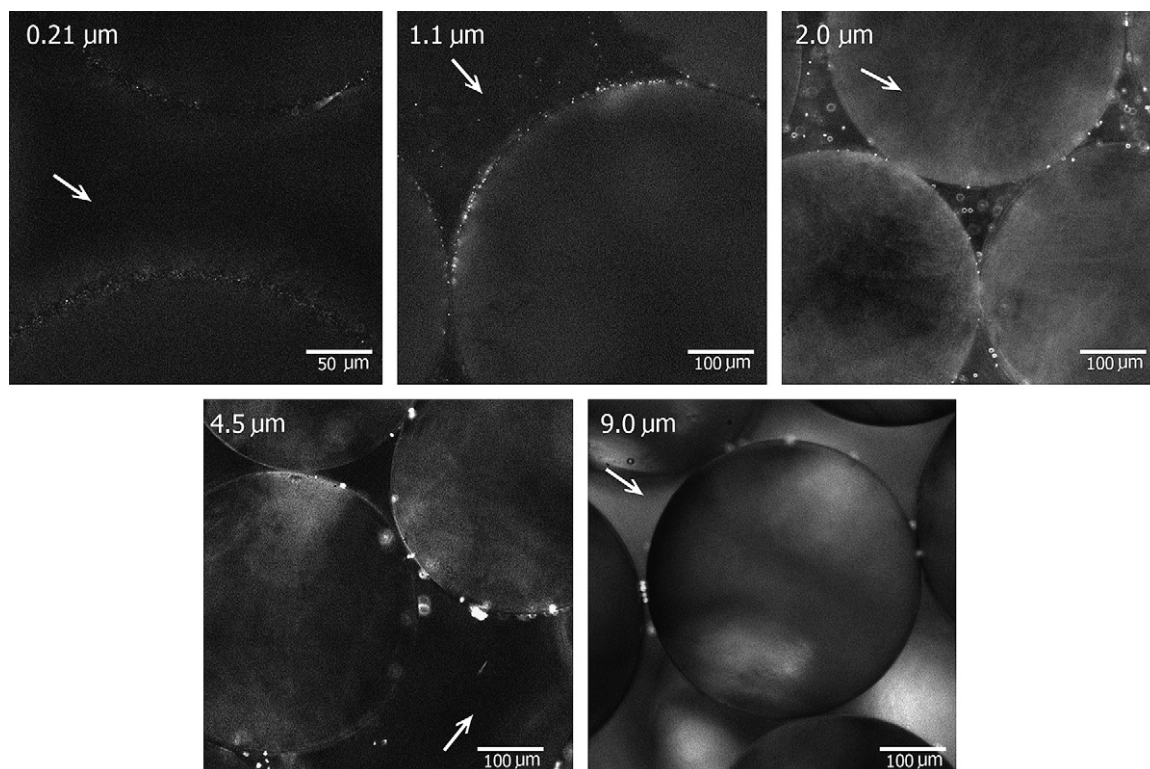


Fig. 3 – Images of later attachment of microspheres in glass bead porous media using white light combined with fluorescence. Focus planes in all panels are at the collector centers (grain to grain contacts). The 0.21- μm image shows two collectors separated by fluid, the bottom collector surface faces upstream. The 1.1- μm image shows portions of four collectors separated by fluid, the bottom-right collector (largest in image) surface faces upstream. Arrows denote principal direction of flow, although it should be noted that flow is three-dimensional in the volume represented by the image.

corresponds to a threshold colloid:collector ratio of approximately 0.004, which is in qualitative agreement with model predictions of Johnson et al. (2007) of the threshold colloid:collector ratio for wedging in grain to grain contacts. This threshold is also consistent with reports placing the threshold for straining at colloid:collector ratios around 0.002 and 0.005 (Bradford et al., 2002; and Xu et al., 2006, respectively). We use the term “wedging”, however, to refer to the observed colloid attachment in grain to grain contacts (e.g. Herzig et al., 1970) since the term “straining” is already used to describe “retention in pore throats too small to pass” (McDowell-Boyer et al., 1986; Bradford et al., 2002, 2003), which clearly does not apply to our system where the colloids are much smaller than the pore throats. For the purpose of incorporating mechanisms of retention in colloid transport models, this distinction is useful since the two mechanisms have different dependencies on colloid size and fluid velocity. A colloid will be entrapped in a too small pore throat regardless of the fluid velocity and energy barrier height, whereas a smaller colloid may or may not wedge in a grain to grain contact depending on the colloid size, fluid velocity, and secondary energy minimum depth, as expected from recent numerical simulations (Johnson et al., 2007). Notably, Auset and Keller (2006) demonstrate colloid retention in pore throats too small to pass (straining) in 2-D micromodels, and argue that the colloid:pore throat ratio is a more appropriate metric than colloid:collector ratio to express the threshold for straining. This sentiment

recognizes the deterministic nature of straining relative to the probabilistic nature of wedging, which results from the fact that grain to grain contacts have no characteristic dimension, as opposed to pore throats.

Under the conditions of our observations, the “wedged” colloids were genuinely attached to the porous media. This highlights a need to more carefully consider how to distinguish between “strained” and “attached” colloids (e.g. Shen et al., 2008). This distinction may be valid in terms of location (strained colloids occurring in pore constrictions); but may be invalid in the sense that strained colloids may also be genuinely attached to the surface(s).

Some authors consider strained colloids to be held reversibly on the basis of their recovery from sediment (after loading) via excavation (or expunging) of the sediment from the column, and addition of the sediment to deionized water (with shaking). These recovered colloids have variously been attributed to strained colloids or colloids held in secondary energy minima (Bradford et al., 2003, 2004, 2007; Foppen et al., 2007; Shen et al. 2007; Kim et al., 2009). However, these recovered colloids may also represent attached colloids, since even if fluid drag and collector abrasion from shaking are insufficient to detach colloids, minor introduction of an air-water interface (e.g. bubbles) during excavation and expunging may generate capillary forces (during submersion in deionized water) that will release even genuinely attached colloids (e.g. Schäfer et al., 1998; Chen, 2008). Furthermore,

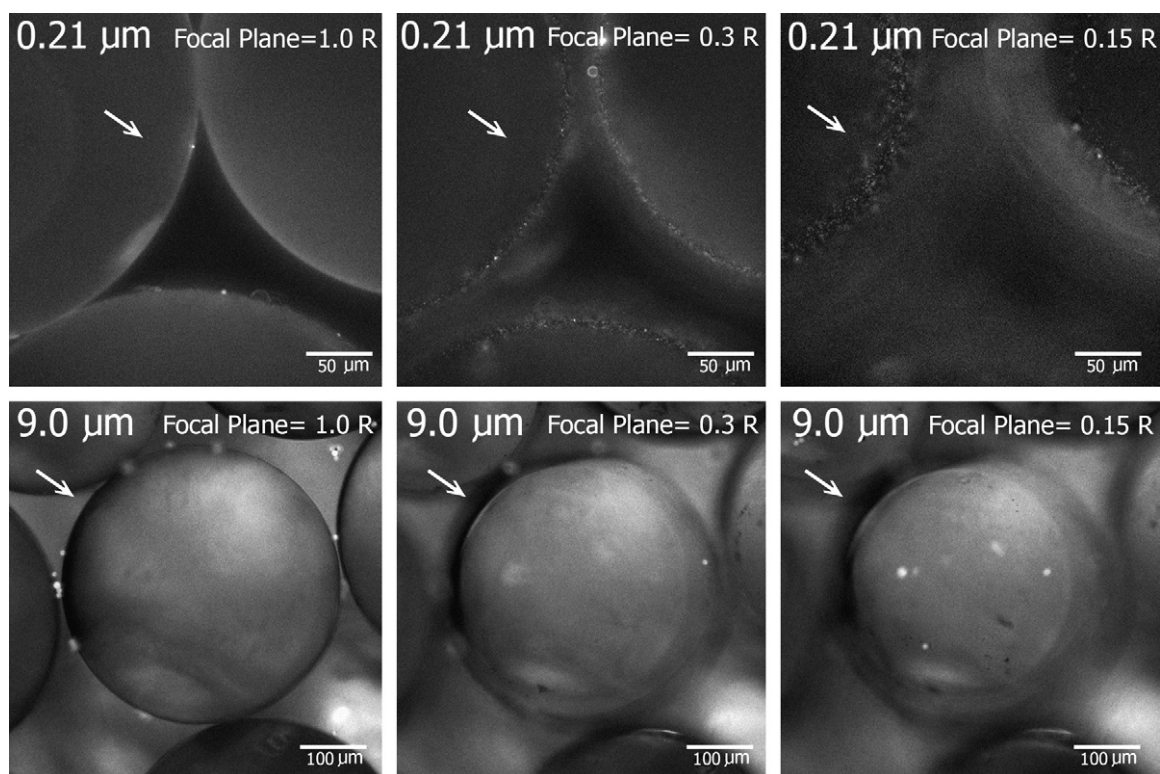


Fig. 4 – Images for two different experiments (0.21 μm and 9.0 μm) at different distances from the glass coverslip (chamber bottom). R, collector radius. Colloid deposition is observed across the open surface of the collectors at different focal planes. The 9.0- μm colloids shown for focal plane at 0.15 R are attached to the glass coverslip rather than the collector. Arrows denote principal direction of flow, although it should be noted that flow is three-dimensional in the volume represented by the image.

genuinely attached colloids (deposited under favorable conditions) are routinely recovered from sediment by dispersion in pure water (Li et al., 2004; Tong and Johnson, 2006). Hence, one cannot rule out attached colloids being recovered by this method unless detachment via abrasion and capillary forces can be ruled out.

The lack of observed re-entrainment of immobilized colloids indicates that the attached colloids could not be re-entrained via the mechanism operating in the Duffadar and Davis (2008) model. This was true despite an aggressive drop in ionic strength to 0.001 M and increased fluid velocity by a factor of 64, which reduce the adhesion force and increase the fluid drag force (according to the Duffadar and Davis model). This is not to say that the Duffadar and Davis (2008) model is invalid; rather, it may indicate that the size and/or frequency of attractive domains is sufficiently high in our system to prevent re-entrainment. Alternatively, the observation may indicate that hetero-domains serve as “holes” in the energy barrier that allow the colloid to move into contact with the surface, and that, once this contact is established, van der Waals attraction and specific adhesion forces prevent detachment despite ionic strength reduction increasing repulsion at greater distances from the surface (the attached colloids are “inboard” of the energy barrier). Further experiments and simulations are needed to explore these possibilities.

Most dramatic in our results was the observation that observable colloid retention was dominated by attachment

to the open surface for the smaller colloids ($<2.0 \mu\text{m}$), which likely reflects the influence of surface charge heterogeneity and roughness. Tong and Johnson (2006) showed that deposition efficiencies were much greater on porous media relative to flat surfaces under equivalent conditions (including similar near-surface fluid velocities). They attributed this excess deposition to pore structure (e.g. wedging and retention in zones of low fluid drag) on the basis that both surfaces were expected to show similar heterogeneities due to their similar composition. However, surface roughness was not compared for the two surfaces, and it is well known that surface roughness can enhance colloid deposition similarly to surface charge heterogeneity (Shellenberger and Logan, 2002; Auset and Keller, 2006; Kemps and Bhattacharjee, 2009; Mitik-Dineva et al., 2008; Khan et al., 2005; Zan et al., 2008). Notably, in addition to retention of secondary energy minimum-associated colloids in rear flow stagnation zones, Kuznar and Elimelech (2007) observed retention of colloids on the open surface of glass beads despite a 1000 kT calculated energy barrier. Although they attributed this retention to the “hairy” surface of the carboxylate-modified colloids, it is also plausible that heterogeneity existed on the glass bead surfaces, particularly given the circum-neutral pH of the solution. Yoon et al. (2006) observed retention on the open surface of “rough” 4-mm glass beads where asperities on the order of 2 μm were observed via scanning electron microscopy.

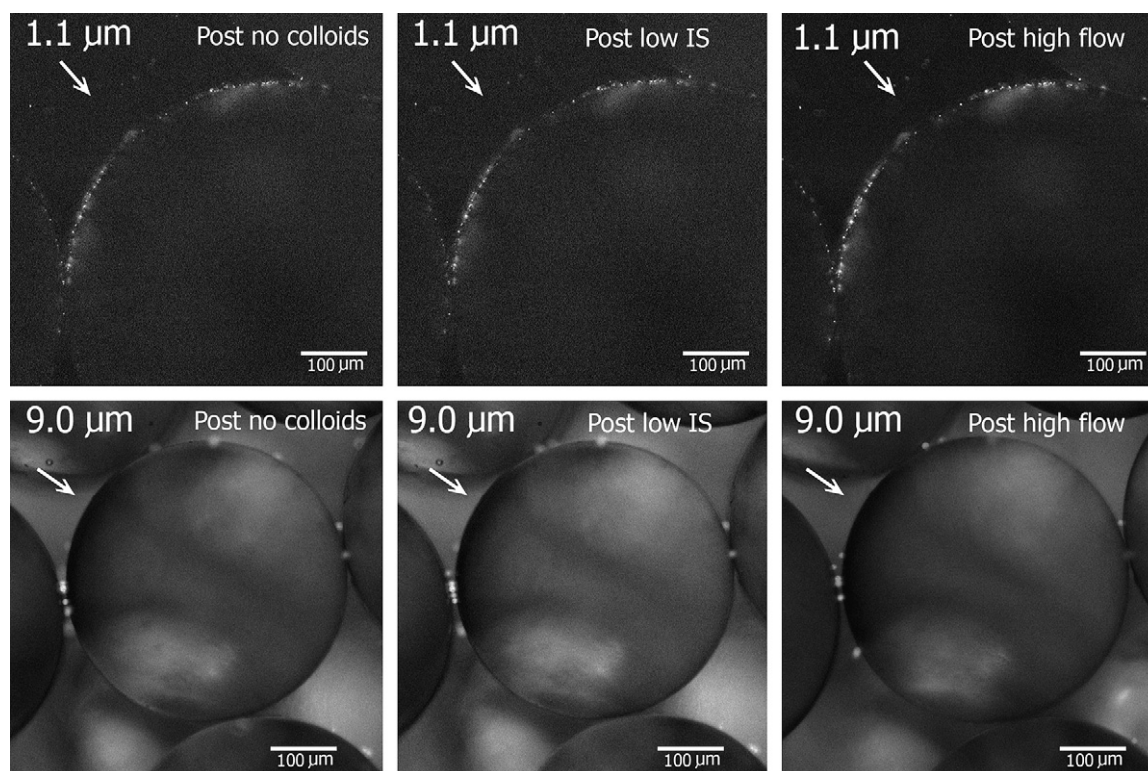


Fig. 5 – Images following cessation of colloid injection, reduction of ionic strength, and increase in flow (factor of 64 for 1 μm , factor of 10 for 9.0 μm). Rotation and vibration of the collectors during high flow resulted in the change of 9.0- μm colloid distribution on the collector surfaces between the post-high-flow and post-low-ionic-strength (IS) conditions. Arrows denote principal direction of flow, although it should be noted that flow is three-dimensional in the volume represented by the image.

The prevalence of retention on the open surface in our experiment (and others) leads us to speculate that interaction with heterogeneities (charge and/or roughness) constitutes an alternative mechanism to straining in the observed retention in porous media under highly unfavorable conditions. Lack of heterogeneity is often assumed under high-pH conditions. For example, Shen et al. (2008) state: “Because the columns were packed with thoroughly cleaned glass beads, and the experiments were conducted using DI water (both measures will minimize attachment), the removal in the packed columns can be attributed to influences of straining, [Xu et al., 2006; Tufenkji et al., 2004].” Xu et al. (2008) make a similar statement. However, it is difficult to rule out heterogeneity on these surfaces. The experiments of Shen et al. (2008) involved glass beads, which contain significant oxide impurities that are assumed (but not confirmed) to carry negative charge under the conditions of the experiments (pH 10). It is also difficult to discount the potential contributions of the 0.01% impurities in the “ultrapure” quartz sand used by Xu et al. (2006), Xu et al. (2008), and Tufenkji et al. (2004), since it is known that the zeta potential of the bulk collector surface that is used in the energy barrier calculations is insensitive to surface heterogeneity (Elimelech et al., 2000). Furthermore, the very significant micro- to nano-scale roughness of the quartz sand, as demonstrated in Tufenkji et al. (2004), may well contribute to local elimination of the energy barrier. Significant roughness may also be expected on acid- and base-treated soda lime glass

beads; e.g. root mean square roughness ranging from 15 to 38 nm was demonstrated by Shellenberger and Logan (2002). “Holes” in the energy barrier from impurities or roughness are very difficult to rule out as an alternative mechanism of retention to straining in the above high-pH experiments. Furthermore, based on our (and others’) observations described above, heterogeneity is a more likely mechanism of retention than wedging or straining for colloid:collector ratios <0.004 .

In addition to retention in spite of large calculated energy barriers, another line of evidence that has been used to infer straining as the mechanism of deposition is the preferential retention of colloids near the source (Bradford et al., 2002, 2003), and non-mechanistic models employing so-called “straining coefficients” have been used to simulate the corresponding “hyper-exponential” profiles. After noting retention in spite of large energy barriers, some papers have concluded straining to be the mechanism of retention on the basis of a good fit of the profiles using the so-called straining coefficient (Xu et al., 2008; Foppen et al., 2005). In actuality, this “straining” coefficient is a distance-dependent coefficient that reduces the attachment rate with increasing transport distance. The observed decrease in attachment rate coefficient as a function of transport distance can alternatively be attributed to heterogeneity among the colloidal population, where the stickier colloids are retained up-gradient of the less sticky colloids (e.g. Li et al., 2004; Tong and Johnson, 2007; Foppen et al., 2007). Since non-mechanistic coefficients may represent multiple alternative

retention mechanisms, we suggest that their names should not evoke specific mechanisms in order to avoid confusion regarding whether a particular mechanism has been proved as a result of a good simulation.

5. Conclusions

Generalizations that we draw from our observations are:

- (1) For the entire range of colloid sizes examined, observed deposition on the open surface was significant (and dominant for $<2.0\text{-}\mu\text{m}$ colloids), and was irreversible with respect to colloid concentration, ionic strength reduction, and fluid velocity increase up to 64 times. This indicates that the mechanism of retention for these colloids was not secondary energy minimum interaction; rather, the mechanism was likely interaction with surface charge heterogeneity or roughness. The irreversibility of this attachment suggests that the size and/or frequency of hetero-domains in our media were sufficient to produce an adhesive force that could not be overcome by the drag force; or alternatively, once contact was established, the colloids were attached via association with the primary energy minimum “inboard” the energy barrier and were not susceptible to increased repulsion via energy barrier increase. Additional experiments are required to determine under what conditions significant detachment of these colloids occurs.
- (2) Entrapment in pore throats too small to pass was absent under all conditions, whereas attachment in grain to grain contacts was significant for colloid:collector ratios greater than about 0.005 (colloids $> 2.0\ \mu\text{m}$). This attachment was irreversible with respect to the above variations in conditions, demonstrating genuine attachment to the surface. We call this form of attachment wedging, and we consider its distinction from straining useful for the purpose of incorporating mechanisms of retention in colloid transport models.
- (3) Comparison to existing literature suggests that our method may not have allowed direct observation of colloids that were reversibly associated with the surface. This can be explained by the possibility that these reversibly associated colloids remained mobile and moved quickly through the focus depth, in trajectories not aligned with the focus plane. This suggests that reversibly-held colloids can move along the surfaces at significant velocities at the micro-scale, but are effectively retained at the macro-scale. This speculation will be clarified and tested as additional experiments accumulate.

The experiments described here were performed in relatively simple porous media; however, their relevance to existing research is evident from the fact that the vast majority of existing work has been performed in relatively simple porous media. We expect that these mechanisms of retention in the presence of energy barriers will also be important in complex porous media having a larger distribution of grain sizes, although new mechanisms may emerge.

In this paper we have provided generalizations of direct observations of colloid retention in the presence of energy barriers, and we have tried to point out alternative conclusions

to those drawn from indirect observations in order to strengthen conclusions that are drawn from those observations.

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Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version at [doi:10.1016/j.watres.2009.12.014](https://doi.org/10.1016/j.watres.2009.12.014).

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