Transport of colloids in saturated porous media: A pore-scale observation of the size exclusion effect and colloid acceleration

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[1] We present experimental evidence of the effect of colloid exclusion from areas of small aperture sizes, using direct observations at the pore-scale using a realistic micromodel of porous media. Four sizes of hydrophobic latex spheres in aqueous suspension, from 0.05 to 3 μm, were introduced into the micromodel at three different pressure gradients. We observed the frequency of occurrence of the size exclusion effect and the influence of relative size of pore throats and colloids (T/C ratio) and flow velocity. From our observations the smallest T/C ratio entered by these different colloids was 1.5. We also observed certain preferential pathways through the pore space for different colloid sizes, such that size exclusion eventually results in distinct pathways. These preferential paths become more important for larger colloids and for greater pressure gradients. Measured colloid velocities were 4–5.5 times greater than estimated pore water velocities. Acceleration factors (ratio of colloid to water velocity) increased for all colloid sizes with increasing pore-scale Pe. Smaller particles appeared to travel along faster streamlines in pore throats, while larger particles travel along with a number of streamlines, thus at a slightly lower velocity than the small colloids. At larger scales the acceleration factor is decreased owing to Brownian motion, adsorption, colloid and straining filtration, and other factors, but these pore-scale results shed light on the size exclusion effect and its role in determining early colloid breakthrough. INDEX TERMS: 1831 Hydrology: Groundwater quality; 1832 Hydrology: Groundwater transport; 5139 Physical Properties of Rocks: Transport properties; KEYWORDS: colloids, advection, Peclet number, accelerated transport, pore size exclusion, retardation


1. Introduction

[2] Colloids represent a group of very fine particles in solution that have effective diameters ranging from 1 nm to 10 μm [Chryssikopoulos and Sim, 1996]. Colloids may be introduced or formed in groundwater. Once colloidal particles occur, they can transport over significant distances. There are several processes involved in colloid removal, such as aggregation, straining or collision filtration, and settling. All of these processes depend on colloid density, colloid size, surface chemistry, water chemistry, and interstitial velocity [McCarthy and Zachara, 1989; O’Melia et al., 1997].

[3] Transport in groundwater of some contaminants, such as radionuclides, can be facilitated in the presence of colloidal particles [e.g., Mill et al., 1991; Corapcioglu and Jiang, 1993; McCarthy, 1998]. In addition, many contaminants are colloidal particle themselves such as viruses and other microorganisms, and this can be a serious latent problem in many circumstances [e.g., Powelson and Gerba, 1994; Abbaszadegan et al., 1999; Schijven and Hassanzadeh, 2000]. Understanding the fate and transport of colloid in porous media has a significant implication on the reduction of the risk of drinking-water-supply contamination.

[4] The migration behavior of colloids and dissolved conservative chemicals in porous media are quite different. In saturated porous media, there is evidence that colloids can migrate at a greater distance than predicted by typical approaches [McDowell-Boyer et al., 1986; Champ and Schroeter, 1988]. In column experiments, colloids have a faster breakthrough compared to solute tracers [e.g., Champ and Schroeter, 1988; Enfield et al., 1989; Niehren and Kinzelbach, 1998]. For example, Reimus et al. [1995] found that synthetic colloids always arrive earlier in the effluent than a nonsorbing solute (iodide) in transport experiments in a fracture system. They hypothesized that this effect is due to the larger size of colloids relative to solutes and that they diffuse too slowly to enter the slow velocity regions (dead zone) along the rough fracture walls. Grindrod et al. [1996] suggested that free colloids have an average migration velocity higher than that of a tracer. Niehren and Kinzelbach [1998] suggested, from their column experiments with colloids and solute tracers, that colloids only flow in pores with diameters several times bigger than their own diameter. They also proposed that the exclusion of colloids from matrix diffusion is the crucial difference between solute and colloid tracer transport. Others have hypothesized that a size-exclusion effect explains the observed behavior [e.g., de Marsily, 1986]. Several researchers also suggested that colloid particles could move along the faster streamlines, therefore enhancing colloid
migration [Powelson et al., 1993; Chrysikopoulos and Abdel-Salam, 1997].

Early breakthrough of microorganisms compared to that of conservative tracer has also been observed or predicted [e.g., Powelson et al., 1993; Bales et al., 1989; Ginn, 1995]. Stochastic analysis of virus transport in aquifers show that increasing heterogeneity in the model results in faster breakthrough of 0.02–0.2 μm colloids [Rehmann et al., 2000]. In a natural sediment core, indigenous groundwater bacteria, 1.2 μm × 0.6 μm in size, exhibited earlier breakthrough when compared to a bromide tracer [Dong et al., 2002].

Although size exclusion is similar to anion exclusion [e.g., James and Rubin, 1986; Gvirtzman and Gorelick, 1991] in that the colloids or anions are focused onto the central streamlines, the underlying forces are different.

The general model described colloid transport in one dimensional, homogeneous, saturated flow, with advection-dispersion and processes, is as follow [Yates and Ouyang, 1992; Jin et al., 1997]:

\[ R_p \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x} - \lambda C - \frac{\rho C^*}{\theta} - K_{att} C. \]  

(1)

Here the retardation coefficient, \( R_p \), can be defined as:

\[ R_p = 1 + \frac{\rho K_d}{\theta}. \]  

(2)

Where, \( C \) is concentration of suspended colloids \( [\text{ML}^{-3}] \); \( C^* \) is mass fraction of colloids sorbed on the liquid-solid interface \( [\text{MM}^{-1}] \); \( D \) is hydrodynamic dispersion coefficient \( [\text{L}^2 \text{t}^{-1}] \); \( U \) is average interstitial velocity \( [\text{L} \text{t}^{-1}] \); \( \rho \) is bulk density of the solid matrix \( [\text{ML}^{-3}] \); \( K_{att} \) is irreversible attachment rate coefficient due to colloid filtration \( [\text{t}^{-1}] \); \( K_d \) is distribution coefficient \( [\text{L}^3 \text{M}^{-1}] \); \( \lambda \) is reaction rate constant of suspended colloids \( [\text{t}^{-1}] \); \( \lambda^* \) is reaction rate constant of colloids sorbed to solid surface \( [\text{t}^{-1}] \); \( \theta \) is porosity of the medium \( [\text{L}^3 \text{L}^{-3}] \); \( t \) is time \([\text{t}]\).

In highly heterogeneous saturated media, the actual breakthrough of colloids (viruses in this case) happened faster than predicted by Equation 2, with actual retardation \( (R) \) lower than the predicted retardation value \( (R_p) \), based on a \( K_d \) calculated from batch experiments [Powelson and Gerba, 1994]. Powelson and Gerba [1994] hypothesized that the discrepancy between \( R \) and \( R_p \) may be due to size exclusion.

In this study, we investigate the size exclusion hypothesis. Furthermore, we also hypothesize that this phenomenon is dependent on ratio of pore throat to colloid diameter \( (T/C) \) ratio. Another hypothesis is that a threshold \( T/C \) ratio is needed to allow colloids to pass through into a new pore space, and that this threshold \( T/C \) ratio is significantly greater than one. Finally, we believe that for colloid transport in the porous media an “acceleration factor” (the ratio of colloid velocity to pore water velocity) is a more appropriate term than a retardation factor, since the size exclusion effect should dominate and transport of colloids should be faster than the pore water velocity. Mathematically, some authors have proposed a retardation factor less than unity, while others have proposed the use of lower effective porosity, as discussed by Ginn [2002]. [11] Size exclusion (i.e., the inability of a colloidal particle to move into a pore space due solely to the ratio of throat to colloid size) can lead to a larger-scale pore exclusion effect, where the larger particles are directed through only certain regions of the porous medium and are excluded from certain pores due to events occurring upstream of the current pore space. [12] This paper presents evidence and information regarding the effect of colloid exclusion from areas of small aperture sizes and how that would influence the colloid transport in saturated porous media. The experiments were setup to investigate at the pore scale the mechanisms of transport of colloid particles of various sizes, using micromodels, under saturated conditions. We control conditions to reduce colloid agglomeration, and focus only on size and pore exclusion. We quantitatively describe the pore size exclusion effect, which is a phenomenon that results in faster transport of colloidal particles, due to restricted transport of colloidal particles only through the higher velocity flow lines in the larger pores. The phenomenon has not been directly observed in natural media, but is inferred from theoretical considerations and works at larger scales [Champ and Schroeter, 1988; Enfield et al., 1989; Abdel-Salam and Chrysikopoulos, 1995].

2. Experimental Setup

The studies were conducted at the pore scale using physical micromodels, based on the experimental setup that has been previously developed and applied by Keller et al. [1997]. Our objective was to observe colloid transport in physical micromodels, containing a realistic pattern of pore networks. A thin slice of porous media (fine sand) was imaged through an optical microscope (approximately 600 by 600 μm) and then digitized. To improve the connectivity in the micromodel, the digitized image was modified slightly. The pattern was then repeated 100 × 100 times. The size of our pore space was chosen based on the physical limitations of our optimal viewing window. Although it is difficult to determine whether 100 units result in a scale-invariant model, it does represent a significant number of correlation lengths, leading toward more realistic behavior. The digital image of the pore space was then transferred to a chrome plated glass mask, without magnification from the original porous media. Using technology similar to the manufacture of microchips, the image was photochemically etched onto a silicon wafer, at a constant etching thickness (for this particular study, micromodels have been constructed with etching depths of about 15 μm). The final etched repeat pattern is shown on Figure 1. Pore diameters range from 2.4 to 30 μm. Figure 2 is a scanning electron micrograph of a section of the repeat pattern, which shows the shape of the grain walls and the regularity of the etching depth. The porosity of the micromodel used here has been experimentally determined to be 37%.

The silicon surface was oxidized after etching, leaving a water-wetting surface, approximately 15 μm deep. The etched silicon wafer was then placed between two glass plates. The top glass plate was attached to the silicon wafer using anodic bonding. Ports were constructed on the top plate to allow independent injection and extraction from different directions. The bottom plate was attached with epoxy to the silicon wafer, and was mainly used to provide
To ensure that the model remains water-wet, carbon dioxide was introduced to displace the air, and then water was injected, which eventually dissolves the carbon dioxide, allowing the wetting fluid to saturate the model completely. This was typically followed by injection of a 10% acetic acid solution into the micromodel for at least 50 pore volumes, to remove any organic deposits and ensure a hydrophilic surface. The acetic acid was flushed out with distilled water for at least 100 pore volumes. In all cases, the model was strongly water-wet in the presence of air. The main component of the surface of the micromodel was silica and silicon hydroxides. The wetted surface in the micromodel was covered with a surface hydroxyl group; this surface was generally negatively charged at neutral pH [Wan and Wilson, 1994].

An industrial microscope (Nikon Optiphot-M) equipped with a Charged-Coupled Device (CCD) camera was used to capture images of the micromodel pore space. We used reflected light to view the fluids and colloids in the pore space. The images were captured with a TV-camera (Sanyo VDC-2972) at a high resolution (1/2” CCD Color Image Sensor, 470 Line Horizontal Resolution). A video image was acquired to the computer using a video frame grabber (Integral Technologies Flashpoint). The digital camera (Sony Digital Handycam) was also connected to the CCD TV system to acquire a video stream of real-time movement of the colloids.

Flow rate was measured at the inlet, using digital flowmeters (using Fischer Scientific Model 1000). Pressure was measured at the inlet and outlet lines using calibrated pressure transducers (Celesco DP-25). The colloids used in this study were fluorescent latex spheres from Sigma-Aldrich, with mean diameter of 3.0, 2.0, 1.0 and 0.05 μm. For each colloidal suspension, 3 samples of 1 mL of the suspension were taken. Each sample was gently filtered on a 0.02 μm pore size Al2O3 Anodisc 25mm membrane filter (Whatman) along with 0.45 μm pore size cellulose nitrate as a backing filter. The concentrations of colloid suspension were calculated in the range of $10^4$ to $10^5$ particles per mL.

Figure 1. Composite image of the etched repeat pattern in the micromodel, which is approximately $509 \times 509$ μm, and etched to a depth of about 15 μm. Pore throats are on the order of 3–20 μm in diameter and the pores may be up to 50 μm across. The pattern is repeated 100 × 100 times in the micromodel, forming a square domain, with the inlet and outlet ports on each of the corners. A scale in μm is shown at the bottom for reference. The numbers in the various pores refer to the pore spaces observed in detail in this study.
The selected pores ranged from 2.4 to 14 μm, having pore bodies with 3 to 9 throats. The throat size of the model were selected (Figure 1). The selected pore spaces model, which include various pore bodies and pore throat streams were taken from selected regions in the micro-under water–saturated conditions. The images and video adhesion to each other. The experiments were conducted colloid solution was buffered at pH 7.8 to minimize colloid size of colloid and pore throat. The relative diameter of the phenomenon should be a preferential path of colloid that associates with large pore throat.

First, the study was focused on finding evidence of the occurrence of the size exclusion phenomenon. For each selected pore, under different flow conditions, the number of colloids that moved in and out was quantified. At least 50 colloidal particles were observed sequentially to determine the frequency with which a given pore throat was used as entry or exit, depending on colloid size and flow velocity. Since the micromodel has a repetitive pattern, the same pore patterns at about the same pressure gradient (i.e., the same distance from the inlet) were also studied as a replicate. The number of the colloids moving through each pore throat was counted. The evidence of the occurrence of this phenomenon should be a preferential path of colloid that associates with large pore throat.

Second, the study quantified the effect of relative size of colloid and pore throat. The relative diameter of the colloids and pores that the colloids moved through were recorded and quantitatively analyzed, under the same pressure gradient.

Third, the velocities of the colloids were calculated. Fixed frames at 100X magnification (approximate area of 600 × 600 μm, slightly larger than the size of one repetitive unit) were selected. The video stream of colloid transport at 200X and 500X magnifications were used to help draw the flow paths and estimate the length of the tortuous path. The slow motion function in the imaging software was used along with a stopwatch (Robic SC–707, 1/1000 s Chronograph) to calibrate time and calculate actual colloid velocity.

Finally, to understand the velocity field in the porous space, we constructed a finite element numerical model of the pore space, using Femlab (COMSOL, Inc.). We solved the Navier–Stokes equation for the micromodel, using a 2–D finite element grid, to obtain the relative water velocity in the streamlines around the grains. We considered no–flow boundaries along the top and bottom of the flow direction and a constant pressure drop across the flow direction. This provided us an estimate of the relative flow velocities in the pore space. The actual pore water velocity is estimated from the available physical data of the micromodel, the measured pressure gradient and the actual discharge.

The experiments were conducted under three pressure gradients: $2.1 \times 10^5$, $5.1 \times 10^4$ and $2.4 \times 10^4$ Pa. The colloid solution was buffered at pH 7.8 to minimize colloid adhesion to each other. The experiments were conducted under water–saturated conditions. The images and video streams were taken from selected regions in the micromodel, which include various pore bodies and pore throat sizes. From the unit pattern, 16 pore spaces in the micromodel were selected (Figure 1). The selected pore spaces have pore bodies with 3 to 9 throats. The throat size of the selected pores ranged from 2.4 to 14 μm.

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The number of colloidal particles moving in and out from observed pores is presented in Figures 3–5, which correspond to the data from pores 10, 13, and 14 (see Figure 1 for locations). We chose to present the data from these pores because they are representative of our more general results and these three pores immediately connected to each other, making it easier for the reader to follow. We have data on sixteen different pore spaces. The numbers of pore throats of each of these pores are 4, 5, and 7 respectively. For each pore, a set of 12 histograms is used to present the data. The histograms are arranged in a matrix of four by three, which consists of four average colloid diameters, and three pressure gradients. Each histogram has two components. The left section represents the frequency of entry for the different T/C ratios of all upper gradient pore throats. The right section represents frequency of exit from a pore for the various T/C ratios of all lower gradient pore throats. The T/C ratio of each pore throat varies because of the different sizes of colloids used in our studies. In each set of plots (for a given pore), the pore throats are presented in the same order in each part of the histograms, from smallest to largest.

For pore 10 for example (Figure 3), colloids can enter or exit through two pore throats. 3 μm colloids only enter through the larger pore throat (T/C ratio = 2.19) and exit through the larger pore throat (T/C ratio = 2.49), independently of pressure gradient. In contrast, for the smallest colloids studied (including 0.05 μm, about twice the size range of Bacteriophage viruses such as MS-2), the colloids enter and exit through either pore throat. The observed frequency of entry or exit is influenced by the overall direction of the pressure gradient as well as the T/C ratios. Note that there was a shift in entry and exit throat from the larger (3 μm) colloids to the smaller ones (2–0.05 μm), while the predominant entry and exit throats were typically the same for all colloids in the range of 2 to 0.05 μm.

For pore 14, (Figure 5), colloids can enter through three pore throats (two of the larger pores are the same size) and exit through four pore throats (two of the medium pores are the same size). The 3 μm colloids enter through only one of the larger pore throats (T/C ratio = 2.49) at the higher pressure gradients. However, at the lowest pressure gradient, there are some particles that enter the pore through another larger pore. Nevertheless, colloids exit through the
largest pore throat (T/C ratio = 2.32), independently of pressure gradient. In contrast, for the smaller colloids studied, the majority of colloids enter the smallest throat. For the smaller colloids, the major exit pore throat is one of the middle size pore throats, not the largest pore throat. Once again, there was a shift in entry and exit throat from the larger (3 μm) colloids to the smaller ones (2–0.05 μm), while the predominant entry and exit throats were typically the same for all colloids in the range of 2–0.05 μm. The shift in entry and exit throats observed in pore 10 and 14, from the larger (3 μm) colloids to the smaller ones (2–0.05 μm) does not occur in pore 13 (Figure 4).

From our observations, the smallest T/C ratio entered by these different colloids was 1.5, which is the smallest

Figure 3. Number of colloids moving in and out of pore 10 for four colloid sizes and three pressures. Frequency of entry or exit is on y axis, and T/C ratio is on x axis.
throat of pore 13 (Figure 4). Although we cannot be certain that 1.5 is an absolute threshold, it seems that for rigid colloids, the threshold must be greater than 1 and possible closer to 1.5. From all observations during the various experiments, there was no observation of any colloids moving into dead-end pores. We assume this has a very low probability, since the colloids are essentially moving along with the faster streamlines and would rarely enter these slow-flow regions.

[27] For each pore, there is a preferential path to traverse from entry to exit, which is described by having high number of colloid particles move through a given set of pore throats. In each pore, for the same pressure gradient (histograms in the same column of Figures 3–5), the preferential flow paths

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**Figure 4.** Number of colloids moving in and out of pore 13 for four colloid sizes and three pressures. Frequency of entry or exit is on y axis, and T/C ratio is on x axis.
become less evident for the smaller colloids. For the same size of colloid (histograms in the same row of Figures 3–5), when the pressure gradient decreases, the preferential flow paths also become less evident. This could be explained by a smaller velocity contrast for the various flow lines under a low-pressure gradient. Hence colloids are less likely to move along a particular flow line. The small size colloids could also be captured in a wider range of flow lines.

[28] The observed preferential paths are quite consistent, i.e., the different size colloids mostly move through the same throats under different pressure gradients. There is no strong evidence that the observed preferential path is

Figure 5. Number of colloids moving in and out of pore 14 for four colloid sizes and three pressures. Frequency of entry or exit is on y axis, and T/C ratio is on x axis.
exclusively related to the largest throats available. However, the effects of colloid size to the change of flow path are observed in the case of 3 \( \mu m \) colloids in pores 10 and 14 (Figures 3 and 5). In these pores, for all pressure gradients, the 3 \( \mu m \) colloids did not move through the same pore throat as the other colloids although those throats are bigger than 3 \( \mu m \). This clearly suggests a size exclusion effect.

[29] The reason that the colloids do not always move through the largest throats, in these particular set of experiments, could be due to a complex flow pattern. There are certain pathways in the micromodel that favor the direction of movement of particles (and flow of water), based on geometry, alignment of the pores, and how the pores connect to each other. A throat that is large enough (based on T/C ratio), but not necessarily the largest, would be preferred if that pore throat aligns with the pressure gradient and if that pore throat has an immediate connection with another open pore. Also in the case of high loading of colloids and with interference from other processes such as coagulation and sorption, the smaller pores might become unavailable due to clogging. This is a subject for further study.

For this work, we specifically adjusted conditions (e.g., pH) to avoid filtration by collision or straining, since our focus was on the size exclusion phenomenon. Filtration might occur further down gradient, but was not the subject of this study.

[30] In Figure 6 the preferential path of the colloids is depicted for each colloid size. The superimposed drawing represents the path that has the highest number of colloids move through, for all pressure gradients. The 0.05 \( \mu m \) colloids sample more pathways; therefore there is the possibility of increased spreading of flow paths, leading to hydrodynamic dispersion (Figure 6d). The finite element flow simulation (Figure 7) shows that there are some relatively high velocity flow regions in the micromodel. The highest flow velocity (fastest streamline) is almost 10 times greater than the slowest flow (slowest streamline). However, most high velocity flow regions are only about 4–6 times faster than the slowest flows. It is generally believed that the high velocities streamlines correspond to the preferential flow path of colloids. Comparing the observed flow paths (Figure 6) to the areas which have relatively high water velocity calculated from the mathematical model (Figure 7),

Figure 6. Most frequent pathway for all colloids in the vicinity of pores 10, 11, 13 and 14, based on at least 20 observations at each pressure gradient. In Figure 6d, path 1 is an entry/exit path, while paths labeled 2–5 represent entry points and paths labeled 6 and 7 represent exit points, with some crossover between entry and exit points.
there is quite good agreement between the actual flow path and the high velocity streamline(s). The small discrepancies in this comparison probably arise from the boundary conditions and the small differences between the actual and simulated pressure gradient orientation.

The velocities of the different colloidal particles are presented in Table 1. The average velocities of the colloids are higher for the higher-pressure gradient and also for the smaller colloids. The differences between the average velocities for the different pressure gradients are all statistically significant (t test, \( p < 0.05 \)). However, the differences between the average velocities among the different colloid sizes are not statistically significant (t test, \( p > 0.05 \)), in all cases. There might be some differences but they could not be detected due to the uncertainties in the measurement, which are greater for the 0.05 \( \mu \)m colloids. The hypothesis is that colloids are transported through streamlines near the center of the flow field, which have greater velocities [Bremer and Gaydos, 1977]. For these experiments, the estimated pore water velocities are about 4 to 6 times less than the colloid velocities, or conversely we see an acceleration factor of 4 to 6 at the pore scale. Although the smaller colloids (0.05 \( \mu \)m) appear to be the fastest, our measurement error does not allow us to state this categorically. These findings are significant for understanding the breakthrough behavior of colloids such as radioactive particles or viruses. In the column experiments by Niehren and Kinzelbach [1998], they found that latex sphere breakthrough is up to 2.25 times faster than the breakthrough of a tracer. The difference might reflect an up scaling effect, as more travel paths are sampled, as well as an increasingly more important sorption/retardation effect as more porous matrix is traversed by the colloids. This might also reflect the differences between 2-D and 3-D pore geometry, although this is probably a minor effect. We intend to study these issues in upcoming core studies.

![Flow Direction](Image)

**Table 1.** Average Colloid and Water Specific Velocities for Four Colloid Sizes and Three Pressure Gradients

<table>
<thead>
<tr>
<th>Pressure, ( \text{Pa} )</th>
<th>Water Flow Rate, ( \text{m}^3/\text{d} )</th>
<th>Water Specific Velocity, ( \text{m} / \text{d} )</th>
<th>Estimated Average Pore Water Velocity, ( \text{m} / \text{d} )</th>
<th>Average Colloid Velocity ± SD(^{a} ), ( \text{m} / \text{d} ) (Actual Range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 ( \times 10^{3} )</td>
<td>7.2 ( \times 10^{-6} )</td>
<td>2.3</td>
<td>18</td>
<td>90 ± 1.1 (87 to 92)</td>
</tr>
<tr>
<td>5 ( \times 10^{4} )</td>
<td>3.8 ( \times 10^{-6} )</td>
<td>1.2</td>
<td>8.0</td>
<td>34 ± 1.4 (32 to 36)</td>
</tr>
<tr>
<td>2 ( \times 10^{4} )</td>
<td>2.0 ( \times 10^{-6} )</td>
<td>0.6</td>
<td>4.1</td>
<td>17 ± 1.2 (14 to 18)</td>
</tr>
<tr>
<td>3 ( \times 10^{4} )</td>
<td>6.0 ( \times 10^{-6} )</td>
<td>1.5</td>
<td>6.0</td>
<td>36 ± 1.6 (34 to 38)</td>
</tr>
</tbody>
</table>

\(^{a}\)This is measured at the outlet of the micromodel and represent the average velocity for the entire pore space. The outlet diameter is 2 mm.

\(^{b}\)Estimated using porosity of 0.37, flow across 7.0 cm length and 15 \( \mu \)m depth.

\(^{c}\)Sample number is 20.
we considered a characteristic length of 7 cm, average colloid velocities for all colloid sizes at each pressure gradient, and an estimated hydrodynamic dispersion (Table 2). We obtained values for the hydrodynamic dispersion by conducting an experiment of colloid transport in a 3 mm × 1.4 m tube at flow rates of 0.10 to 0.14 mL/s. The dispersion was then calculated according to Levenspiel [1998] from the breakthrough curve analysis.

4. Conclusions

[34] We provide direct observation of the size exclusion phenomenon for colloids traveling through porous media. This phenomenon is important to understand the behavior of colloids. The observed threshold T/C ratio was 1.5, although this might not be the absolute minimum. However, evidence from the wide number of experiments indicates that the threshold ratio is closer to 1.5 than 1.0, since the colloids preferentially enter larger pore throats where most of the flow is directed.

[35] We clearly observed that certain flow patterns are followed by the colloids in this porous media, and the patterns are similar for all colloid sizes and ranges of pressure gradient applied in these experiments. We did not observe colloids entering dead-end pores (out of several in the micromodel), indicating that this is a low-probability process. The observed preferential flow paths are less evident in the case of the smaller colloid (0.05 μm) compared to the case of the larger colloid sizes (1–3 μm). These preferential flow paths are not only determined by the ratio of colloid to pore throat dimensions, but also by the pore geometry, the alignment and the connection between pores. Nevertheless, the smaller colloids have more diverse flow path because they can travel more easily through a range of pore throats.

![Figure 8.](image1.png)

**Figure 8.** Relationship between pore-scale Peclet number and acceleration factor (colloid to pore water velocity ratio).

![Figure 9.](image2.png)

**Figure 9.** Sketch of different colloids moving along a velocity profile in a pore throat. The larger colloid (shaded) moves with lower mean velocity compared to the smaller colloid (open) since the smaller colloid moves in the region of higher average velocity. Increasing pore water velocity will increase the velocity of smaller colloid more relative to the larger colloid.
The transport of colloids along the faster streamlines, as observed directly, results in a velocity ratio of 4 to 5 at the pore scale, considering the average velocity of colloids to water or a conservative nonsorbing tracer. These velocity ratios are within the simulated range of streamline velocities in the pore space, but are higher than those observed in core studies, possibly due to an up-scaling effect, since at the core scale the colloids sample a wider range of streamlines due to Brownian motion.

The pore-scale Péclet numbers (Pe) indicate an overwhelmingly advective dominated regime, since at the pore scale even these low water flow velocities are much greater than the corresponding thermal diffusion, with Pe values range from 10^2 to 10^5. For the micromodel as a whole, Pe was on the order of 10^1 to 10^2, since hydrodynamic dispersion is very significant at this scale. The relationship between pore-scale Pe and the acceleration factor indicates larger acceleration with increasing Pe. The effect of Pe is more pronounced for smaller particles, since they are traveling along the fastest streamlines. This increased acceleration factor might be reduced as the particles migrate through the porous medium and sample more dead-end pores, slower streamlines and other obstacles.

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References
Chrysikopoulos, C. V., and Y. Sim, One-dimensional virus transport in homogeneous porous media with time dependent distribution coefficient, J. Hydrol., 185, 199 – 219, 1996.

Table 2. Hydrodynamic Dispersion of Colloids and Calculated Pe for the Entire Micromodel

<table>
<thead>
<tr>
<th>Colloid Diameter, μm</th>
<th>Hydrodynamic Dispersion, μm^2 s^-1</th>
<th>Characteristic Length, μm</th>
<th>Velocity, m s^-1</th>
<th>Pe</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>1.70 × 10^-4</td>
<td>0.07</td>
<td>1.04 × 10^-3</td>
<td>1.06 × 10^-1</td>
</tr>
<tr>
<td>1.00</td>
<td>5.22 × 10^-4</td>
<td>0.07</td>
<td>3.94 × 10^-4</td>
<td>5.28 × 10^-2</td>
</tr>
<tr>
<td>0.05</td>
<td>6.88 × 10^-4</td>
<td>0.07</td>
<td>1.97 × 10^-4</td>
<td>8.10 × 10^-2</td>
</tr>
</tbody>
</table>
Figure 7. Relative pore water velocity in the vicinity of pores 10, 13 and 14, calculated by solving the Navier-Stokes equations in a 2-D finite element grid.