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Hydrodynamic and Chemical Factors in Clogging by Montmorillonite in Porous Media

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Abstract

Clogging by colloid deposits is important in water treatment filters, groundwater aquifers, and petroleum reservoirs. The complexity of colloid deposition and deposit morphology preclude models based on first principles, so this study extends an empirical approach to quantify clogging using a simple, one-parameter model. Experiments were conducted with destabilized suspensions of sodium- and calcium-montmorillonite to quantify the hydrodynamic and chemical factors important in clogging. Greater clogging is observed at slower fluid velocity, consistent with previous investigations. However, calcium-montmorillonite causes one order of magnitude less clogging per mass of deposited particles compared to sodium-montmorillonite or a previously published summary of clogging in model granular media. Steady state conditions, in which the permeability and the quantity of deposited material are both constant, were not observed, even though the experimental conditions were optimized for that purpose. These results indicate that hydrodynamic aspects of clogging by these natural materials are consistent with those of simplified model systems, and they demonstrate significant chemical effects on clogging for fully destabilized montmorillonite clay.

Introduction

Permeability reduction caused by deposition of colloidal particles in porous media, or clogging, is important in numerous environmental processes, including water treatment (*e.g.*,¹), aquifer storage and recovery (*e.g.*,²), surface water-ground water interaction (*e.g.*,³), formation damage in petroleum reservoirs (*e.g.*,⁴, chapter 8) and the influence of earthquakes on hydrology (*e.g.*,⁵). Filtration theory (^{6–8}) assists in understanding particle clogging, because it predicts the porosity reduction that results from particle accumulation. However, filtration theory is not sufficient to predict clogging because there is no unique relationship between porosity and permeability (9). The thrust of this study is to investigate the factors that control the degree of clogging for a given quantity of deposited particles. This focus makes the present study distinct from, but complimentary to, parallel approaches that predict permeability from the geometry of the porous medium in the absence of particles (*e.g.*,¹⁰), and from network models that predict permeability from an assumed porosity-permeability relationship in elements with particle accumulation (*e.g.*,¹¹).

Clogging is known to depend on physical factors, which control hydrodynamic effects, and on chemical factors, which control the colloidal stability of the particles (12). In order to investigate hydrodynamic effects on clogging, Mays and Hunt (13) analyzed published data sets from constant-flow filtration experiments that measured particle accumulation and head

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loss over a range of fluid velocities. Data were analyzed using a one-parameter clogging model based on the work of O'Melia and Ali (14), who predicted clogging based on the surface area within the porous media, which increases with particle deposition:

$$\frac{\Delta H}{\Delta H_o} = (1 + \gamma \sigma)^2, \quad (1)$$

where ΔH is the head loss, ΔH_o is the clean bed head loss, σ is the specific deposit, defined as the dimensionless ratio of deposit volume to total filter volume, and γ is an empirical clogging parameter that quantifies clogging per specific deposit. Because of the difficulty in measuring specific area (15), this model requires an empirical approach. The fact that γ is not constant reflects the important role of deposit morphology. One physical interpretation of γ is that its inverse is a critical specific deposit such that for $\sigma > 1/\gamma$, deposited particles contribute most of the surface area within the porous medium, resulting in greater clogging per unit of additional particle accumulation.

The analysis of published clogging data by Mays and Hunt (13) revealed a power-law correlation between the empirical clogging parameter and the Peclet number of the flow, $\gamma = 10^6 N_{Pe}^{-0.55 \pm 0.09}$, consistent across the various data sets, that indicated greater clogging at smaller Peclet numbers, where the Peclet number is defined as

$$N_{Pe} = \frac{ud_c}{D_p}, \quad (2)$$

and D_p is the particle diffusivity given by

$$D_p = \frac{\kappa T}{3\pi\mu d_p}, \quad (3)$$

where κ is Boltzmann's constant, T is temperature, μ is dynamic viscosity, and d_p is the primary particle diameter. Three of the data sets analyzed by Mays and Hunt (13) used kaolinite clay, but with a relatively small range of velocity. The most extensive data set analyzed was Veerapaneni's (16, chapter 5), who used a velocity range of almost two orders of magnitude, but these results were for latex microspheres depositing on glass beads. Considering these limitations, the first goal of the present study was to investigate whether the power-law correlation between clogging and hydrodynamic loading reported by Mays and Hunt (13) also extends to clogging by natural materials conducted over a wide range of velocity.

With regard to chemical effects, cation valence is known to affect the permeability of soils containing clays (*e.g.*, ¹⁷⁻¹⁸) and to influence the morphology of clay aggregates (*e.g.*, ¹⁹⁻²¹). However, experiments using soils or cores make it difficult to quantify the relationship between chemical conditions, permeability, and deposit morphology for clays because of two confounding factors: First, with soil or core samples, one cannot quantify particle accumulation by mass balance on the influent and effluent suspensions, which prevents the analysis of clogging for a given specific deposit. This is important, because knowing the specific deposit is required to determine the role of deposit morphology. Second, most studies on soil permeability focus on the dramatic effects that result when chemical changes, illustrated on Quirk-Schofield diagrams (22), create newly stabilized or newly destabilized particles. This focus on chemical changes makes it difficult to isolate the role of cation valence for a given degree of particle stabilization. Accordingly, the second goal of this study is to isolate the effect of cation valence on clogging during filtration experiments using a fully destabilized natural clay mineral.

A third goal of this study is to investigate long-term clogging. The conventional application of filtration theory to granular filters, which are frequently backwashed, provided little incentive to consider long-term effects. In contrast, these effects are important in natural environments where backwashing is not possible. Particle transport and clogging may be conceptualized as a dynamic feedback process between fluid flow and particle deposition: Flow transports particles, which form deposits, which cause clogging, which reduces or redirects subsequent fluid flow. Although classic filtration studies simultaneously modeled particle transport and clogging (14, 23), contemporary studies on environmental particle transport seldom address clogging. However, an appreciation for the feedback process between fluid flow and particle deposition is demonstrated by reports showing that fluid shear (24) or hydrodynamic drag (25) can mobilize previously deposited particles (26, 27). As long-term deposition proceeds under constant flow conditions, one might expect this dynamic feedback process to approach a limit, or steady state condition, in which the average deposition rate matches the average mobilization rate, with constant permeability and specific deposit. Steady state conditions could then be used as a baseline from which to evaluate permeability changes resulting from hydraulic, mechanical, or chemical perturbations. In the filtration literature, several reports document either permeability (28) or specific deposit (29) approaching a constant value, but simultaneous observations of steady state for both variables have not been reported. The third goal of the present study, therefore, was to investigate the potential for steady state clogging in long-term experiments.

Materials and Methods

The apparatus was designed to promote rapid achievement of steady state, with large approach velocities and concentrated influent suspensions to maximize particle delivery, destabilized particles to maximize particle accumulation, a short column to minimize the volume in which deposition and mobilization must reach equilibrium, and durations of tens of thousands of pore volumes. The filter column had a diameter of 1.4 cm, a length of 2.0 cm and was packed with Clementine silica (Prime Equipment, South San Francisco, CA), with density 2.65 g/cm^3 , passing a #80 (177 μm) mesh and retained on a #100 (150 μm) mesh, resulting in a geometric mean diameter of 163 μm . Sieved sand was rinsed with and then stored in distilled water. The column was wet-packed in short lifts and a carbon dioxide flood was used to remove trapped air bubbles. The porosity was 0.35 and the pore volume was 1.09 cm^3 . The sand was kept in place by a stainless steel mesh at the top and bottom of the column. Pressure ports were installed at the top, bottom and an intermediate location 0.7 cm from the top. No samples were collected from the intermediate pressure ports, since such an effort would have disturbed the deposits (23). The head loss across the entire filter and across the top section was measured with Validyne DP15 pressure transducers (Validyne Engineering, Northridge, CA).

Montmorillonite was selected as a model particle because it is a common clay mineral that is present in soils from temperate regions, sedimentary rocks, and poorly drained environments (30), whose morphology depends on cation valence (20, 31, chapter 10), allowing investigation of chemical effects on clogging. Montmorillonite SWy-2 was purchased from the Source Clays Repository (Clay Minerals Society, West Lafayette, IN). Clay was mixed with deionized water and then centrifuged at 100 G to remove particles with equivalent diameter greater than 2 μm , assuming Stokes settling, clay density of 2.33 g/cm^3 , and a settling path of 7 cm perpendicular to the centrifuge axis. This method of size fractionation has been shown to be superior to membrane filtration for colloidal suspensions (32). A series of ion exchange rinses were used to convert the raw clay into Na-montmorillonite or Ca-montmorillonite (33). Suspensions of 100 mg/L Na-montmorillonite or Ca-montmorillonite, with pH in the range of 6.0-6.2, were stirred rapidly and continuously to minimize aggregation, then pumped by a peristaltic pump at constant flow through the column. Destabilized conditions were imposed by using a background solution of 100 mM NaCl or 2 mM CaCl_2 , which are approximately one order of

magnitude above the critical coagulation concentrations of 8 ± 6 mM for Na-montmorillonite or 0.12 ± 0.02 mM for Ca-montmorillonite (31, chapter 10). The column was flushed with at least 15 pore volumes of particle-free brine prior to each experiment, which determined the clean bed head loss ΔH_o . Ca-montmorillonite suspensions included 3 g/L of 2-chloroacetamide biocide, added as a precaution to extend the shelf life of effluent samples before turbidity measurements. This concentration of 2-chloroacetamide did not change the pH nor electrical conductivity of a 2 mM CaCl_2 solution, and caused no significant increase in turbidity, indicating that the biocide had no influence on particle stability.

Effluent samples were collected by an automatic 25 mL fraction collector. The turbidity of these samples and the influent suspension was measured with a Hach 2100A turbidimeter (Hach Company, Ames, IA) with a nominal error of ± 0.07 NTU for 100 mg/L Na-montmorillonite and ± 0.7 NTU for 100 mg/L Ca-montmorillonite, converted to concentrations using clay-specific calibration curves, and then used to calculate the specific deposit, σ , as a function of time by mass balance.

Mass recovery was determined by comparing the measured specific deposit determined by extrusion to the calculated specific deposit from an overall mass balance. The extruded sample was vigorously shaken to ensure complete clay mobilization into a particle-free brine matching that used in the relevant experiment (100 mM NaCl or 2 mM CaCl_2). The contribution from suspended particles in the pore space was negligible. Preliminary experiments were conducted to confirm that flow through the filter was one-dimensional, that there was no deposition in the supply tubing, that particle mobilization from the silica sand was negligible, and that the magnitude of peristaltic pulsing was within the ± 2.2 cm nominal error of the pressure transducers. Further details are available the Supporting Information and in (34, chapter 4). Experimental conditions are listed in Table 1.

Results and Discussion

Raw data for experiment 1 are shown in Figure 1, with corresponding results for other experiments shown in Figures S5-S12 of the Supporting Information. The first few concentration measurements indicate that breakthrough occurred rapidly, so the influent concentration was only slightly higher than the effluent during the remainder of the experiment. This observation was typical and reflects the objective of rapidly achieving steady state. The head loss, shown in the lower panel, increased with time in both the top and bottom sections of the filter. Mass balance results are discussed in the Supporting Information.

Montmorillonite Clogging in Silica Sand

Clogging data were analyzed by plotting the normalized increase in head loss, $\Delta H/\Delta H_o - 1$, versus the specific deposit, σ , for the first 3500 pore volumes of each experiment, both averaged over the whole filter. This duration provides a uniform basis to compare results across experiments, and eliminates the effect of head loss through the cake deposit that formed in experiments operated beyond 5000 pore volumes, which is modeled differently (35). Results for Na-montmorillonite with $u = 0.021$, 0.11, and 0.53 cm/s are shown in Figures 2-4, respectively. To illustrate the profound effect of cation valence, Figure 2 also shows results for Ca-montmorillonite at $u = 0.021$ cm/s. The Na-montmorillonite results in Figure 2 correspond to the data of Figure 1. For clarity in this and similar figures, data were selected to display up to 25 points, but all concentration data and their corresponding head loss data were used for model fitting by least squares. Error bars were estimated using the method described in the Supporting Information. Figure 2 also shows the fitted clogging model, which on average differs from the data by a factor of e^{RMSE} , where $RMSE$ is the root mean squared error, defined in the Supporting Information. For experiment 1, $RMSE = 0.52$, so on average the model differs from the data by a factor of $e^{0.52} = 1.7$. During the first 3500 pore volumes, the critical specific

deposit $\sigma = 1/\gamma$ was exceeded only for experiments 1, 2A, and 4, shown as dotted vertical lines on Figures 2 and 3. Fitted parameters for all experiments are given in the “whole filter” column of Table 1, and results for Ca-montmorillonite at $u = 0.21$ and 0.53 cm/s, which maintained essentially clean bed conditions, are shown in Figures S13-S14 of the Supporting Information.

Although the fitted models do not replicate the observations in detail, they do provide an average description that can be used to parameterize hydrodynamic and chemical effects. For a given specific deposit, the data clearly show major differences in clogging. The model serves to quantify those differences, because its single parameter is uniquely defined by the given data. The fitted values of γ are plotted against Peclet number, N_{Pe} , in Figure 5 along with a power-law correlation for Na-montmorillonite and for Ca-montmorillonite, assuming primary particle diameter $d_p = 1$ μm , consistent with the clay preparation procedure. The uncertainty of the power-law exponent is a 95% confidence interval calculated using the standard error for the slope of the linear regression of $\ln(\gamma)$ versus $\ln(N_{Pe})$. The resulting exponents are significantly different from 0 and -1, but not significantly different from each other.

The first goal of this study was to determine whether clogging by natural materials is consistent with the empirical correlation reported in Mays and Hunt (13), shown on Figure 5. Both Na- and Ca-montmorillonite have power law exponents that are comparable to previously reported results. This analysis indicates that the hydrodynamic effect on clogging is also applicable to natural materials, which supports the apparently general nature of this scaling relationship for porous media clogging by destabilized, abiotic particles at constant flow. This empirical relationship is consistent with simulations predicting that at higher flow rates, the resulting ballistic deposits will be more streamlined, and therefore require more colloids in order to exert the same drag on the fluid (36).

Cation Valence

The second goal of this study was to isolate the effect of cation valence on clogging with a fully destabilized clay. As shown in Figure 5, the Peclet number scaling is consistent across data sets, but the magnitude of the clogging parameter depends strongly on cation valence. Assuming that the biocide did not affect the Ca-montmorillonite experiments, which is reasonable given that it was non-ionic and had no significant impact on turbidity, Figure 5 shows that Na-montmorillonite causes approximately 20 times more clogging per mass of deposited clay than Ca-montmorillonite. This difference is consistent with the known swelling behavior of Na-montmorillonite (30) that would cause increased clogging per mass of clay, and with the formation of multi-plate quasi-crystals by Ca-montmorillonite (20) that would cause decreased clogging per mass of clay. The formation of quasi-crystals results from the outer-sphere complexation of Ca^{2+} between two opposing siloxane cavities on the montmorillonite surface, resulting in a characteristic plate spacing of approximately 2 nm (31, chapter 10).

A speculative interpretation of this 20-fold difference in clogging is that quasi-crystal formation by Ca-montmorillonite increases the *effective* particle size from the perspective of clogging. Specifically, if characteristic particle size for Ca-montmorillonite were 100 times larger than Na-montmorillonite, then the calculated Peclet number would shift to the right by two orders of magnitude, yielding a more consistent correlation for γ .

Steady State

To investigate the potential for steady state clogging, the raw head loss data were analyzed for the full duration of each experiment. In order to eliminate clogging by cake deposits, only data from the lower 1.3 cm of the filter were considered, which prevented inclusion of experiment 2B, for which no intermediate head loss data were available. The final slope was determined

by linear regression of head loss versus pore volumes for the final 20% of each experiment, with a 95% confidence interval determined from the standard error of the estimated slope. The 20% interval was arbitrary, but was chosen to focus on the final slope while avoiding erroneous results caused by noise in final few head loss data. The results, given in the “lower filter” column of Table 1, indicate that only experiments 1, 2A, and 4 had significant particle accumulation that exceeded the critical specific deposit of $\sigma = 1/\gamma$. These experiments were associated with low fluid velocity ($u \leq 0.11$ cm/s) and large final head loss ($\Delta H/\Delta H_0 > 5$) that was still increasing upon termination (slope > 1 cm/10,000/ ΔH_0), indicating a lack of steady state. Minimal deviation from clean bed conditions was observed in the remaining experiments: high fluid velocity ($u \geq 0.21$ cm/s) appears to have prevented significant deposit accumulation ($\sigma < 1/\gamma$ during the first 3500 pore volumes), resulting in small final head loss ($\Delta H/\Delta H_0 < 2$) with minimal head loss increase at termination (slope < 1 cm/10,000/ ΔH_0).

These experiments suggest that no steady state clogging should be expected for fluid velocities characteristic of slow sand filtration ($u \approx 0.01$ cm/s), groundwater flow ($u \approx 0.001$ cm/s), or soil infiltration ($u \approx 0.0001$ cm/s). This negative result does not prove steady state clogging is impossible, but it was surprising given that the experiment was specifically designed for this goal (small filter, concentrated influent suspension, destabilized particles, and up to 61,000 pore volumes of influent). Deposition in natural environments is subjected to variations in suspension concentration, composition, aqueous chemistry, and hydrodynamic loading that would likely preclude steady state clogging in nature.

Hydrodynamic Shear

Head loss can be interpreted in terms of hydrodynamic shear, either as a shear rate or a shear stress with a mean shear rate, G , in porous media (37) given by:

$$G = \left(\frac{\rho g u \Delta H}{\varepsilon \mu L} \right)^{1/2}, \quad (4)$$

where ρ is fluid density, g is gravity, ΔH is head loss in the lower $L = 1.3$ cm of the filter, and porosity is $\varepsilon = 0.35$. The mean shear stress, $\tau = \mu G$, provides insight into the strength of the particle deposits. The results, shown in Table 2, indicate significant clogging occurs when clean bed shear rates, G_0 , are less than or equal to 700 s^{-1} , and negligible clogging occurs for $G_0 \geq 1400 \text{ s}^{-1}$. This suggests a critical shear rate between 700 s^{-1} and 1400 s^{-1} or shear stress between 7 and 14 dyne/cm² that will prevent significant accumulation of destabilized montmorillonite. Although this hydrodynamic shear appears to have prevented deposit initiation, it was not sufficient to remove existing deposits, as evidenced by the final shear stress of 16 dyne/cm² in experiment 2A, which did not reach steady state. The apparent deposit shear strengths in experiments 1, 2A, and 4 between 4 and 16 dyne/cm² are similar to those for Na-montmorillonite depositing in fractures, $\tau = 1\text{--}8$ dyne/cm² (33), and to kaolinite depositing in porous media, $\tau = 2.7\text{--}4$ dyne/cm² (38). The continued increase in head loss, hydrodynamic shear, and deposit strength reflects the dynamic feedback between fluid flow and particle deposition leading to dynamic deposits that evolve over time.

The results of this study indicate that the specific deposit is not sufficient to predict clogging by montmorillonite, since the data clearly show hydrodynamic and chemical effects. The order-of-magnitude differences in clogging for a given specific deposit indicate an important role for deposit morphology. The empirical parameter γ can be used to quantify the important role of macroscopic hydrodynamic and chemical effects on clogging (Figure 5), but continued progress toward a mechanistic understanding of deposit morphology, extending the work of Veerapaneni and Wiesner (36), will require experimental techniques that non-invasively

quantify deposit structure (*e.g.*, ^{39, 40}). This effort, in turn, would provide the basis for improved pore-scale clogging models.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Effluent concentration (top) and head loss (bottom) versus pore volumes eluted, experiment 1. The influent concentration, C_o , is shown as a solid line with an error of one standard deviation shown by dashed lines. The error bars on the head loss data, which were selected to display only 40 measurement times, are smaller than the plotted symbols. Head loss measurements in the top section were discontinued when the head loss exceeded the transducer capacity at approximately 100 cm.

Figure 2.

Normalized increase in head loss versus specific deposit for experiments with $u = 0.021$ cm/s. Experiment 1 (Na^+) is shown with solid circles. Experiment 4 (Ca^{2+}) is shown with open squares. For each, the solid line is the fitted clogging model, and the dashed lines are plus or minus one root mean squared error (RMSE). The critical specific deposit occurs at 5.6×10^{-4} with Na^+ and at 4.5×10^{-3} with Ca^{2+} .

Figure 3.

Normalized increase in head loss versus specific deposit for experiment 2. The bold line is the fitted model and the dashed lines are $\pm$ RMSE for replicate A; the regular line is the fitted model and the dotted lines are $\pm$ RMSE for replicate B. Rapid clogging in experiment 2A is expected above the dotted vertical line at $\sigma = 1/\gamma$.

Figure 4. Normalized increase in head loss versus specific deposit for experiment 3. The bold line is the fitted model and the dashed lines are $\pm$ RMSE for replicate A; the regular line is the fitted model and the dotted lines are $\pm$ RMSE for replicate B.

Figure 5.

Fitted clogging parameter γ versus Peclet number for Na-montmorillonite (circles) and Ca-montmorillonite (squares). Note there are two squares at $N_{Pe} = 2 \times 10^6$. The dashed line is the empirical correlation reported by Mays and Hunt (13), which summarized the effect of fluid velocity on clogging in six previously published data sets.

Details on the filtration experiments, with influent concentration, C_o , averaged over the whole experiment and duration in pore volumes. Na^+ experiments used a background of 100 mM NaCl; Ca^{2+} experiments used 2 mM $CaCl_2$. The Peclet number, N_{Pe} , is defined by equation (2). The clogging parameter γ in equation (1) was fitted to whole filter data from the first 3500 pore volumes. On average the model differs from the data by the given factor. The final normalized head loss, $\Delta H/\Delta H_o$, and final slope were determined for the lower 1.3 cm of the column, with the slope and 95% confidence interval calculated for the final 20% of each experiment. The slope has units of centimeters of head loss per ten thousand pore volumes, normalized by clean bed head loss [cm/10,000/ ΔH_o].

Table 1

#	general			whole filter			lower segment	
	cation	u [cm/s]	C_o [mg/L]	duration	N_{Pe}	γ	factor	final $\Delta H/\Delta H_o$ slope
1	Na^+	0.021	102	3,700	7.8×10^4	1,800	1.7	98
2A	Na^+	0.11	101	3,600	4.1×10^5	600	1.4	440 ± 17
2B	Na^+	0.11	102	61,000	4.1×10^5	660	1.2	34 ± 1
3A	Na^+	0.53	101	4,100	2.0×10^6	360	1.3	-0.056 ± 0.004
3B	Na^+	0.53	99	3,500	2.0×10^6	510	1.2	0.14 ± 0.10
4	Ca^{2+}	0.021	102	59,000	7.8×10^4	220	1.6	1.6 ± 0.1
5	Ca^{2+}	0.21	103	60,000	7.8×10^5	100	1.8	0.16 ± 0.02
6A	Ca^{2+}	0.53	106	4,700	2.0×10^6	80	2.2	0.065 ± 0.017
6B	Ca^{2+}	0.53	96	43,000	2.0×10^6	81	1.8	0.21 ± 0.03

Table 2
Average shear rate G , calculated with equation (4) for the lower 1.3 cm of the filter, and corresponding shear stress, τ , assuming a dynamic viscosity of $\mu = 0.01$ g/cms. Results in the “clogged” column were calculated at the termination of each experiment.

#	general			clean bed		clogged	
	u [cm/s]	G_o [s^{-1}]	τ_o [dyne/cm ²]	G [s^{-1}]	τ [dyne/cm ²]	G [s^{-1}]	τ [dyne/cm ²]
1	0.021	100	1	1000	10	1000	10
2A	0.11	700	7	1600	16	1600	16
3A	0.53	3000	30	3200	32	3200	32
3B	0.53	3100	21	3300	33	3300	33
4	0.021	100	1	400	4	400	4
5	0.21	1400	14	1700	17	1700	17
6A	0.53	3200	32	3200	32	3200	32
6B	0.53	3500	35	4100	41	4100	41