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Stopping clay colloid formation in engineered barrier systems

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Abstract

Clays have many positive attributes leading to their use in waste isolation scenarios. One negative of their use is the formation of clay colloids that can transmit otherwise strongly sorbing contaminants long distances. In this work, we introduce a material combining a layered double hydroxide and a montmorillonite clay. This material is functionally characterized in an advective column under conditions where clay colloid formation is extensive. The material is shown to retard clay colloids once formed, and to help limit the initial formation of clay colloids. Adding this material to a waste barrier will help to limit the erosion of the clays in the barrier and limit the colloidal transport of contaminants.

Introduction

Clays have many favorable qualities leading to their use in waste isolation scenarios. Both in nuclear waste disposal and as a barrier material in hazardous waste landfills, the desired properties are exceedingly low hydraulic conductivity, high sorption capacity for metals/radionuclides, and swelling capacity to self-seal fractures or damage caused by construction of the waste repository [1]. Swelling clays, such as bentonite, have all of these characteristics. Many of the listed properties are related to the plate like nature and small particle size characteristic to clay minerals [2]. However, these small particle sizes also make clays prone to the formation of colloidal particles that can enhance the transport of contaminant species.

The formation of clay colloids has been studied extensively. Colloid formation is enhanced by chemical and physical attributes of the water in contact with the clay. Clay colloid formation is enhanced when the ionic strength of the solution is low, pH is high and porewater velocity is fast. Specifically, there is a critical salt concentration [3], or critical coagulation concentration [1], above which clays from a hydrated gel, and colloids are not released. Depending on the clay identity, the percent composition of the clay in a soil, and the salts used to generate the ionic strength, the critical salt concentration can range from 10^{-4} M - 10^{-1} M [3-8]. The other major chemistry control on colloid formation is pH. Colloid formation is enhanced at higher pH [8]. At higher pH values, the edge sites deprotonate and become negatively charged. Under these conditions both the edge and faces of the clay plates are negatively charged, thus electrostatic repulsion leads to more clay colloid release [8]. The main physical attribute of water related to colloid formation is flow rate. The larger the flow rate of the water, the larger the shear forces are on the individual particles. When shear forces are large, particle generation is also high [9].

The larger pore velocities also stabilize the particles in solution leading to increased transport [10].

Once the colloids are formed, the distance they are transported depends on the interactions between the colloids and the porous media and on the physical characteristics of the porous media [11]. If the attraction between the colloids and the porous media are weak, deposition due to chemical or electrostatic forces is unlikely. However, in heterogeneously charged porous media, small areas of attraction have been shown to be sufficient to lead to particle removal [12]. As colloids are transported, pore constrictions can lead to the physical entrapment of particles even when there is a repulsive force between the colloid and the porous media [3, 13].

Minimizing clay colloid transport away from a repository site is important to both maintain the engineered properties of the liner, and to minimize colloid facilitated transport. In nuclear waste repositories the total mass loss due to colloid migration is expected to be small, though there are still considerable differences between modeled and experimental erosion rates [1, 4]. In nuclear and other waste isolation scenarios, clays may be mixed with sands to achieve specific physical properties. Under these conditions, the hydraulic conductivity is higher than that of clay alone, the average pore diameters are larger, and erosion of clay particles is expected to be larger [9]. In both nuclear and other waste isolation scenarios, colloid facilitated contaminant transport is the second critical issue [1, 4, 14, 15]. The formation of a colloidal phase creates a ternary system where a contaminant can be in the dissolved phase, sorbed to the colloid, or sorbed to the porous media [16]. If conditions favor colloid transport, any contaminant sorbed to the colloid will be transported as well. This migration mechanism has been to shown to be particularly important for any metal that is strongly sorbing, most notably the actinides, U, Pu, Am, Cm.

While understanding contaminant-colloid interactions and colloid transport mechanisms have been well studied, far less effort has been placed on stopping the initial formation of colloids. Poly-electrolyte materials have been used to stop particles [17]. This technology requires active management, which is unrealistic for nuclear waste scenarios, and the polymers used are organic which have increased potential to breakdown under high heat or high radiation fields during the long waste isolation periods. In this work, we describe a novel, inorganic material that is a mixture of a layered double hydroxide and a swelling clay. The material is functionally characterized and demonstrates the capability to reduce colloid formation under low ionic strength and highly advective conditions. This material could be added to the outer fringes of waste barriers to minimize the formation of colloids.

Methods

Synthesis

The synthesis of the material occurred in two steps. The first was to create the layered double hydroxide (LDH). To create the LDH materials, aqueous mixtures of $AlCl_3$ and either $MgCl_2$ or $ZnCl_2$ were mixed in a 1:3 Al^{3+}:M^{2+} ratio, where M is either Mg or Zn. With constant stirring and over the course of several hours, 4.5M NaOH was added to the mixture until a pH of 8.62 +/- 0.05 was achieved. The solution was covered and placed in an 80°C oven overnight. After heating, the solution was centrifuged to separate it from the remaining solution. The clear solution was decanted, and the material was rinsed with DI water and re-centrifuged. The rinsing procedure was repeated two more times. Once rinsed, the material was placed in a 40°C oven overnight. The material is then calcined for four hours at 600°C with a ramp of 5°C/minute. The two LDH samples (LDH-Mg and LDH-Zn) were ground by hand to a fine powder.

To make the colloid trap material, the LDH was allowed to coagulate with a montmorillonite sample. They clay used was the Na-rich montmorillonite (SWy-2) available from the Clay Minerals Society. Two different mass ratios were used, 1:1 and 1:9 LDH:clay. The clay was added to ~300-400 mL of de-ionized water. The clay slurry was vigorously stirred for several minutes to ensure hydration of the clay minerals. The LDH was then added, and the slurry was actively mixed for another minute, at which point the stirring was ceased. The combination of the materials behaved similarly to other coagulants with a clear water layer forming above the sludge layer. Settling was rapid, and was typically completed in 2-3 minutes. The water was decanted and the sludge was collected, air-dried and calcined at 600°C for 2 hours. The completed material was ground by hand to a fine powder. Four different materials were tested, a 1:1 mass ratio of LDH-Mg:montmorillonite, a 1:9 mass ratio of LDH-Mg:montmorillonite, a 1:1 mass ratio of LDH-Zn:montmorillonite, and a physical mixture of 1:1 mass ratio of LDH-Mg:montmorillonite that had not been coagulated and calcined.

Functional Characterization

The goal of the functional characterization was to compare colloid transport properties with and without the new materials. This was completed in a 1-D column, 15 cm long and 2.49 cm in diameter. The column was packed in thirds perpendicular to flow. The first and last thirds were clean uniform sand. The sand had been cleaned in ~8 M boiling HNO_3. The sand was then rinsed with deionized water until the pH of the water was circum-neutral. The middle zone was filled with a mixture of sand and the newly created materials. In each experiment the materials were physically mixed with the sand in a 1:9 mass of material:mass of sand ratio. The sand and sand/material mixtures were loaded in lifts and compacted with a glass rod. As more material was added, the water level was increased so that compaction occurred under water. Once packed, steady state flow was established through the column with deionized water and a peristaltic pump set at 1 mL/min. Once steady state was achieved, the influent was switched to a colloid suspension made with montmorillonite suspended in deionized water. The suspension was made by adding ~1g of montmorillonite to 1 L of deionized water. The solution was mixed by hand and allowed to settle for several days. The solution was decanted from any settled solid materials. This same solution was used for all the column experiments. Samples from this reservoir were removed at the start of each experiment to normalize for any variation caused by further settling.

The effluent from the column was directed to sampling tubes, and fractions were collected every three minutes for one hour, or about 2 pore volumes. The solutions were acidified with HNO_3 and analyzed for dissolved aluminum via inductively coupled plasma-optical emission spectroscopy. The dissolved aluminum concentration was used as a proxy for particle concentration.

To help evaluate the material effectiveness two baseline experiments were completed. In the first, clean sand was packed throughout the column, and the colloid suspension was pumped through the clean sand. This gives a baseline for colloid migration in the absence of the novel materials. The second baseline experiment was again packed in thirds, but the middle third consisted of a 0.5:9.5 mass montmorillonite:mass sand physical mixture. This experiment gives a baseline for colloid creation.

Analysis

The data was modeled with a 1-D analytical solution to the advective-dispersive equation for a step input change with retardation (eqn 1):

$$C(x,t) = \frac{C_0}{2}\left(erfc\left[\frac{(RL-v_x t)}{(4RDt)^{0.5}}\right] + \exp\left(\frac{v_x L}{D}\right) erfc\left[\frac{(RL-v_x t)}{(4RDt)^{0.5}}\right]\right) \qquad \text{eqn. 1}$$

where C = concentration, C_0 = influent concentration, R = retardation coefficient, v_x = linear flow velocity, t = time, D = dispersion coefficient, and L = column length. Using the physical dimensions of the column and the mass of water added to the column during packing, the porosity was determined to be 0.44. For 1 mL/min volumetric flow this gives a linear flow velocity of 0.47cm/min. The only parameters used to fit the data were the dispersion retardation coefficients. The model was fit to the data using the solver function in Excel, minimizing the sum of the squared difference between the model and the data.

Results and Discussion

The breakthrough curve for the baseline experiment where only montmorillonite was added to the middle third of the column is shown in Figure 1. For the majority of the experimental timeframe, the effluent colloidal concentration was noticeably higher than the influent concentration. Implying that for the conditions studied, and without the layered double hydroxide present, montmorillonite is expected to delaminate and flow out of the column. The decreasing normalized concentration as a function of time maybe caused by increasing pore clogging of the colloids within the porous media or to depletion of the montmorillonite supplied.

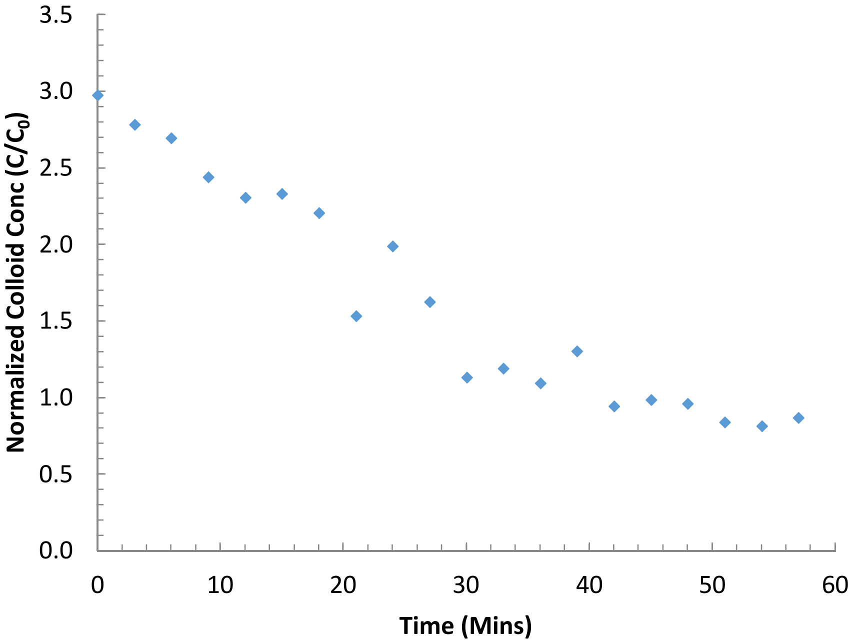

Figure 1- Normalized colloid breakthrough from a sand column with a montmorillonite/sand mixture packed in the middle third of the column.

Figure 2 shows the normalized breakthrough curves for all of the other experimental conditions. The sand only data is the second of the baseline experiments. It will be used for comparative purposes in the data analysis. For all of the cases when the novel materials are present, the breakthrough curve shifts to later timepoints implying retardation of the colloidal materials. This is seen explicitly in Table 1, which summarizes the values for the model fitting under each condition.

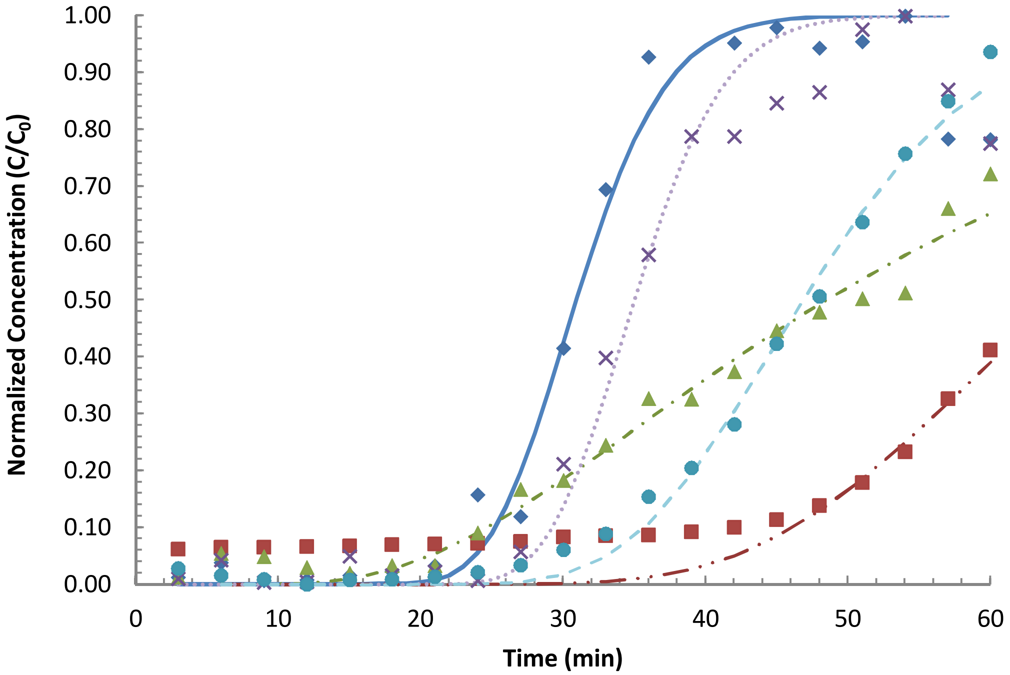

Figure 2- Breakthrough curves for clay colloid passage through the column. Sand only (—◆—), 1:1 LDH-Zn:montmorillonite (··×··), 1:1 physical mixture of LDH-Mg:montmorillonite (- -●- -), 1:1 LDH-Mg:montmorillonite (– ·▲· –), and 1:9 LDH-Mg:montmorillonite (—■· ·).

Table 1- Modeled retardation and dispersion coefficients for model fits in Figure 2.

	Model Values	
	R (unitless)	D (cm^2/sec)
Sand Only	0.98	1.48E-3
1:9 LDH-Mg:Mont	2.11	5.17E-3
1:1 LDH-Mg: Mont	1.64	1.87E-2
1:1 Physical mixture of LDH-Mg:Mont	1.49	2.67E-3
1:1 LDH-Zn:Mont	1.10	1.17E-2

In the sand only column, the transport of the colloids was nearly ideal, with low dispersion and a retardation value near one, signifying the colloids are behaving conservatively. This behavior is expected based on the fixed negative charge of the montmorillonite, and on the likely de-protonated surface sites of the silica sand at the pH of deionized water. Of the novel materials the 1:1 LDH-Zn:Mont was the least effective at retarding the injected colloids with a retardation value only slightly larger than the colloids moving through clean sand. All of the LDH-Mg compounds fared much better, with the 1:9 LDH-Mg:Mont doubling the retardation value compared to the clean sand column.

In comparing the different mass percents and introduction methods, it does not appear that the calcining of the material truly helps the material retard colloid migration. The retardation values are similar for both of the 1:1 materials with LDH-Mg. However, the dispersion coefficients are markedly different, implying alterations to the flow regime. The dispersion value was an order of magnitude higher for the 1:1 LDH-Mg:Mont material than in any of the other materials tested. Visually examining the breakthrough curve, this material also had the least ideal breakthrough behavior, having a breakthrough time near that of the sand only column. It is not clear why the calcining leads to less ideal behaviors.

Surprisingly, the 1:1 LDH-Mg:Mont material did not retard the colloids to the same extent as the 1:9 LDH-Mg:Mont material. Since the 1:1 material is much richer in the positively charged layered double hydroxide, the assumption would be that it would attract more of the clay particles out of solution, and therefore retard the clays to a greater extent. And yet, it is the 1:9 material that performs the best in terms of retardation. Since electrostatic reasoning does not help explain the data, there may be physical reasons for such behavior. For example, upon coagulation, the 1:9 material may have larger particle sizes which alters the size distribution of the pores in the sand leading to more filtration of the injected colloids. Despite the better colloid retardation, the pre-breakthrough colloid concentration is the highest in the 1:9 material. The average normalized concentration prior to breakthrough for the 1:9 material is 0.066. For all of the other materials, the highest pre-breakthrough concentration is 0.032. Since these colloids are breaking through before the injected colloids could have passed through the column, the eluted colloids must be coming from the material itself. At this mass ratio, the cohesion between the LDH and the montmorillonite may be too low to keep the clays in the material in place. This small amount of colloid present at early timepoints also complicated the fitting of the model to the data. When the solver function was applied to all of the data, the transport parameters were $R = 2.59$, and $D = 1.53E\text{-}2\ cm^2/sec$. Visually this was a poor fit to the data, and so the initial data points with the low, constant concentration of colloids were ignored. The values in Table 1 were fitted from the final seven data points. A different solution to the advective-dispersive equation, with a constant source term, would likely give a better overall fit to the data. This was not completed to maintain the ability to compare the model values between the different column packings.

Conclusions

The material created and tested can clearly retard and stop the formation of clay colloids, even under conditions where large amounts of colloids are expected. The materials are inexpensive, and could be easily added to the fringes of a clay barrier. They are inorganic, meaning they will likely survive the disposal environment for extended periods of time. Since the material properties are based on structural charges, slight changes to solution conditions (e.g., ionic strength or pH) will not change their behavior. Although it would need to be tested, it is expected that under conditions less favorable to clay colloid formation (i.e., diffusion dominated conditions), the materials would have similar mitigating effects on colloid formation.

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