EFFECTS OF STRUCTURAL IRON REDUCTION ON THE HYDRAULIC CONDUCTIVITY OF Na-SMECTITE

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Abstract—The long-term impermeability of clay barriers in waste disposal facilities and hydraulic structures is of critical importance to environmental, agricultural, and industrial concerns. Changes in the oxidation state of Fe in the constituent clays of compacted clay barriers may degrade the hydraulic conductivity of these structures because other properties related to hydraulic conductivity, such as swelling, gel microstructure, and particle size, are greatly altered by the oxidation state. Two Na-saturated smectites (SWa-1 and API 25) were reduced by sodium dithionite ($Na_2S_2O_4$), both in suspension and *in situ* after consolidation, to examine the effects of structural Fe reduction on hydraulic conductivity. Results indicated that the hydraulic conductivity depended on both the oxidation state and the consolidation history of the clay. The hydraulic conductivity of clay reduced in suspension before consolidation was lower than that of oxidized clay. Initially reduced smectite, thus, may be compactable to a less-permeable material with higher bulk density. But reduction of smectite *in situ* after consolidation increased the hydraulic conductivity and its variability. The oxidized state of clay liners should, therefore, be preserved.

Key Words—Barriers, Bulk density, Clay, Hydraulic conductivity, Iron, Liners, Permeability, Reduction, Smectite, Water.

INTRODUCTION

Clay liners are widely used as containment barriers in waste disposal facilities (e.g., landfills, waste piles, surface impoundments) and hydraulic structures (canals, dams, reservoirs). The effectiveness of these barriers is determined by their impermeability to water, organic compounds, and dissolved inorganic species, and by their ability to remain impermeable over long periods of time (Weeks, 1986; Goldman *et al.*, 1988; Albrecht and Cartwright, 1989). Smectite is one of the most effective clay minerals to be used in these liners because of its high swelling pressure, low hydraulic conductivity, and high cation exchange capacity.

While the initial hydraulic and cation exchange characteristics of smectites are favorable for the purposes of clay liners, their long-term stability in liners is uncertain, especially in highly reactive and widely varying chemical environments. Studies of clay-chemical interactions on the permeability of smectites reveal significant degradation or variation depending on chemical and physical factors that may change with time (Buchanan, 1964). Permeability to organic compounds seems to be greater than to water (Anderson, 1981), probably because of the hydrophilic nature of clay surfaces; but the accumulation of an organic compound over time may alter the water-retention capacity of the clay. Also, the permeability to water changes with the water content of the compacted clay (Monserrate, 1982).

Studies by Stucki and co-workers (Stucki *et al.*, 1984b, 1984c; Lear and Stucki, 1987, 1989; Stucki and Tessier, 1991; Khaled and Stucki, 1991) revealed that the oxidation state of structural Fe in smectite produces large differences in many properties which are fundamental to the performance of clay liners, swelling pressure, cation exchange capacity, total layer charge, specific surface area, and microstructure or texture.

Because hydraulic conductivity and swelling pressure depend on the forces which govern clay-water interactions (Blackmore and Marshall, 1965), these two properties are strongly correlated even though a uniform, quantitative relationship has yet to be established. Hydraulic conductivity is also closely related to the microstructure or texture of the clay-water fabric. Because the reduction of structural Fe(III) to Fe(II) causes changes in swelling pressure and in other physico-chemical properties of smectites, oxidation and reduction might change hydraulic conductivity as well. The purpose of this study was to determine how the oxidation state of structural Fe affects the hydraulic conductivity of consolidated smectite gels.

MATERIALS AND METHODS

Sample clays

Smectite clay minerals used in this research were ferruginous smectite SWa-1 (Source Clay Minerals Repository of The Clay Minerals Society) from Grant County, Washington, and montmorillonite API 25 (Wards Natural Science Establishment) from Upton, Wyoming. The structural formulae of these smectites were reported by Goodman *et al.* (1976) and Stucki *et al.* (1984b), respectively, *viz.*,

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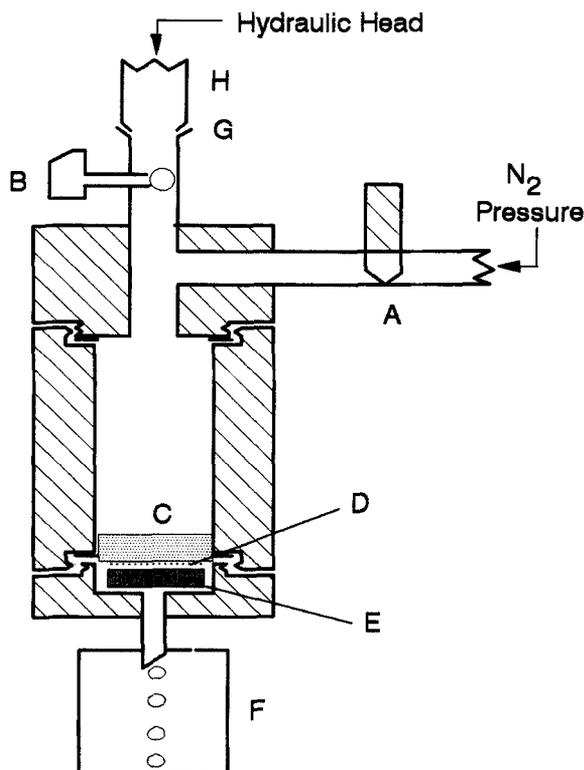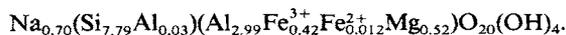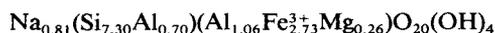
Figure 1. Diagram of flow cell used in experiments for consolidated clay sediment preparation and for hydraulic conductivity measurements. Key: A—needle valve; B—ball valve; C—consolidated clay; D—porous, membrane filter (<0.025 μm pore diameter); E—porous, stainless-steel filter; F—effluent collection flask (covered with parafilm punctured with one pin hole); G—fitting attaching glass stand-pipe to ball valve; H—glass stand pipe.

$$Na_{0.81}(Si_{7.30}Al_{0.70})(Al_{1.06}Fe^{3+}_{2.73}Mg_{0.26})O_{20}(OH)_4$$

$$Na_{0.70}(Si_{7.79}Al_{0.03})(Al_{2.99}Fe^{3+}_{0.42}Fe^{2+}_{0.012}Mg_{0.52})O_{20}(OH)_4.$$

The clays were Na saturated using 1 M NaCl, fractionated to <2 μm, dialyzed, and freeze-dried prior to use.

Structural iron reduction

Experiments were differentiated by the order in which Fe reduction and clay consolidation occurred. The designation *in-suspension* refers to experiments in which the smectite was reduced in suspension then consolidated under low pressure in the hydraulic conductivity cell; *in-situ* is the designation for experiments in which the smectite was consolidated in the cell prior to reduction. All samples were initially in the oxidized state, which is referred to here as the "unaltered" state.

Smectite reduction in suspension was carried out using the methods and apparatus described by Stucki *et al.* (1984a). A 150-mg portion of clay was added to each of two reaction tubes, and suspended in 40 ml of citrate-bicarbonate (C-B) buffer solution, which was prepared by combining 8 parts of 1 M NaHCO$_3$ with 1 part of 0.3 M Na$_3$C$_6$H$_5$O$_7$·2H$_2$O. The clay sample in one tube was reduced with 200 mg of Na$_2$S$_2$O$_4$ at 70°C for 2 hr. We added 134 mg NaCl to the other tube, giving the same amount of Na as in the first tube but without altering the oxidation state. Otherwise, the two samples were treated identically. Samples were then washed three times with a deoxygenated solution of 5 × 10^{-3} M NaCl and one time with deoxygenated, deionized water (18 Mohm-cm resistivity) using the procedure and apparatus described by Stucki *et al.* (1984a). The supernatants were saved in 50-ml flasks, then analyzed for Na$^+$ by atomic emission spectroscopy. After decanting the final supernatant (about 5 × 10^{-4} mole/liter Na$^+$), the clay was resuspended in 10 ml of deoxygenated, deionized H$_2$O.

A 2-ml portion of suspension from the reaction tube was transferred to a plexiglas flow cell (Figure 1) under virtually O$_2$-free conditions using an air-tight syringe. The clay was then consolidated in the cell by applying 0.5 bar O$_2$-free N$_2$ gas pressure to the top of the suspension through needle valve A with ball valve B closed (see Figure 1), causing water to be extruded from the clay through a porous, membrane filter (<0.025 μm pore diameter, D) and the clay (C) to be consolidated on the base (E) of the cells. Cells for oxidized and reduced samples were always paired; four or five pairs were used in each experiment.

For the *in situ* reduction experiments, the clay was first treated the same as the oxidized sample in suspension, including consolidation in the conductivity cell. Hydraulic conductivity of the clay sediment was monitored, by the method described below, until it reached a stable value. Then 2 ml of freshly-prepared Na$_2$S$_2$O$_4$ solution (0.115 M Na$^+$) were added to the cell through valve B to reduce the clay sediment *in situ*. For each cell in which *in situ* reduction occurred, a second cell was prepared in which the unaltered (oxidized) clay was treated identically as that in the reduced cell, except Na$_2$SO$_4$ solution was added instead of the reducing agent. This preserved the oxidized state but introduced a comparable effect of ionic strength as that experienced by the sample reduced *in situ*.

Hydraulic conductivity measurements

Valve A in Figure 1 was closed after the consolidation of clay. A hydraulic head of 110 cm was established by carefully filling the cell with degassed, O$_2$-free water through ball valve B. We attached fitting G to a glass stand-pipe (H) in which degassed, O$_2$-free water was raised to the appropriate level. As water moved through the clay, the water level in tube H decreased. The time and change in height was recorded after each 6–10 cm decrement, and the hydraulic head restored to its original value. This process was repeated until the flow rate was stable for 5 days. The flow

Table 1. Clay gel bulk density (ρ_b) and hydraulic conductivity (K) under different hydraulic heads (ΔH). (Number of samples = 3.)

Sample		ΔH = 100–110 cm H$_2$O		ΔH = 30–40 cm H$_2$O	
		ρ_b (g/cm^3)	$K(10^{-7}$ cm/s)	ρ_b (g/cm^3)	$K(10^{-7}$ cm/s)
SWa-1	Oxidized	0.13	0.56	0.08	2.06
	Reduced	0.16	0.48	0.09	1.66
API 25	Oxidized	0.14	0.60	0.10	1.65
	Reduced	0.15	0.33	0.11	1.19

Table 2. Hydraulic conductivity (K) and Fe(II) content of smectites from *in-suspension* experiments under hydraulic head of 100–110 cm. (Number of samples = 5.)

Clay	Treatment	Hydraulic conductivity		Fe(II)/Total Fe	
		Mean (10^{-7} cm/s)	SD	Mean	SD
SWa-1	Reduced	0.33[1]	0.04	0.332	0.065
	Oxidized	0.43[1]	0.02	0.004	0.005
API 25	Reduced	0.66[2]	0.08	0.112	0.001
	Oxidized	0.80[2]	0.04	0.035	0.001

[1] Statistically significant difference at the 99% confidence interval (t-test).
[2] Statistically significant difference at the 95% confidence interval (t-test).

volume was calculated based on the cumulative change in water level and on the tube and cell inside diameters. Effluent water was also collected in flask F (which was covered with pin-hole-vented parafilm to prevent evaporation) and measured gravimetrically to verify water balance with input values. Flow rates were then obtained by dividing the volume by the total time elapsed. The thickness of the clay sediment was also measured. Hydraulic conductivity, K (cm/sec), was calculated by the equation (Klute and Dirksen, 1986):

$$K = \frac{zd^2}{D^2(t - t_0)} \ln\left(\frac{h_0}{h}\right) \qquad (1)$$

where z is the sample thickness; h_0 and h are the initial and ending hydraulic heads at times t_0 and t, respectively; d is the diameter of the stand-pipe tube; and D is the diameter of the flow cell.

Analysis for Fe(II) and total Fe

At the end of the experiment, the flow cell was dismantled and the clay was quickly transferred to a polypropylene tube containing an indicator for Fe(II) (1,10 phenanthroline) and an acid digestion solution (HF-H$_2$SO$_4$). The ratio of Fe(II) to total Fe was determined by the method of Komadel and Stucki (1988).

RESULTS AND DISCUSSION

Effects of cell diameter and hydraulic head

The effect of flow-cell diameter on K was checked by comparing results from both 9- and 21-mm diameter cells, using oxidized clay SWa-1. The original concern was that the higher ratio of wall circumference to filtrate area of the smaller diameter cell would magnify wall effects on the hydraulic conductivity. A diameter of either 9 or 21 mm, however, was determined to have little effect on the hydraulic conductivity (only 3% difference) even though the change of the circumference to area ratio was a factor of 2.3-fold. All subsequent measurements were obtained using 9-mm diameter cells.

Preliminary tests were also made of the effect of lowering the hydraulic head from 110 to 35 cm, using unaltered and reduced samples of clays SWa-1 and API

25 in suspension. Decreasing the head resulted in a lower bulk density in the sediment ranging from 27% to 44%, depending on the smectite and oxidation state (Table 1). The value of K increased by as much as 3.7 fold (Table 1). The hydraulic head was, therefore, maintained between 100 and 110 cm throughout the experiments.

In-suspension experiments

The reduction of structural Fe in suspension decreased the hydraulic conductivity of smectites SWa-1 and API 25 to 77% and 83% of that in their respective oxidized states (Table 2). Thickness measurements of the consolidated gels also revealed that the reduced clays had higher bulk density than the oxidized clay. The average bulk density of reduced SWa-1 was 71% higher than that of the oxidized sample (Figure 2), and in smectite API 25 it was about 79% higher (Figure 3). Iron oxidation state thus effects changes in hydraulic conductivity, apparently by altering the bulk density of the consolidated matrix.

The effect of oxidation state on bulk density is understandable in light of earlier studies which revealed that Fe reduction decreases the water content of the clay at a given applied pressure (Stucki et al., 1984c), decreases the specific surface area (Lear and Stucki, 1989), and increases the particle size (Stucki and Tessier, 1991). The reduction of structural Fe(III) to Fe(II) consolidates smectite particles from an extensive network of small crystals (1–6 layers thick) to distinct particles of limited size in the a–b direction and about 20–40 layers thick (Stucki and Tessier, 1991). The stacking of layers is also more ordered when the clay is reduced. All of these factors would contribute to a more compact gel structure in the reduced state, with smaller and fewer pores. And because structural Fe was reduced in suspension, sufficient time and space existed during sedimentation for particle rearrangement and, therefore, for these factors to manifest themselves strongly in the sediments. The result was higher bulk density and less void space, and thus a lower hydraulic conductivity, in the reduced state.
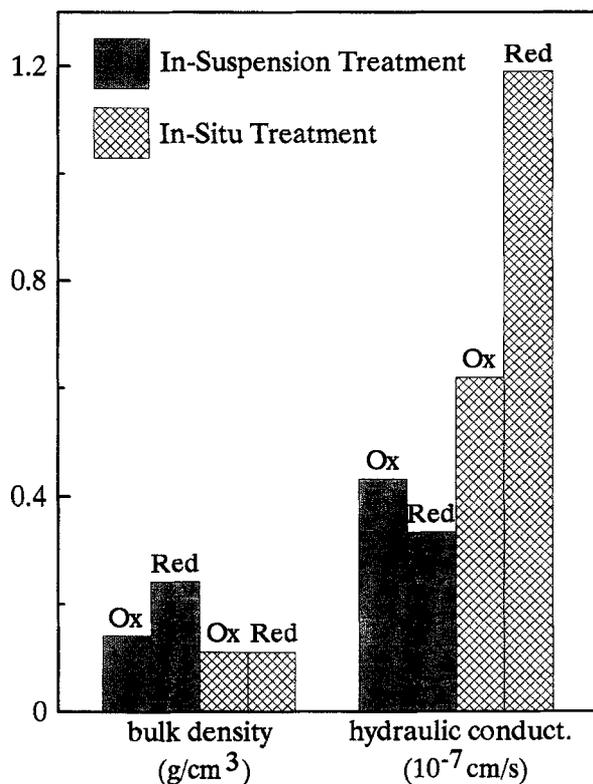
Figure 2. Bulk density and hydraulic conductivity of smectite SWa-1 oxidized (Ox) and reduced (Red), with treatment either *in-suspension* or *in-situ*.
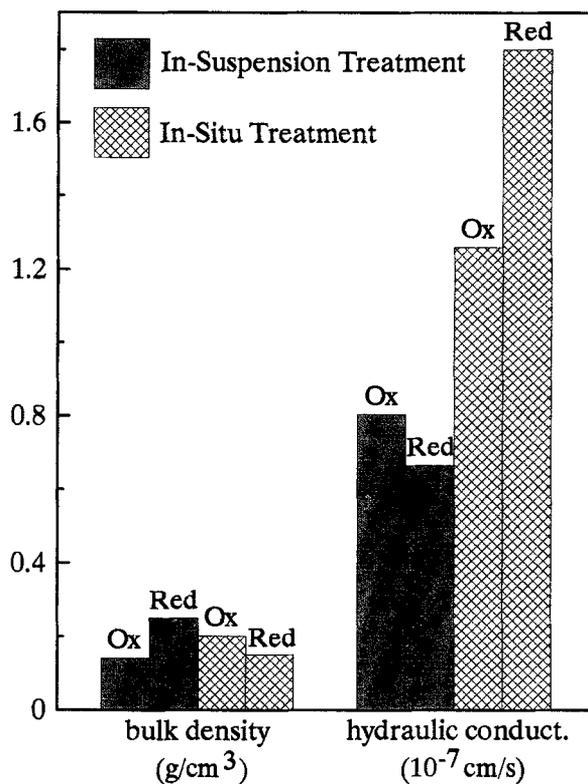

Figure 3. Bulk density and hydraulic conductivity of smectite API 25 oxidized (Ox) and reduced (Red), with treatment either *in-suspension* or *in-situ*.

In situ experiments

When the oxidized, consolidated clay sediments were reduced *in situ,* their hydraulic conductivities increased significantly (Table 3), which is opposite the effect observed in the *in suspension* experiments; but little change was observed in the bulk density (Figures 2 and 3). Notice in Figures 2 and 3 that treatment of the clay gel with a Na electrolyte (Na_2SO_4), without reduction,

Table 3. Hydraulic conductivity (K) and Fe(II) content of smectites from *in situ* experiments under hydraulic head of 110 cm. (Number of samples = 5.)

Clay	Treatment	Hydraulic conductivity		Fe(II)/Total Fe	
		Mean (10^{-7} cm/s)	SD	Mean	SD
SWa-1	Reduced	1.19[1]	0.47	0.507	0.001
	Oxidized	0.62[1]	0.20	0.005	0.004
API 25	Reduced	1.80[2]	0.27	0.413	0.007
	Oxidized	1.26[2]	0.08	0.056	0.016

[1] Statistically significant difference at the 90% confidence interval (t-test).
[2] Statistically significant difference at the 99% confidence interval (t-test).

increased the hydraulic conductivity (compare *in-suspension* and *in-situ* Ox), probably because of the dampening effect of increased solute concentration on clay swelling and clay-water interactions. Compared with the oxidized samples treated with the same amount of Na electrolyte (in the form of Na_2SO_4), the hydraulic conductivity of reduced SWa-1 and API 25 increased by 92% and 43%, respectively. These results indicate that the *in situ* reduction of structural Fe in clay liners may substantially increase their permeability.

Understanding the underlying basis for the effect of *in situ* Fe reduction on K is less straight-forward than for the *in suspension* experiments because the bulk density was largely unchanged *in situ* (Figures 2 and 3). An increase in K without a change in bulk density indicates that the particles in the consolidated matrix must rearrange upon reduction in such a way as to create larger pores while maintaining approximately the same total void space. This could be accomplished if some of the pores were made smaller or eliminated by the collapse of some layers to form micro-aggregates, while simultaneously creating larger pores between the aggregates (see illustration in Figure 4). In effect, the void volume, although approximately constant, would become redistributed among fewer, larger

pores. The larger pores, in turn, would increase the hydraulic conductivity of the system.

This hypothesis is plausible in light of previous studies using clay gels formed under similar conditions. Several studies (Stucki *et al.,* 1984b; Chen *et al.,* 1987; Lear and Stucki, 1989; Khaled and Stucki, 1991; Stucki and Tessier, 1991) revealed that attractive forces between reduced clay layers are greater than between oxidized layers, which creates thicker, more discrete particles. Structural Fe reduction causes parallel layers to collapse (Wu *et al.,* 1989), but it also causes them to rotate in the face-to-face plane until they form a more ordered (non-turbostratic) stacking sequence (Stucki and Tessier, 1991). As Fe reduction introduces these forces into a previously consolidated clay sediment, the movement of parallel layers toward one another decreases the pore space between them but creates larger pores in the space left behind. If the whole clay matrix maintains its volume during this layer rearrangement, the result will be a system with fewer, but larger, pores which are less resistant to water flow. A further pore-size redistribution may occur because of the lower energy of the non-turbostratic structure. As the layers seek the lower energy state upon Fe reduction, the relatively high density of the consolidated clay presents a resistive force which hinders the free rotation of the layers. The net result of these opposing forces could be a distorted arrangement of clay particles. The resulting stresses may enlarge the pores.

Variability

Comparing the mean values reported in Tables 2 and 3, the differences in K between oxidized and reduced samples appears to be much greater in the *in situ* experiments than in the *in suspension* experiments. Because of the much larger variability among replicates in the *in situ* experiments, however, the true magnitude of these differences is uncertain. The greater variability *in situ* may be attributed partially to the greater difficulty of achieving spatial uniformity in the Fe(II) content of the compacted clay because of diffusion and tortuosity barriers. Homogeneous *in situ* reduction of the clay gel is difficult because some clay surfaces may be inaccessible due to the particular flow patterns of the water carrier and the consolidated nature of the system. The variability in hydraulic conductivity may also be due, in part, to an inherently chaotic process of particle rearrangement occurring when the reducing agent (or Na_2SO_4 salt) was added *in situ*.

CONCLUSIONS

The effect of Fe oxidation state on the hydraulic conductivity of consolidated smectite clays depended on the order in which Fe reduction and clay compaction occurred. If the clay was initially reduced in suspension, then compacted, it was less-permeable to water and had a higher bulk density than in the oxidized
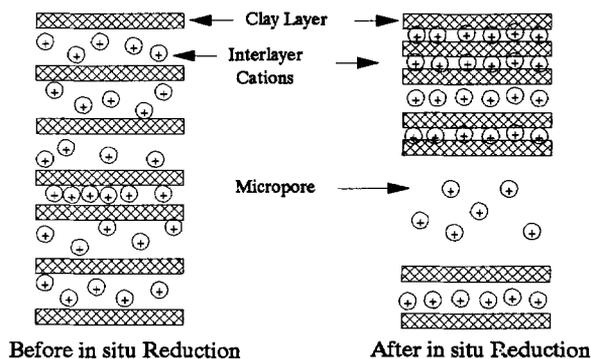

Figure 4.   Diagram of clay layer stacking and micropore formation in oxidized and reduced smectite.

state. Interlayer forces are greater in reduced smectite, resulting in a lower swelling pressure and larger particle size, as compared to the oxidized state. Reduced smectite consolidates from suspension to a higher bulk density with fewer and/or smaller pores, and thus a lower hydraulic conductivity. If the clay was first compacted and then reduced, the hydraulic conductivity increased, probably due to the formation of larger pores as a result of distortions in the gel structure of the sediment produced by the greater interparticle forces. In this case, the oxidation state was the primary factor controlling the hydraulic conductivity.

These results indicate that changes in redox conditions may alter the integrity of clay liners in waste disposal sites and other hydraulic barriers, but the magnitude of the effect may be only secondary to other factors. Ideally, clay barriers should be installed and maintained in the reduced state. Where this is impractical, reduction *in situ* should be avoided.

ACKNOWLEDGMENTS

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