

EFFECT OF Na-HEXAMETAPHOSPHATE ON THE HYDRAULIC CONDUCTIVITY OF KAOLINITE-SAND MIXTURES¹

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Abstract—Mixtures of kaolinite clay and quartz sand were packed in columns and leached with NaCl-CaCl₂ solutions of different concentrations (ranging from 0.5 M to distilled water) having sodium adsorption ratios (SAR) of 5, 10 and 20. Sodium hexametaphosphate (NaHMP) (10 g/m³) was added to each solution. Changes in the hydraulic conductivity (HC) and clay concentration in the effluent were measured, and the dispersion of the clay was evaluated. In the absence of NaHMP, using distilled water instead of 0.01 M solutions caused some reduction in the HC; the reduction became more severe as the SAR increased. At SAR 20 the HC dropped to 73% of that obtained when the 0.5 M salt solution was used. This reduction in HC was related to increases in the pH of the effluent and partial dispersion of the clay. On adding the NaHMP to the leaching solutions, a marked decrease in the HC and severe clay dispersion were observed at all SAR levels, if the kaolinite-sand mixtures were leached with dilute solutions and distilled water. The HC dropped to 40% of that obtained when leaching with 0.5 M salt solution, and dispersed clay in the effluent peaked at about 1% in the SAR 20 treatment following leaching with distilled water. The observed reduction in the HC of the kaolinite-sand mixture when NaHMP was added to the leaching solutions was due to the dispersive effect of NaHMP and sodium on the kaolinite. The polyanion NaHMP reduced the edge-to-face particle interactions, thereby enabling the diffuse double-layer repulsion forces to predominate. Following addition of the polyphosphate, the response of kaolinite to sodium and electrolyte concentration was similar to that reported in the literature for smectite.

Key Words—Dispersion, Hexametaphosphate, Hydraulic conductivity, Kaolinite, Sand, Sodium adsorption ratio.

INTRODUCTION

The saturated hydraulic conductivity (HC) of a soil is determined mainly by the microstructure of the soil matrix, which in turn depends, partly, on the type of the clay mineral present in the soil, the composition of the exchangeable cations, and the electrolyte concentration in the soil solution. The ease with which flocculation or deflocculation and swelling of a clay mineral takes place affects the structure of the pores and, hence, the HC during water flow through the soil profile (Quirk and Schofield, 1955).

A study of the behavior of kaolinite in suspension has shown that pure Na-kaolinite flocculated at pH < 7 under conditions that dispersed illite and montmorillonite (Schofield and Samson, 1954). The acidified kaolinite retained exchangeable Na, indicating that the clay crystals were negatively charged. In the presence of dilute NaCl solution, Cl⁻ was adsorbed, indicating that the edges were positively charged. The attraction of the positively charged sites on the edges to the neg-

atively charged sites on the planar surfaces, the “edge-to-face” (EF) model, was considered as the cause of the flocculation of kaolinite (Schofield and Samson, 1954). On addition of NaOH to the salt free suspension, however, the kaolinite dispersed. At pH 8, Cl⁻ was desorbed from the crystals indicating that the edges were no longer positively charged. Hence, eliminating the positive charges at the edges of the kaolinitic clay plates, dispersed the clay (Schofield and Samson, 1954).

van Olphen (1977) suggested the following particle-particle interactions in kaolinite: (1) At pHs less than the isoelectrical point of the edge surface of the crystals, the edges are positively charged, and an electrostatic attraction is promoted between the edges and the negatively charged faces, leading to an EF structure; (2) at high ionic strength the electrical double layers are compressed and face-to-face (FF) flocculation is promoted. A third type of interaction, the edge-to-edge (EE) mode was introduced by Flegmann *et al.* (1969), who postulated that conditions of low ionic strength and pHs near the isoelectric point of the edges favor such interaction.

Deflocculation of kaolinite can also be brought about by adding small amounts of polyanions, such as so-

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dium oxalate, sodium pyrophosphate, and polymetaphosphate (Schofield and Samson, 1954; Durgin and Chaney, 1984). A polyvalent anion not only satisfies any positive charge on the kaolinite edge, but also provides an excess of negative charge, thus preventing edge-to-face (EF) flocculation. If EF interaction is prevented, diffuse double layer forces between planar surfaces probably predominate, and kaolinite dispersion will depend on the electrolyte concentration and composition of the clay suspension (Oster *et al.*, 1980).

From these studies the addition of a polyanion to kaolinite apparently causes kaolinite dispersion to be similar to that of smectite. The objective of the present study was to investigate the effect of sodium and electrolyte concentration on the deflocculation and HC of kaolinite-sand mixtures in the presence and absence of sodium hexametaphosphate. The dispersion of, and HC changes in kaolinite-sand mixtures were also examined and compared with the behavior of smectite-sand mixtures (Shainberg *et al.*, 1987, 1988).

MATERIALS AND METHODS

A kaolinitic clay, Peerless no. 2 (Ward's Natural Science Establishment, Rochester, New York), was used in this study. The cation-exchange capacity (CEC) of the clay at pH 7 was 4.0 meq/100 g. Total chemical analysis of the clay was obtained using the method developed by Norrish and Hutton (1969). The percentage of K_2O was used to calculate the mica content in the clay, assuming 10% K_2O to be equal to 100% mica. The percentage of mica impurities was found to be 5% of the clay.

Clay-sand mixtures were prepared by mixing 5 g of dry, powdered clay (no pretreatment) with 95 g of acid-washed quartz sand. Two size fractions of sand were used, 0.075–0.3 mm and 0.075–0.42 mm. The clay sand mixtures were thoroughly mixed and wetted with 10 ml of distilled water. Following 3 hr of equilibration at room temperature, the wetted mixtures were dried at 40°C and then cooled in a desiccator at room temperature. Wetting of the clay-sand mixtures bonded the clay platelets to the sand grains and prevented clay and sand segregation when the columns were packed.

Columns of the clay-sand mixtures were prepared by packing 100 g of the mixture into 50-mm diameter plastic cylinders to a bulk density of 1.35 g/cm³. Assuming particle density of 2.65 g/cm³, the pore volume of the columns was 36.3×10^3 mm³. Bottom support for the clay-sand mixtures consisted of a rubber stopper with a hole to accommodate an outflow tube. A circle of 20-mesh bronze screen cut to fit the inside of the cylinder and covered with a 10-mm layer of sand served as a filter. Dispersed clay particles could, therefore, be washed freely out of the columns.

The columns were initially wetted from the bottom with a 0.5 M Cl^- solution having the desired sodium

adsorption ratio (SAR) of 5, 10, or 20, and kept saturated. The saturated hydraulic conductivity (HC) was determined by leaching the column with the solutions using a constant head device (height = 5 cm) and an hydraulic gradient of 1.32. The effluent was collected incrementally using a fraction collector, and the drainage rate was calculated. The HCs of the columns obtained using 0.5 M solutions were taken as the "base" HC. The columns were then leached with solutions of the same SAR but of successively decreasing salt concentration (0.05 M and 0.01 M) to which sodium hexametaphosphate (NaHMP) was added in the amount of 10 mg/liter (i.e., 10 ppm). Leaching lasted until steady state flow and effluent composition were achieved. The columns were then differentially leached with solutions of the same SAR and containing 10 mg/liter NaHMP, but with salt concentrations of 3.0, 2.0, 1.0, or 0 mM Cl^- . The 3.0, 2.0, and 1.0 mM Cl^- treatments were followed by more leaching with distilled water to which NaHMP had been added. The control treatments included leaching the columns with solutions having the same SARs and salt concentration of 0.5, 0.05, 0.01, and 0.0 M, but without the addition of NaHMP. The leaching solutions were not pretreated to remove atmospheric CO_2 , and their pH was in the range 6.15–6.30. The volume of leachate at a given time interval, pH, electrical conductivity (EC), and weight of dispersed clay were recorded. Each treatment was repeated twice, and the agreement between replicates was good (coefficient of variance <10%).

RESULTS AND DISCUSSION

Hydraulic conductivity

The experimental results are shown as curves of relative HC vs. the effluent volume. The relative HC is the ratio between treatment HC and the HC obtained for leaching with the 0.5 M salt solution. The HC values obtained when leaching with the 0.5 M salt solution were 9.3 and 14.9 cm/hr for sand size fractions of 0.075–0.3 and 0.075–0.42 mm, respectively. The effects of replacing the 0.01 M solutions (with and without addition of 10 ppm NaHMP) with distilled water, at different sand sizes, is shown in Figure 1.

Leaching the Peerless clay-sand (0.075–0.3-mm size fraction) mixtures with distilled water resulted in no decrease in HC for the SAR 5 treatment, whereas a drop of 5% in the HC was observed in the SAR 10 treatment. Increasing the SAR to 20 caused a moderate decrease in the relative HC to 73% (Figure 1). The pHs of the effluent solutions were 6.9, 7.1, and 7.6 for the SAR 5, 10, and 20, respectively. Bar-On and Shainberg (1970), who also observed increases in pH with the increases in exchangeable sodium, associated this phenomenon with the hydrolysis of adsorbed sodium when clay was leached with distilled water. The reduction in the HC in the SAR 10 and 20 treatments probably was

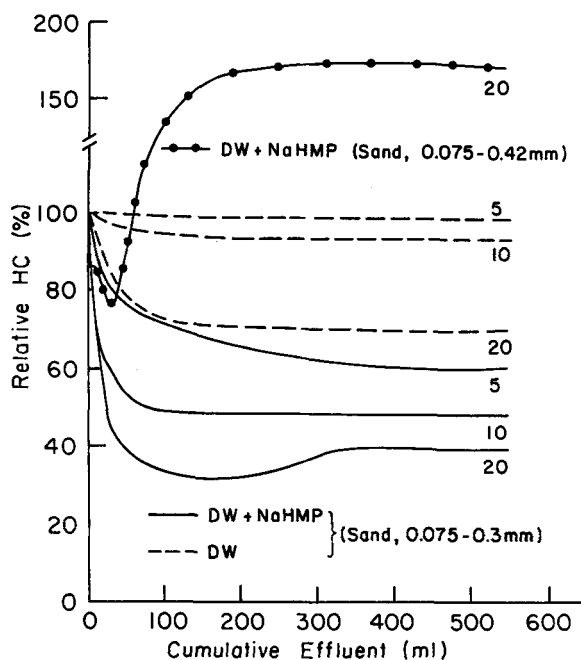


Figure 1. Relative hydraulic conductivity of clay-sand mixtures leached with distilled water (DW) as affected by the sodium adsorption ratio (SAR) (indicated by the numbers next to the curves), the presence of sodium hexametaphosphate (NaHMP), and sand size (0.075–0.3 mm and 0.075–0.42 mm).

due to the high pHs of the solutions. The pHs were close to and even exceeded the pH of the isoelectric point of the edge surfaces of kaolinite (pH 7.3, according to Rand and Melton, 1977). At pHs less than the isoelectric point, the edges were positively charged and an EF particle interaction mode prevented the dispersion of the kaolinite. Thus, the HC did not decrease on leaching with distilled water, as was noted in the SAR 5 treatment (Figure 1). If the pH exceeded the isoelectric point, the charge on the edges became increasingly more negative, the EF particle interaction was eliminated, and the diffuse double layer repulsion forces predominated. According to Shainberg *et al.* (1971) these planar repulsion forces increase with an increase in sodium in the exchangeable complex, thus, leading to some clay deflocculation and a reduction in the HC.

Another possible explanation for the reduction in the HC upon increasing the SAR to 10 and 20 could be the presence of 2:1 clay impurities. Schofield and Samson (1954) recognized that only a pure kaolinite would remain flocculated if it were saturated with Na. They suggested that the presence of some micaceous and smectitic impurities in a kaolinitic clay caused the attraction of the negatively charged platelets of these two clay minerals to the positive charges on the edges of the kaolinite, thereby neutralizing these positive

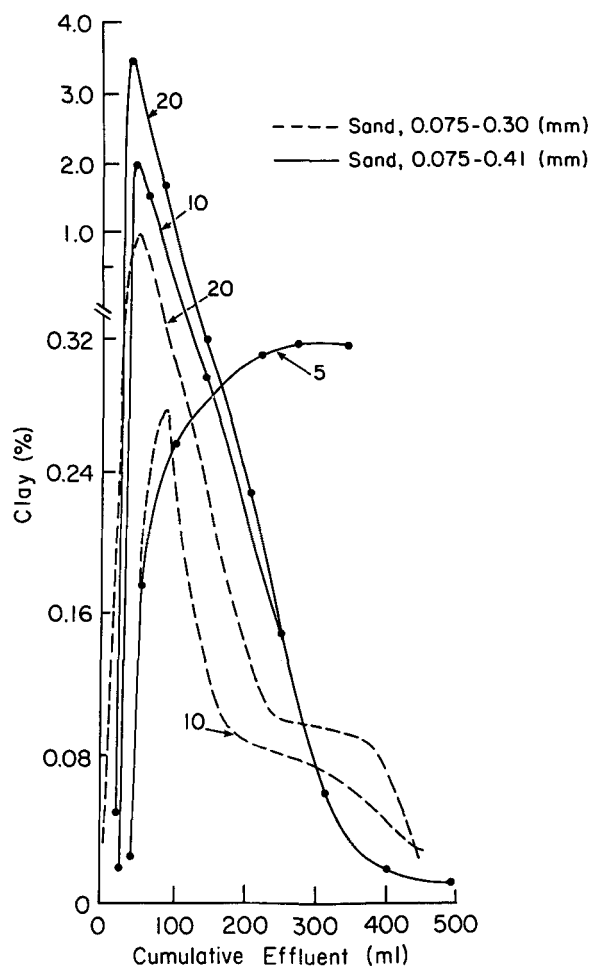


Figure 2. Concentration of clay in effluent during leaching with distilled water following leaching with 0.01 M solution of various sodium adsorption ratios (SAR) and as affected by sand size. Numbers next to curves indicate SAR.

charges and diminishing EF flocculation. The chemical analysis of the Peerless clay suggested the presence of about 5% mica, which could have caused the kaolinite to disperse under the prevailing sodic conditions (i.e., SAR 10 and 20) and distilled water.

No clay particles were detected in the effluent in any of the SAR treatments. Possibly, the short distance migration of dispersed clay particles that only partly clogged some of the conducting pores of the clay-sand mixture took place; hence, only a limited reduction in the HC was noted.

The addition of NaHMP to the various leaching solutions (0.05 M, 0.01 M, and distilled water) decreased the HC slightly if the 0.05 M solution was replaced by the 0.01 M solution (relative HC of 95% and 90% for the SAR 10 and 20 treatments, respectively). Replacing the 0.01 M solution with distilled water reduced the HC of the clay-sand mixtures (Figure 1). The effect of

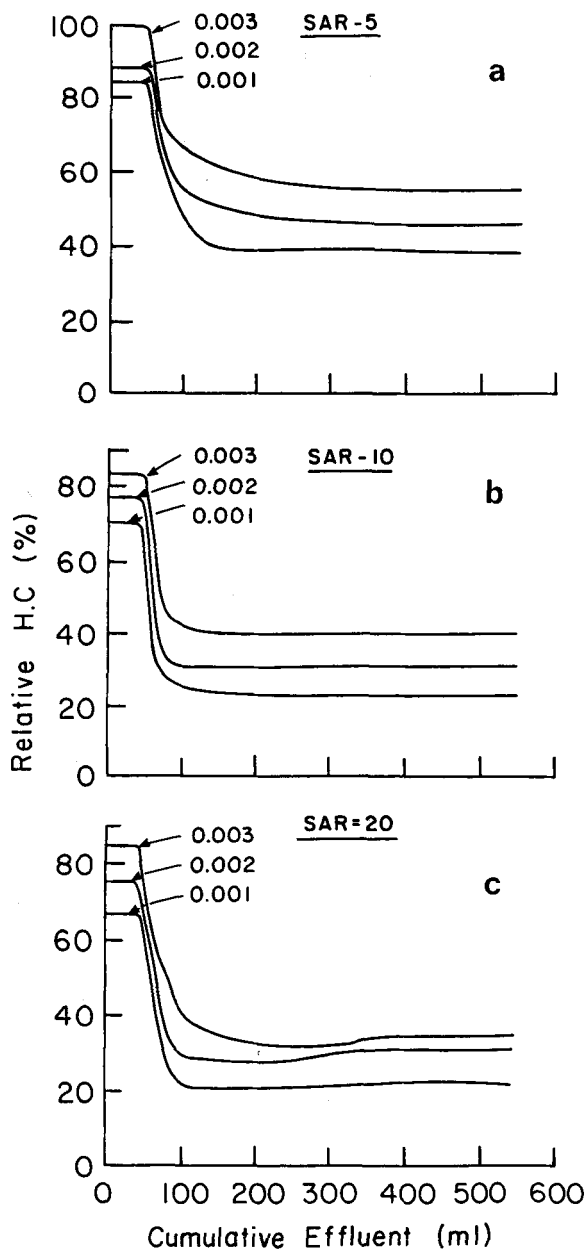


Figure 3. Relative hydraulic conductivity of clay-sand mixtures leached with dilute salt solutions (numbers next to curves indicate concentration of dilute solutions), which after two pore volumes were replaced with distilled water. All solutions concerned contain sodium hexametaphosphate. Sand size fraction = 0.075–0.3 mm.

sodium was pronounced on not only the final relative HC but the rate at which the relative HC decreased. In the SAR 5 treatment, the decrease in HC was gradual and reached its final value after 11 pore volumes. In the other two SAR treatments (SAR 10 and 20), the HC dropped sharply, and a relative HC of 50% was obtained after 2 and 1 pore volumes for the SAR 10

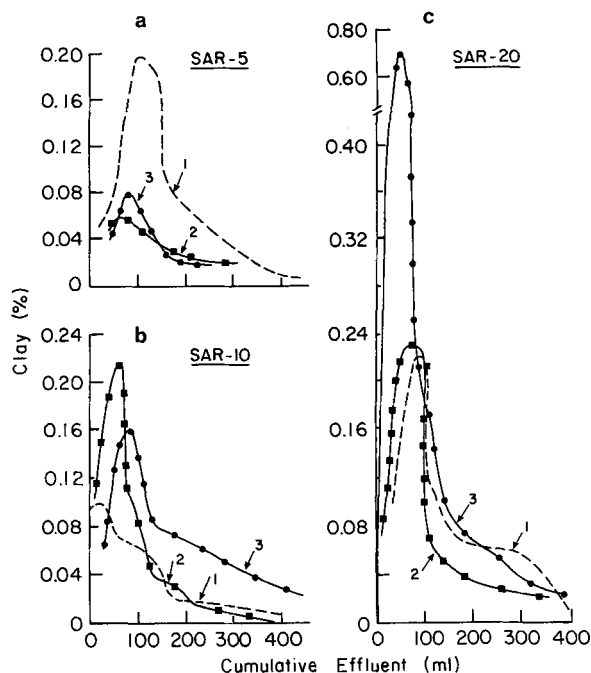


Figure 4. Concentration of clay in effluent during leaching with distilled water following leaching with dilute salt solutions (numbers next to curves indicate concentration of dilute solution) being replaced by distilled water. Sand size fraction = 0.075–0.3 mm.

and SAR 20 treatments, respectively (Figure 1). Furthermore, dispersed clay was observed in the effluent if leaching was with distilled water, peaking at nearly 1% in the SAR 20 treatment (Figure 2).

These adverse effects of NaHMP on the HC and clay dispersion were even more pronounced if coarser sand grains (0.075–0.42 mm) were used to prepare the clay-sand mixtures (Figures 1 and 2). In the SAR 20 treatment, equilibrating the clay-sand mixture with 0.01 M solution, the relative HC of the mixture was maintained at 90%. Leaching with distilled water produced a sharp decrease in the relative HC to a minimum of 78% at an effluent volume of 30 ml which is less than one pore volume. With further leaching of about 6.5 pore volumes, the relative HC increased markedly to 180% (Figure 1). This sharp increase in the relative HC was associated with extensive clay dispersion (Figure 2). Similar phenomena, although less pronounced, were found for the SAR 10 solutions. Alperovitch *et al.* (1985) also noted the effect of coarse sand and the sudden sharp increase in relative HC for smectite-sand mixtures. The presence of clay in the effluent of our clay-sand mixtures indicated severe dispersion and long-distance movement of clay particles. Using the coarser sand resulted in larger pores in which the dispersed clay particles could move more freely. Thus, the concentration of clay in the effluent increased (Fig-

Table 1. Properties of solutions obtained by leaching kaolinite-sand mixtures with dilute NaCl solutions.¹

Sodium adsorption ratio	Solution concentration (mM)											
	10			3			2			1		
	RHC (%)	pH	Clay (%)	RHC (%)	pH	Clay (%)	RHC (%)	pH	Clay (%)	RHC (%)	pH	Clay (%)
5	100	6.9	—	100	6.9	—	88	7.0	—	85	7.0	tr ²
10	95	6.9	—	84	7.0	—	77	7.0	tr	70	7.1	0.02
20	90	7.0	—	82	7.2	tr	75	7.3	0.04	66	7.3	0.05

¹ pH = pH at end of leaching; RHC = relative hydraulic conductivity; clay = concentration of clay in leachate solution.

² tr = traces.

ure 2). The abrupt increase in the HC in the smectitic clay-sand mixtures was explained by Alperovitch *et al.* (1985) as due to a change in the pattern of flow. As the clay dispersed in the distilled water, the flow changed from flow of a solution in a sandy clay matrix, in which the sand particles were coated with a skin of clay, to a flow of a suspension in a sand matrix. Removing the clay from the sand particles increased both the pore radii and the HC (Figure 1).

The deflocculation of, and HC changes in the kaolinite-sand mixtures of the present investigation after NaHMP was added were compared with those of smectite-sand mixtures (Alperovitch *et al.*, 1985; Shainberg *et al.*, 1987, 1988). The comparison reveals that both the kaolinite, to which NaHMP had been added, and the smectite were very sensitive to the electrolyte concentration and SAR of the percolating solution. Severe clay dispersion followed by a reduction in the relative HC on decreasing the electrolyte concentration and increasing SAR were observed in both the kaolinitic and smectitic-sand mixtures. Moreover, once the clay became highly dispersive, detachment of the clay skin from the sand particles in the clay-sand mixtures occurred, leading to an increase in pore radii that enabled an increase in the relative HC to 180% in the kaolinite-sand mixture and to 125% in the smectite-sand mixture (Shainberg *et al.*, 1987).

NaHMP being a polyanion satisfies positive charges on the edges of kaolinite crystals and provides them with excess negative charge (van Olphen, 1977). Consequently, the EF mode of attraction and flocculation is eliminated, and the interaction between the edges and planar surfaces of the kaolinite particles is controlled by the diffuse double layer forces. Hence, under conditions defined as favorable for deflocculation (i.e., high levels of sodium and low electrolyte concentration) in 2:1 clay minerals, in particular for smectite, the presence of NaHMP causes kaolinite to behave similarly to smectite. This conclusion is supported by the results of the present study with dilute solutions (*vide infra*).

Effect of dilute solutions on hydraulic conductivity

The relative HC values obtained for 0.01 M solutions replaced with the different dilute solutions (in which all solutions concerned contained NaHMP) are

presented in Table 1. Similar to the results obtained from the experiments in which the 0.01 M solutions were replaced by distilled water, the HC was directly related to the concentration of the solution and inversely related to the SAR. Furthermore, the present results are comparable with those of Shainberg *et al.* (1987, 1988), who described the effects of dilute solutions on the HC of smectite-sand mixtures. The similar sensitivity of the two types of clays with respect to HC and clay dispersion to low levels of electrolytes and to sodium suggest that the clay deflocculation mechanism and, hence, particle interaction was similar for kaolinite and montmorillonite after small amounts of NaHMP had been added to the former.

Leaching with distilled water after leaching with the dilute solutions provided a further decrease in the relative HC (Figures 3a–3c). The data indicate that in all of the SAR treatments, the concentration of the dilute solutions used prior to the leaching with distilled water determined the relative HC during the actual leaching with distilled water. Leaching with dilute solutions prior to leaching with distilled water also had a significant effect on the amount of dispersed clay found in the effluent during leaching with the dilute solutions, as well as on the amount of dispersed clay in the effluent during the subsequent leaching with distilled water (Table 1 and Figures 4a–4c). The graphs show: (1) An increase in dispersed clay in the effluent as the SAR increased, and (2) for each SAR treatment, the most extreme clay dispersion was produced after preleaching with a different dilute solution, namely 1, 2, and 3 mM for the SAR 5, 10, and 20 treatments, respectively. The results suggest an interaction between the electrolyte concentration and level of sodium with regard to their effect on clay dispersion and consequently on the HC of the clay.

In the SAR 5 treatment, diluting the 1 mM interclay solution during leaching with distilled water resulted in an electrolyte concentration in the interclay solution that was low enough to support severe clay dispersion (Figure 4a), thereby leading to a low relative HC. Conversely, leaching with the 3 and 2 mM solutions, prior to leaching with distilled water, resulted in concentrations of the interclay solution sufficiently high to produce only limited clay dispersion and, hence, to maintain relatively high relative HC (Figures 3a and 4a). In

the SAR 20 treatment, leaching with the more dilute solutions (i.e., 2 and 1 mM) produced some leaching of dispersed clay particles (Table 1), as well as some blocking of pores, mainly the smaller pores. Subsequent leaching with distilled water decreased the HC further but did not appear to wash out large amounts of clay. The absence of dispersed clay in the effluent probably resulted from the fact that the dispersed clay particles were prohibited from moving in the pores of the clay-sand mixture because of the partial blocking and narrowing of the pores, which took place in the preceding leaching by the diluted solutions. On the other hand, because only traces of clay were found in the leachate, a concentration of 3 mM was apparently high enough to produce only limited dispersion of the clay. Thus, almost no reduction in pore size occurred during the leaching with the 3 mM solution. During subsequent leaching with distilled water, which diluted the interclay solution and enhanced clay dispersion, the dispersed clay moved freely in the pores and was leached from the column. Consequently, a large amount of dispersed clay particles, which peaked at 0.69% of the leachate, was produced (Figure 4c). In the moderate SAR treatment (SAR 10), the most dispersed clay in the leachate was observed during leaching with distilled water after leaching with the 2 mM solution (Figure 3b). Diluting a 3 mM interclay solution with distilled water caused only limited dispersion of the clay in this SAR treatment. Leaching with the 1 mM solution, however, resulted in a measurable clay content in the leachate (0.02%) and blocking of the pores. Thus, in the subsequent leaching with distilled water further dispersed clay was prevented from moving in the reduced-size pores of the clay-sand mixture and, hence, low relative HC coupled with little dispersed clay were observed in the leachate (Figures 3b and 4b).

Considering these results, the dispersivity of the Peerless kaolinite, similar to smectite, is very susceptible to low levels of electrolytes and sodium in the interclay solution, if NaHMP is added to the solution. Conversely, in the absence of NaHMP, the Peerless

kaolinite is relatively stable under extreme conditions of low salinity and high sodium.

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