

## EFFECT OF EXCHANGEABLE POTASSIUM ON THE HYDRAULIC CONDUCTIVITY OF SMECTITE-SAND MIXTURES<sup>1</sup>

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**Abstract**—Changes in hydraulic conductivity of smectite-sand mixtures (using four reference smectites) as a function of the concentration (0.01, 0.003, 0.002, 0.001 M Cl<sup>-</sup> and distilled water) and potassium adsorption ratio (of 2, 4, and 6) of the percolating solution were measured. Swelling and dispersion of the clays were evaluated from the changes in hydraulic conductivity of the mixture and from the clay concentration in the effluent.

The effect of exchangeable potassium percentage (EPP) on the hydraulic conductivity of the smectites depended on the charge density of the clays. The effect of potassium at EPPs <20 on the hydraulic conductivity of smectites having high charge density was negligible. Conversely, the hydraulic conductivity of smectites having low charge density (smectites from Wyoming and Belle Fourche, South Dakota), changed markedly when leached with dilute solutions as the EPP of the clay increased. The dispersive effect of exchangeable potassium on low-charge smectites was similar to that of exchangeable sodium. The low hydration energy of the K<sup>+</sup> cations, coupled with the strong electrostatic attraction forces between platelets of smectites with high charge density account for the “inefficiency” of K<sup>+</sup> in dispersing these smectites.

**Key Words**—Hydraulic conductivity, Potassium, Salinity, Sand, Smectite, Swelling.

### INTRODUCTION

The permeability of montmorillonitic soils is strongly dependent on the type of exchangeable cation and the salt concentration of the percolating solution; the permeability tends to decrease with increasing exchangeable sodium percentage (ESP) and decreasing salt concentration (Quirk and Schofield, 1955). Few reports on the effects of K<sup>+</sup> on soil permeability have been published, and the results seem to vary or conflict, possibly due to differences in soil mineralogy and sample preparation procedures. Generally, soil permeability relates to exchangeable cations in the following order: Ca = Mg > K > Na (Ahmed *et al.*, 1969; Quirk and Schofield, 1955). Some researchers, however, report larger aggregates of greater stability in K<sup>+</sup>-saturated soils than in those saturated with divalent cations (Ceccconi *et al.*, 1963; Ravina, 1973), suggesting that K<sup>+</sup> in the exchange sites increases soil permeability.

Swelling and dispersion of clay have been proposed to explain the decrease in soil permeability due to monovalent exchangeable cations. Quirk and Schofield (1955), for example, suggested that the swelling of clay particles, which increases with a rise in the percentage of monovalent exchangeable cations, could result in

total or partial blockage of the conducting pores. McNeal *et al.* (1968) found a linear relationship between the reduction of hydraulic conductivity (HC) and macroscopic swelling of extracted soil clays, with a correlation coefficient ranging from .94 to .97.

Deflocculation, dispersions, and clay movement into the conducting pores were proposed as second mechanisms for the plugging of the soil pores (Quirk and Schofield, 1955). The importance of dispersion in soil permeability was recognized by Frenkel *et al.* (1978), Pupisky and Shainberg (1979), and Shainberg *et al.* (1981).

The differences between swelling and dispersion are important. Whereas a change in soil permeability due to swelling is essentially a reversible process, changes due to dispersion and particle movement are essentially irreversible and may produce an impermeable clay layer in the soil profile. Clay swelling is not greatly affected by low ESP values (i.e., <10–15) and increases markedly as ESP increases >15 (McNeal *et al.*, 1968; Oster *et al.*, 1980). Conversely, clay dispersion is highly sensitive to low levels of sodicity and increases markedly at low ESP (Oster *et al.*, 1980). Finally, whereas dispersion of clay is prevented by dilute solutions whose concentrations exceed the flocculation value, swelling decreases continuously and gradually with an increase in solution concentration.

The effect of clay mineralogy on the response of

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Table 1. Sources and properties of the clays used in the study.<sup>1</sup>

Mineral <sup>2</sup>	CEC <sup>3</sup> (meq/100 g)		S <sup>3</sup> (m <sup>2</sup> /g)	Octahedral substitution (atoms/unit cell)		Tetrahedral substitution (atoms/unit cell)	Charge density (meq/cm <sup>2</sup> × 10 <sup>7</sup> )
	Low (1980)	This study		Mg	Fe		
Smectite, Upton, Wyoming (API 25)	85	90.7	800	0.65	0.32	0.18	1.13
Smectite, Belle Fourche, South Dakota (API 27)	85	92.4	776	0.57	0.36	0.20	1.19
Smectite, Polkville, Mississippi (API 21)	105	103.4	760	0.90	0.29	—	1.36
Smectite, Otay, California	120	122.2	552	1.20	0.11	0.05	2.21

<sup>1</sup> Based on Low (1980).

<sup>2</sup> Obtained from Ward's Natural Science Establishment, Rochester, New York; numbers are American Petroleum Institute reference clay numbers.

<sup>3</sup> CEC = cation-exchange capacity; S = specific surface area.

smectite-sand mixtures to sodic and saline conditions was studied by Alperovitch *et al.* (1985). They found that the HC and dispersion of smectites with low charge density (Wyoming montmorillonite) were more susceptible to exchangeable sodium than smectites with high charge density (Polkville and Otay smectites). The purpose of the present study was to investigate the effect of exchangeable K<sup>+</sup> on the HC of smectite-sand mixtures. Smectites of various charge densities were studied, and the hypothesis that the charge density on the smectites determined the HC response of the clay to exchangeable K<sup>+</sup> was tested.

## MATERIALS AND METHODS

### Materials

Four smectites from Ward's Natural Science Establishment, Rochester, New York, were selected for this study. Their source, identifying API numbers, amount of octahedral and tetrahedral substitution, cation-exchange capacity (CEC), and specific surface area (S) as reported by Low (1980) are presented in Table 1. The charge on the four clays is due mainly to ionic substitution in the octahedral layer.

Clay-sand mixtures were prepared by mixing 5 g of dry, powdered raw (no pretreatment) clay with 95 g of acid-washed quartz sand (0.1–0.6 mm diameter). 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 60°C and then cooled in a desiccator to room temperature. Wetting of the clay-sand mixtures bound the clay platelets to the sand grains and prevented clay and sand segregation upon packing of the columns. Columns of the clay-sand mixtures were prepared by packing 100 g of the mixture into 5-cm diameter plastic cylinders to a bulk density of 1.35 g/cm<sup>3</sup>. Based on a particle density of 2.65 g/cm<sup>3</sup>, the pore volume of the columns was 36.3 cm<sup>3</sup> and the length of the mixture column was 3.8 cm. Bottom support for the clay-sand mixtures consists of a rubber stopper with a hole to accommodate an outflow tube. A circle of 20-mesh bronze screen cut so as to fit on the inside of the cylinder and covered with 1.0-cm layer of sand served as a filter.

Dispersed clay particles could be leached freely out of the columns.

### Methods

The saturated hydraulic conductivity of the columns was used to measure the effect of the treatment. Each column was initially wetted from the bottom with 0.5 M Cl<sup>-</sup> solution having an appropriate potassium adsorption ratio (PAR = (K)/(Ca)<sup>1/2</sup>, where ionic concentrations are in mmole/liter) or sodium adsorption ratio (SAR = (Na)/(Ca)<sup>1/2</sup>), and kept saturated. Saturated HC was determined by leaching the column with the solutions, by means of a constant head device and measuring the drainage rate. Effluent was collected incrementally using a fraction collector. The HCs of the clay-sand mixture obtained using 0.5 M solutions were taken as the "base" HC. Columns were then consecutively leached with 0.05 and 0.01 M Cl<sup>-</sup> solutions of the treatment PAR and SAR until steady state flows and effluent compositions were achieved. The columns were then differentially leached with solutions of the same PAR or SAR but with salt concentration of 0, 1.0, 2.0 or 3.0 mmole Cl<sup>-</sup>/liter. Each treatment was replicated two or three times; the agreement between replicates was satisfactory.

### Ion-exchange equilibria

PAR solutions of 0, 2, 4, and 6 and SAR solutions of 10 and 20 were applied in the column experiment. The exchangeable K and Na on the clay in equilibrium with the ionic composition in solution was determined by equilibrating 0.5 g of the clay with 0.5 M solutions of the treatment PAR or SAR solution in batch experiments. The suspension was centrifuged, the supernatant was decanted, and another solution of the same PAR (or SAR) and same concentration was added. Following three washings with 0.5 M solutions, the clay was washed three times with 0.01 M Cl<sup>-</sup> solutions of the same PAR (or SAR). Finally, the suspension was centrifuged, the supernatant was analyzed for Ca and K or Na, and the clay was washed with 60% ethanol-water solutions until free of electrolytes. Exchangeable

Table 2. Exchangeable potassium percentage (EPP), exchangeable sodium percentage (ESP), and Gapon's constants ( $K_G$ ) for the four smectites in equilibrium with the treatment solutions.

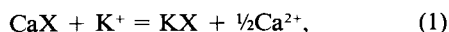
Cation composition	PAR (or SAR)	Wyoming		Belle Fourche		Polkville		Otay	
		EPP (or ESP)	$K_G$	EPP (or ESP)	$K_G$	EPP (or ESP)	$K_G$	EPP (or ESP)	$K_G$
K-Ca	2	6.6	0.036	7.3	0.038	9.5	0.054	14.6	0.090
	4	11.1	0.031	11.8	0.032	15.9	0.047	23.2	0.076
	6	16.2	0.032	16.9	0.033	22.3	0.048	34.0	0.082
Na-Ca	10	10.5	0.0115	9.7	0.0105	12.0	0.0135	10.3	0.0113
	20	21.6	0.0139	19.7	0.0124	22.0	0.0142	21.2	0.0136

cations were extracted from the clay with 1.0 M  $\text{NH}_4\text{OAc}$  solution and determined spectroscopically.

## RESULTS AND DISCUSSION

### Exchange characteristics

The EPP-PAR and ESP-SAR relationships for the four clays are given in Table 2. Whereas the affinity of the clay for sodium ions is independent of its source, the affinity for potassium ions depends on the charge density on the smectite. With an increase in charge density of the smectite, the affinity of the clay for  $\text{K}^+$  increases. This phenomenon was discussed by Shainberg *et al.* (1987) and is demonstrated here through the effect of charge density on Gapon's selectivity coefficients ( $K_G$ ). For the exchange reaction



$$K_G = \frac{\text{KX}}{\text{CaX}} \cdot \frac{(\text{Ca})^{1/2}}{(\text{K})} = \frac{\text{EPP}}{(100 - \text{EPP})} \cdot \frac{1}{(\text{PAR})}, \quad (2)$$

where CaX and KX are the exchangeable cations (meq/100 g) and ( ) is the concentration of the cation in the equilibrium solution (mmole/liter). Whereas the Gapon's constants for Na-Ca exchange were similar for the four smectites, these selectivity coefficients for K-Ca exchange increased with a rise in the charge density on the clay. The composition of the exchangeable ions in equilibrium with a given solution was considered in comparing the effect of the monovalent cations on the swelling, dispersion, and HC of the various clay-sand mixtures.

### Hydraulic conductivity

The experimental results are shown as curves of relative HC, as a function of the mixture EPP or ESP and effluent volume. The relative HC is the ratio between treatment HC and the HC of a 0.5 M salt solution. In Figures 1 and 2 relative HC is presented as a function of the effluent volume for the treatment where distilled water displaced 0.01 M solution. In Figures 3 and 4 the 0.01 M solution was displaced by the more dilute

solutions. The intercept of each curve is the relative HC for 0.01 M solutions of the various treatments.

Leaching the smectite-sand mixtures with distilled water showed the effect of PAR (and EPP) and charge density on the relative HC (Figure 1). The numbers in brackets next to the smectite's name give the EPP on the clay in equilibrium with the given PAR solution. When distilled water displaced 0.01 M of  $\text{CaCl}_2$  solution (EPP = 0), no change in the HC of the mixtures, even for the Wyoming and Belle-Fourche smectites, was noted (data not presented). As the EPP of the clay increased, the relative HC of the clay-sand mixtures decreased.

The effect of clay swelling on the relative HC of the clay-sand mixtures leached with 0.01 M  $\text{Cl}^-$  solutions was evaluated from the y-axis intercepts (Figure 1). The decrease in HC in 0.01 M  $\text{Cl}^-$  solutions was due

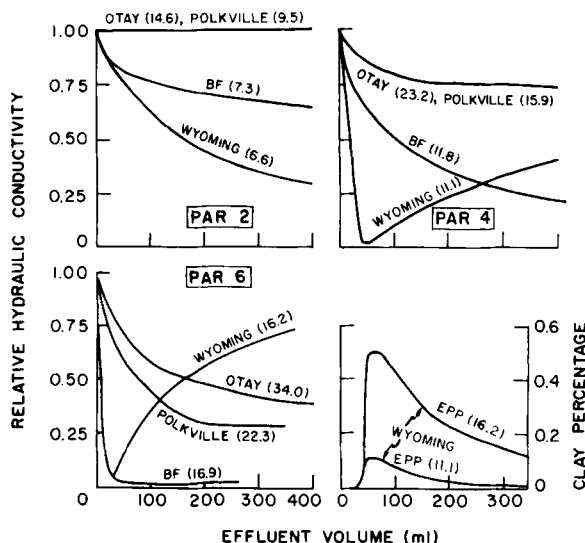


Figure 1. Relative hydraulic conductivity of smectite-sand mixtures as a function of the effluent volume. 0.01 M  $\text{Cl}^-$  solutions of potassium adsorption ratio (PAR) of 2.0, 4.0, and 6.0 are displaced with distilled water. Exchangeable potassium percentage (EPP) is given in parenthesis next to the smectite name. Clay concentration in the effluent of the Wyoming-sand mixtures is given in the bottom-right graph. BF = smectite from Belle Fourche, South Dakota.

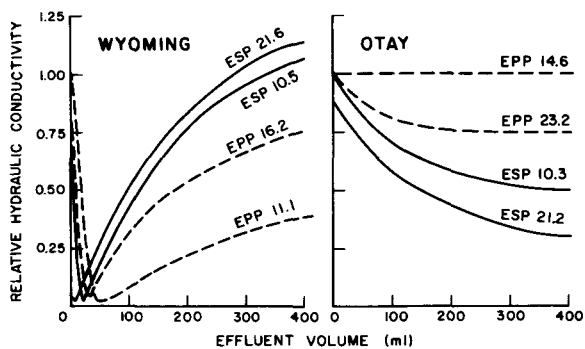


Figure 2. Effect of exchangeable sodium percentage (ESP) and exchangeable potassium percentage (EPP) on the hydraulic conductivity of two smectite-sand mixtures leached with distilled water.

mainly to clay swelling (Alperovitch *et al.*, 1985). Smectite dispersion was not expected at this electrolyte concentration, which is well above the flocculation value of the clay (Oster *et al.*, 1980). In 0.01 M  $\text{Cl}^-$  solution of PAR 2.0 and 4.0, no swelling of the clay was observed, whereas the relative HC of Wyoming and Belle-Fourche smectites at equilibrium with a solution of PAR 6.0 dropped to 0.82, and the relative HC of the smectites from Polkville and Otay decreased to 0.95. The effect of sodium on the swelling of the same smectites in similar mixtures was discussed by Alperovitch *et al.* (1985) and is presented in part in Figure 2. The swelling of Na-Wyoming clay with ESPs of 10.5 and 21.6 caused the relative HC of the mixtures to drop to 0.70 and 0.03, respectively. Conversely, the swelling of the same clay with EPP of 11.1 had no effect on the relative HC and EPP of 16.2 caused the relative HC to drop to 0.82. A similar difference between Na and K swelling was observed for the other smectites. Electrolyte concentration of 0.01 M prevented the swelling and HC drop of the smectites saturated with EPPs <20.

When the 0.01 M  $\text{Cl}^-$  solutions of PARs of 2.0, 4.0, and 6.0 were displaced with distilled water (Figure 1), the relative HC of the various clay-sand mixtures varied markedly. EPPs of 9.5 and 14.6 had no effect on the relative HC of the mixtures of smectites from Polkville and Otay, respectively. Only a small change in HC was noted when the EPPs of these clays increased to 15.9 and 23.2 (in equilibrium with PAR 4 solutions). These smectites with high charge density are not sensitive to exchangeable K in the range that might be found in cultivated soils, even if they are leached with distilled water.

At the other extreme was the Wyoming montmorillonite. Introducing 6.6%  $\text{K}^+$  into the exchange complex resulted in dispersion of the clays and a drop in the relative HC of the mixture. Leaching the mixtures of EPP of 11.1 and 16.2 with distilled water caused large changes in HC. The relative HC of the mixtures

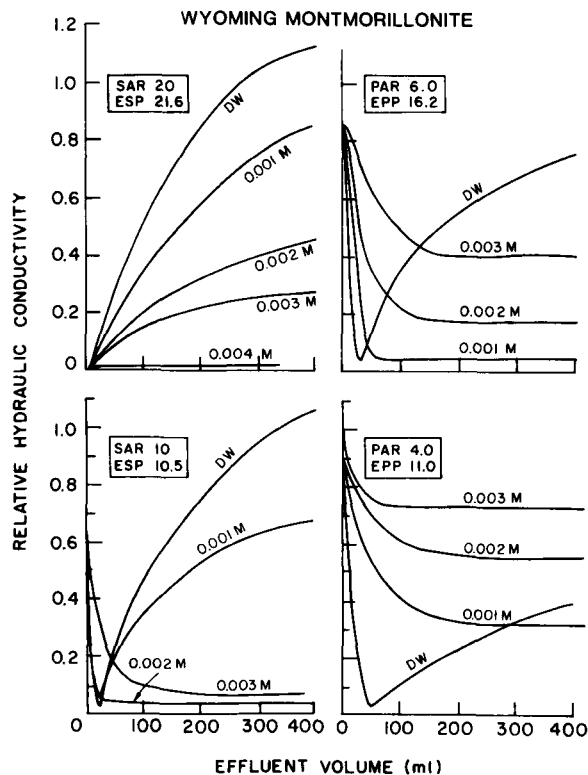


Figure 3. Relative hydraulic conductivity of (Na-Ca)- and (K-Ca)-Wyoming smectite-sand mixtures leached with dilute salt solutions. (DW = distilled water, SAR = sodium adsorption ratio, PAR = potassium adsorption ratio, ESP = exchangeable sodium percentage, EPP = exchangeable potassium percentage.)

dropped sharply to <0.05, followed by an increase in relative HC (Figure 1). Also, dispersed clay appeared in the effluent (Figure 1). Similar HC curves were reported by Alperovitch *et al.* (1985) for Na-smectite-sand mixtures (Figure 2). The presence of clay in the effluent indicated that dispersion and long-distance movement of the clay particles took place. Swelling and deposition of the clay particles in pore spaces led to the sharp drop in the HC values. The subsequent increase in the HC was explained by Pupisky and Shainberg (1979) as due to a change in the mechanism of flow. As the clay dispersed in the distilled water, the flow changed from flow of solution in a sandy clay matrix where the sand particles are covered with a skin of clay, to flow of suspension in a pure sand matrix. Removing the clay skin from the sand particles increased both the pore radii and the HC (Figure 1).

The relative effects of exchangeable K and exchangeable Na on the HC of Wyoming (a smectite with low charge density) and Otay (a smectite with high charge density) smectite-sand mixtures are summarized in Figure 2. In the comparison, the K or Na percentages in the exchange complex were maintained at similar values. The effect of exchangeable K at EPPs <20 on



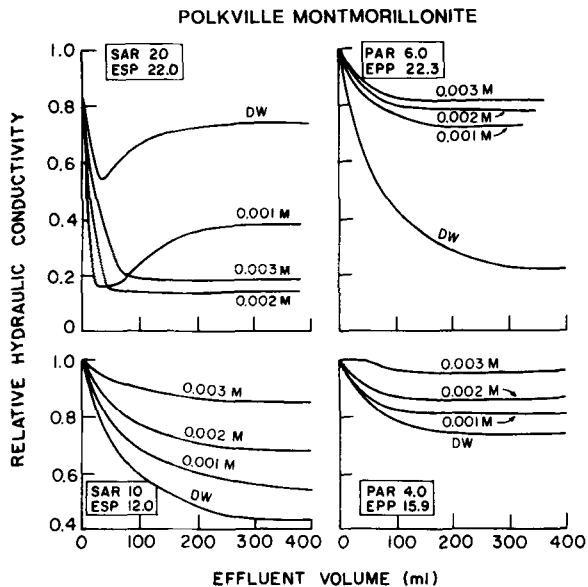


Figure 4. Relative hydraulic conductivity of (Na-Ca)- and (K-Ca)-Polkville smectite-sand mixtures leached with dilute salt solutions. (DW = distilled water, SAR = sodium adsorption ratio, PAR = potassium adsorption ratio, ESP = exchangeable sodium percentage, EPP = exchangeable potassium percentage.)

the HC of low-charge smectite in equilibrium with 0.01 M solutions is negligible. Conversely, the effect of ESP on the HC of Na-smectite in equilibrium with 0.01 M is large. Exchangeable Na in this ESP range effectively breaks up the Ca-tactoids, increases the swelling, and decreases the HC of the mixture (Shainberg and Letey, 1984). Conversely, exchangeable K penetrates between the Ca-tactoids without effectively breaking them apart, and no increase in swelling and decrease in HC is observed at EP < 20.

When Wyoming clay-sand mixtures were leached with distilled water, the relative HC initially dropped and thereafter increased in both K-Ca and Na-Ca systems (Figure 2). Na<sup>+</sup> was more dispersive than K<sup>+</sup>, but K<sup>+</sup>, even in small percentages, actively dispersed the Wyoming smectite.

The relative HC of the Otay-sand mixture in equilibrium with 0.01 M solutions dropped only slightly as the ESP increased (Figure 2). Similarly no drop in HC was obtained in K-Ca Otay systems. The high charge density in the Otay clay resulted in strong electrostatic attraction forces which prevented the swelling and change in HC in both monovalent cations. When the Otay smectite-sand mixtures saturated with ESP of 10.3 and 21.2 were leached with distilled water, the relative HC gradually decreased (Figure 2). When the Otay-clay-sand mixture having an EPP of 14.6 was leached with distilled water, the relative HC did not change (Figure 2). Even if the Otay clay was saturated with 23.2% K, the change in the HC was very gradual and small. The low hydration energy of the K cations

coupled with the strong electrostatic attraction forces between the platelets account for the "inefficiency" of exchangeable K in dispersing smectites having high charge density.

#### *Effect of dilute solutions on hydraulic conductivity*

The effects of displacing 0.01 M NaCl + CaCl<sub>2</sub> solutions of SAR 10 and 20, and KCl + CaCl<sub>2</sub> solutions of PAR of 4.0 and 6.0 with solutions of the same SAR or PAR, respectively, but with electrolyte concentrations of 0.003, 0.002 or 0.001 M Cl<sup>-</sup> are presented in Figure 3 for the Wyoming smectite and in Figure 4 for the Polkville smectite. Displacing the SAR 10, 0.01 M Cl<sup>-</sup> solution with 0.002 and 0.003 M solution of the same SAR resulted in a decrease in relative HC of the Wyoming smectite from 0.70 to 0.03 and 0.06 of the "base HC" value, respectively. No clay was leached from the columns, indicating that solutions exceeding 0.002 M Cl<sup>-</sup> were sufficiently concentrated to prevent macroscopic movement of the clay. Swelling and short-range movement of the clay by which the conducting pores were plugged, however, were so pronounced that the relative HC dropped to 0.03–0.06. Inasmuch as more swelling was expected in the 0.002 M compared with the 0.003 M solution, the relative HC was lower. Displacing the SAR 10 0.01 M solution with 0.001 M Cl<sup>-</sup> solution resulted in a curve similar to that found for distilled water (DW), i.e., a sharp drop in relative HC followed by a sharp increase in relative HC. A concentration of 0.001 M Cl<sup>-</sup> was not enough to prevent dispersion, and the HC of the suspension flow increased. Clay dispersion in 0.001 M solutions and the resulting increase in relative HC, however, were appreciably less in 0.001 M solutions compared with the distilled water. As the ESP of the Wyoming clay-sand mixtures increased to 21.6, the clay dispersed and the relative HC increased at electrolyte concentration of 0.001, 0.002, and 0.003 M. The extent of clay dispersion and the increase in relative HC decreased, of course, as the electrolyte concentration increased. An electrolyte concentration of 0.004 M Cl<sup>-</sup> was enough to prevent the Wyoming clay having ESP 21.6 from dispersing.

If 0.001–0.003 M Cl<sup>-</sup> solutions of PAR 4.0 and 6.0 displaced solutions of 0.01 M Cl<sup>-</sup> of the same PAR (EPP of 11.1 and 16.2, respectively), a pronounced drop in HC was obtained which was not followed by an increase in relative HC (Figure 3). The sharp drop in HC indicates that exchangeable K caused swelling and short-distance migration of the clay platelets which upon deposition in the conducting pores plugged the pores and reduced the HC. Only in the effluent of the 0.001 M solution having PAR 6.0 were traces of clay observed. This clay dispersion was not sufficient to cause an increase in the relative HC (Figure 3). Likewise, only in the distilled water effluent was the inten-

sity of clay dispersion sufficient to cause an increase in relative HC. These curves suggest that K-Ca systems were less dispersive than corresponding Na-Ca mixtures, and very low electrolyte concentrations (0.001 M) were sufficient to prevent appreciable dispersion.

The effect of leaching with dilute solutions (0.001–0.003 M  $\text{Cl}^-$ ) on the relative HC of the Polkville smectite in equilibrium with 0.01 M  $\text{Cl}^-$  solutions of SAR 10 and 20 and of PARs of 4.0 and 6.0 is presented in Figure 4. Polkville smectite behaved differently from Wyoming smectite. Polkville clay having ESP 12.0 did not disperse in distilled water, and only a gradual decrease in relative HC was noted. As the electrolyte concentration in the leaching solutions increased, the amount of swelling decreased and higher HC values were maintained. Macroscopic clay dispersion with clay in the effluent and an increase in relative HC were obtained only in mixtures having an ESP of 22.0, and leached with distilled water or 0.001 M solutions. The minimum in the relative HC curve for 0.001 M  $\text{Cl}^-$  solution was lower than that for distilled water. The minimum in the HC curves was due to two opposing tendencies: swelling of the clay which decreased the HC, and intensive clay dispersion, which increased HC. In distilled water dispersion of Polkville clay predominated, and the HC curve was high. In 0.001 M  $\text{Cl}^-$  solutions, the dispersion of the clay was limited, swelling predominated, and the relative HC was lower.

The relative HC curves of K-Ca-Polkville clay-sand mixtures are also presented in Figure 4. In the clay-sand mixtures of EPP 15.9, the relative HC decreased slightly as the mixture was leached with distilled water. The decrease was even smaller as the concentration increased (Figure 4). In Polkville clay of EPP 15.9, swelling and dispersion were so small that in soils containing smectites having a high charge, K is probably not a dispersive cation. At an EPP of 22.3 (corresponding to PAR 6.0 solutions), only in distilled water leaching was a significant decrease in relative HC noted. At electrolyte concentrations 0.001 M  $\text{Cl}^-$ , the decrease was insignificant. In most soils, even those leached with distilled water (simulating rain water), the electrolyte concentration in the soil solution does not drop below 0.001–0.002 M (due to clay hydrolysis or  $\text{CaCO}_3$  and Ca-feldspar dissolution; Shainberg *et al.*, 1981). If these soils contain smectite of the high charge-density type,

the clay will not disperse at EPPs <22.3, and the changes in relative HC will be insignificant.

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