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CHARGE DENSITY AND Na-K-Ca EXCHANGE ON SMECTITES[1]

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Abstract—Ca-K-, Na-K-, and Ca-Na-exchange isotherms on four reference smectites were studied. The electric charge on the four smectites was due predominantly to cationic substitution in the octahedral layer and varied between 90 and 122 meq/g (cmole(+)/kg) clay. The affinity of the clays for K increased with a decrease in the fraction of K in the exchange phase. The selectivity coefficients of the smectites for K increased with an increase in charge density. The effect was similar in the Na-K- and Ca-K-exchange isotherms. Charge densities on the smectites had no effect on the Ca-Na-exchange isotherm. The electrostatic attraction forces between the platelets increased with increase in charge density. The low hydration energy of adsorbed K was apparently not enough to overcome these attraction forces as the charge density on the smectites increased. Equilibrium between the low hydration energy of adsorbed K and the electrostatic attraction energies between the platelets is postulated to explain the results.

Key Words—Cation exchange, Charge density, Selectivity coefficient, Smectite, Swelling.

INTRODUCTION

The exchange of K for Na or Ca on clays has been studied extensively. The selectivity of the clays for K is in the order illite > vermiculite > smectites. Whereas in the first two minerals fixation of K may take place, no fixation of K appears to take place in wet smectite (Carson and Dixon, 1972). The high selectivity of illites and vermiculite for K is explained by the facts that (1) the charge density in illite and vermiculite is 1.5 times that in montmorillonites, and (2) the negative layer charge in illite and vermiculite is concentrated in the tetrahedral layer, whereas in montmorillonite the negative charge is due mostly to cationic substitutions in the octahedral layer. The objective of the present research was to study the effect of charge density of reference smectites having predominantly octahedral substitution on their selectivity for K.

Reference smectites may contain impurities of illite and vermiculite that have high selectivities for K at low levels of adsorbed potassium. Thus, the selectivity of the smectites for K was determined only at exchangeable-potassium percentage (EPP) >5. Because of the heterogeneity of charge density in reference smectites (Talibudeen and Goulding, 1983), the change in the selectivity constants with the fraction of exchangeable K was also evaluated.

THEORETICAL CONSIDERATIONS

For the exchange reaction

$$CaX_2 + 2\,K^+ = 2\,KX + Ca^{2+}, \qquad (1)$$

the thermodynamic exchange equilibrium constant is represented by

$$K = \frac{(KX)^2(Ca^{2+})}{(CaX_2)(K^+)^2}, \qquad (2)$$

where X is one mole of charge of the anionic part of the exchanger and ( ) refers to the activity of the chemical species.

In Eq. (2) only the activity of the cations in the solution phase is easily computed in terms of molar ion concentration, m, and molar activity coefficient. The activity of a species in the adsorbent phase is not computed as easily. If the activities of the exchangeable cations are equal to their equivalent fraction, the Gaines-Thomas selectivity coefficient, K_{GT}, is obtained:

$$K_{GT} = \frac{(E_K)^2(Ca^{2+})}{(E_{Ca})(K^+)^2}, \qquad (3)$$

where E_K and E_{Ca} are the equivalent fractions of the total exchange capacity occupied by the ions specified.

If the activity of an exchangeable cation is equal to its mole fraction, N, Eq. (2) gives the Vanselow selectivity coefficient, K_V:

$$K_V = \frac{(N_K)^2(Ca^{2+})}{(N_{Ca})(K^+)^2}. \qquad (4)$$

The U.S. Salinity Laboratory Staff (1954) advocated the use of an empirical Gapon's equation,

$$K_G = \frac{E_K(Ca^{2+})^{1/2}}{E_{Ca}(K^+)} \qquad (5)$$

or

$$\frac{E_K}{E_{Ca}} = K_G\frac{(K^+)}{(Ca^{2+})^{1/2}}. \qquad (5a)$$

If exchange between two monovalent ions is considered,

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Table 1. Sources and properties of the clays used in the study.[1]

Mineral[2]	CEC[3] (meq/100 g) Low (1980)	CEC[3] (meq/100 g) This study	S[3] (m^2/g)	Octahedral substitution (atoms/unit cell) Mg	Octahedral substitution (atoms/unit cell) Fe	Tetrahedral substitution (atoms/unit cell)	Charge density (meq/100 g) (mmole(+) $cm^{-2} \times 10^{10}$)
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 (API 24)	120	122.2	552	1.20	0.11	0.05	2.21

[1] Based on Low (1980).
[2] Obtained from Ward's Natural Science Establishment, Rochester, New York; numbers are American Petroleum Inst. Reference clay numbers.
[3] CEC = cation-exchange capacity; S = specific surface area.

$$NaX + K^+ = KX + Na^+. \quad (6)$$

The three selectivity coefficients condense into one, as follows:

$$K = \frac{(N_K)(Na^+)}{(N_{Na})(K^+)}. \quad (7)$$

EXPERIMENTAL

Materials

Four montmorillonites from Ward's Natural Science Establishment, Rochester, New York, were selected for this study. Their source and identifying API numbers are given in Table 1, as are the amounts of octahedral substitution and their cation-exchange capacities (CEC), as reported by Low (1980). Also in Table 1, the CECs as determined in the present study and the resultant charge densities are presented. The CECs determined here agree well with those reported in the literature: thus, the mineralogical compositions of the samples are assumed to be similar to those of the reference samples.

Methods

Na-clays were prepared by treating the natural clays with 1 M solutions of NaCl. The clays were then washed with distilled water by centrifugation until the electrical conductivities of the equilibrium solutions were <0.5 dS/m. Suspensions of 1–2% clay were prepared, and clay-size fractions of the clays were separated from coarser fractions by sedimentation. Following centrifugation, the clays were freeze-dried and stored in a desiccator.

Triplicate 0.5-g samples of the clays were equilibrated with 0.5 M solutions having ionic ratios, $(K)/(Ca)^{1/2}$, of 0.0617, 0.129, 0.189, 0.316, and 0.475 (the concentrations are given in mole/liter). When the concentrations are given in mmole/liter, these ionic ratios, called potassium adsorption ratios (PAR), have the values 2.0, 4.0, 6.0, 10.0, and 15.0, respectively. Following leaching three times with 30 ml of the 0.5 M solutions in the centrifuge, the clay was leached three more times with 30 ml of 0.01 M solutions of the same ionic ratio. The supernatants of the final 0.01 M solutions were analyzed. The clay samples then were washed with 60% ethanol solution until free of electrolytes. Exchangeable cations were extracted from the clays with three, 30-ml batches of 1.0 M NH_4OAC solution, K and Ca in the solution were determined by atomic absorption spectroscopy.

Na-K-exchange isotherms on the four smectites were studied by a similar method; clay samples were equilibrated with 0.5 and 0.01 M solutions containing Na/K ratios of 1/9, 2.5/7.5, 5/5, 7.5/2.5, and 9/1, and the compositions of the equilibrium solutions were determined. The clay samples were then washed with 60% ethanol-water solution, and the exchangeable cations were extracted with NH_4OAC 1.0 M solution.

Na-Ca-exchange isotherms were determined using solutions having a sodium adsorption ratio (SAR) of 10, 20, and 40 [$SAR = (Na)(Ca)^{1/2}$), where the values in parentheses are the concentrations in mmole/liter]. The procedure was similar to that described above.

RESULTS AND DISCUSSION

The composition of the equilibrium solution and the exchangeable ions, the selectivity constants, and some statistics for K-Ca exchange on the four smectites are presented in Tables 2 and 3. The ionic ratios in the equilibrium solutions are presented in terms of concentration and not activities because the total electrolyte concentration in all equilibrium solutions was low, (0.01 M Cl^-); therefore, the error introduced by neglecting the activity coefficient ratios is small.

Of the three selectivity coefficients (K_V, K_{GT}, and K_G) describing the exchange isotherms of K-Ca on the four smectites, Gapon's selectivity coefficient was the variable that was least dependent on the fraction of K in the exchange complex. Vanselow's selectivity coefficient was the variable that changed most with exchangeable K percentage (EPP). Similar observations were made by, e.g, Bolt *et al.* (1963), Carson and Dixon (1972), and Shaviv *et al.* (1985). Furthermore, the affinity of Wyoming montmorillonite for K decreased as

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Table 2. Ionic ratio ($(K^+)/(Ca)^{½}$) in equilibrium solutions, composition of exchanger phase, and selectivity coefficients in K-Ca-exchange.

Smectite mineral	Ionic ratio[1]	KX (meq/100 g)	CaX (meq/100 g)	EPP (%)	K_G[2]	K_{GT}[3]	K_V[4]
Upton, Wyoming	0.062	6.02	86.14	6.05	1.13	1.19	4.48
	0.129	10.11	80.45	11.2	0.97	0.83	3.00
	0.189	14.66	76.13	16.2	1.01	0.86	3.00
	0.316	22.27	68.63	24.5	1.03	0.80	2.56
	0.475	29.66	59.30	33.3	1.04	0.74	2.23
Belle Fourche, South Dakota	0.062	6.73	86.52	7.3	1.25	1.47	5.47
	0.129	10.81	81.95	11.7	1.02	0.94	3.35
	0.189	15.65	76.8	16.9	1.07	0.96	3.31
	0.316	23.26	69.2	25.2	1.06	0.840	2.70
	0.475	30.76	61.69	33.3	1.05	0.74	2.21
Polkville, Mississippi	0.062	9.87	92.92	9.6	1.71	2.69	9.90
	0.129	16.46	86.58	15.9	1.49	1.80	6.36
	0.189	23.05	80.48	22.3	1.52	1.78	5.91
	0.316	33.17	70.61	32.0	1.49	1.51	4.52
	0.475	45.12	59.64	43.1	1.58	1.49	4.04
Otay, California	0.062	17.84	102.04	14.8	2.85	6.81	23.81
	0.129	28.29	91.69	23.6	2.41	4.30	14.08
	0.189	41.59	84.54	33.0	2.59	4.60	13.78
	0.316	57.5	66.76	46.3	2.72	4.10	10.904
	0.475	74.13	48.01	62.3	3.20	4.13	10.3

[1] Concentrations in mole/liter. The corresponding ratios (in mmole/liter)^{½} are 2.0, 4.0, 6.0, 10.0, 15.0.
[2] Gapon selectivity coefficient.
[3] Gaines-Thomas selectivity coefficient.
[4] Vanselow selectivity coefficient.

the EPP increased from 6.1 to 11.2. In the EPP range 11.2 and 33.3, the Gapon coefficient was constant, whereas the two other selectivity coefficients tended to decrease, indicating that the affinity of the clay for K decreased as the percentage of exchangeable K increased. The three other clays behaved similarly. At a low EPP, the selectivity coefficients were higher than at higher EPPs. The presence of impurities (such as illite and vermiculite) having high affinities for K may explain this observation for the low EPP range. The gradual decrease in affinity for K with increase in EPP >10 suggests that some charge heterogeneity was present in the smectites (Talibudeen and Goulding, 1983), and that sites with higher affinity for K were neutralized first by exchangeable K. Thus, for an increase in EPP, sites with lower affinity for K were occupied, and the

Table 3. The average ($\bar{X}$) and coefficient of variation (CV) of the selectivity coefficients for Ca-K, Na-K, and Ca-Na exchange on the four smectites.

Treatment	Selectivity coefficient	Wyoming		Belle Fourche		Polkville		Otay		
		$\bar{X}$	CV	$\bar{X}$	CV	$\bar{X}$	CV	$\bar{X}$	CV	r[1]
K-Ca, all data	K_G[2]	1.04	5.7	1.082	6.2	1.552	6.4	2.75	10.8	.9943
	K_{GT}[3]	0.89	20.2	0.959	22.9	1.85	25.3	4.80	23.2	.9982
	K_V[4]	3.05	28.2	3.405	36.97	6.129	36.85	14.57	37.20	.9975
K-Ca, without lowest EPP	K_G	1.00	3.0	1.053	2.05	1.520	2.8	2.73	12.38	.9945
	K_{GT}	0.81	6.3	0.87	11.65	1.64	10.23	4.28	5.36	.9984
	K_V	2.70	13.92	2.89	18.72	5.23	20.73	12.26	15.84	.9973
K-Na	K	1.908	34.5	2.074	23.6	3.108	11.5	5.418	16.9	.9899
Na-Ca, all data	K_G	0.455	22.4	0.412	22.3	0.471	12.3	0.445	21.8	
Na-Ca, without lowest ESP	K^*_G	0.50		0.452		0.493		0.489		
	$K^K_{G_{Ca}}/K^K_{G_{Na}}$	0.54		0.52		0.50		0.51		

[1] Linear correlation coefficients between the selectivity coefficients and the charge density on the smectites (Table 1).
[2] Gapon selectivity coefficient.
[3] Gaines and Thomas selectivity coefficient.
[4] Vanselow selectivity coefficient.

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Table 4. Ionic ratio (K/Na) of equilibrium solution, the exchanger phase, and the selectivity coefficient in K-Na exchange.

Clay[1]	Ionic ratio K/Na	NaX	KX	CEC	KX/Na	K_{eq}	$\bar{K}$	CV (%)
		(meq/100 g)						
Wyoming	0.11	49.22	16.07	65.29	0.33	2.97		
	0.33	39.7	26.5	66.2	0.67	2.00	1.908	34.5
	1.0	24.32	44.54	68.86	1.83	1.83		
	3.0	12.27	56.14	68.41	4.58	1.51		
	9.0	6.36	70.22	76.58	11.04	1.23		
Belle Fourche	0.11	52.83	16.95	69.78	0.32	2.88		
	0.33	42.61	27.83	70.44	0.65	1.95		
	1.0	23.26	50.0	73.26	2.15	2.15	2.074	23.6
	3.0	11.74	62.61	74.35	5.33	1.76		
	9.0	5.64	83.4	89.05	14.76	1.63		
Polkville	0.11	68.53	27.56	96.09	0.40	3.6		
	0.33	50.24	46.83	97.07	0.93	2.79		
	1.0	23.17	78.05	101.22	3.37	3.37	3.108	11.5
	3.0	10.49	90.97	101.46	8.67	2.86		
	9.0	3.66	96.12	99.78	26.26	2.92		
Otay	0.11	66.82	50.34	117.16	0.75	6.75		
	0.33	44.54	75.00	119.54	1.68	5.04		
	1.0	16.82	100.45	117.27	5.97	5.97	5.418	16.9
	3.0	7.95	110.70	118.65	13.92	4.59		
	9.0	2.72	116.25	118.97	42.74	4.74		

[1] Sources listed in Table 1.

selectivity coefficient for K decreased. One exception to this generality is the high Gapon's constant for Otay clay which had an EPP of 62.3. Possibly, some collapse of the platelets of the smectite having high charge density took place at this high EPP (Norrish, 1954). The collapse increased the affinity of the clay for K.

The averages of the selectivity coefficients for each of the smectites and the coefficients of variation (CV = standard deviation/average), as calculated for all the ionic ratios and by omitting the selectivity coefficients that correspond to the lowest EPP, are presented in Table 3. By omitting the selectivity coefficients for the lowest EPP, the variability of the data for each clay is diminished. Considering the CV values, Gapon's selectivity coefficient clearly varies the least, whereas the two other selectivity coefficients vary more. Also, the effect of charge density at the smectite surface on the selectivity coefficients is pronounced. The affinity of the smectites for K increased linearly with an increase in charge density, despite the fact that in the four smectites the cationic substitution was predominantly in the octahedral layer. The linear correlation coefficients between the selectivity coefficients and the charge density are also presented in Table 3.

Ca-montmorillonites aggregate into tactoids or quasicrystals (Blackmore and Miller, 1961). Each tactoid consists of several (4–9) clay platelets in parallel array, with interplatelet distances of 9 Å. In K-montmorillonites the platelets are separated if they are in equilibrium with dilute salt solution, and the clay swells to infinite layer thickness (Schramm and Kwak, 1982). In a mixture of monovalent and divalent ions, the two ions may be mixed at random throughout the exchange sites, i.e., for any ratio of adsorbed K/Ca, as many K ions exist on the internal surfaces of the tactoids as on their external surfaces. Another possibility for the distribution of K/Ca is that the cations "demix" such that some interlayer spaces contain mainly K ions, and others mainly Ca ions. For a Na-Ca-montmorillonite having an ESP <40, Shainberg *et al.* (1980) suggested that the Na ions were concentrated on the external surfaces of the tactoids, whereas the Ca ions concentrated on the internal surfaces of the tactoids. This "demixing" affected the selectivity coefficients of Na-Ca-exchange isotherms. K-Ca-smectites may behave similarly, and the effect of charge density on the selectivity coefficients may be due to the effect of charge density on tactoid formation.

To rule out the possibility of tactoid formation and its effect on the selectivity coefficients, the effect of charge density on K-Na exchange was studied. The data listed in Table 4 suggest that: (1) The measured CEC of Wyoming montmorillonite was a function of the exchangeable cation; it diminished as the fraction of Na in the exchange phase increased. The Belle Fourche montmorillonite behaved similarly. During the equilibration of Na- and K-montmorillonite (Wyoming) with dilute salt solution (0.01 M) and the leaching of excess salt with a 60% ethanol-water solution, the exchangeable cation hydrolyzed (Shainberg *et al.*, 1980). The rate of hydrolysis of Na-smectites was higher than that of K-smectites; hence, the CEC increased from Na- to K-montmorillonite. The cation saturation of the Polkville and Otay clays was affected only slight-

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Table 5. Ionic ratio $(Na)/(Ca)^{1/2}$ in the equilibrium solutions, the exchanger phase, and Gapon's selectivity coefficient in Na-Ca exchange.

Clay[1]	Ionic ratio	SAR[2]	NaX	CaX	ESP[3]	CEC[4]	K_G[5]	K'_G[6]
Wyoming	0.322	10.19	9.4	80.3	10.5	87.7	0.363	.0115
	0.628	19.87	19.3	69.9	21.6	89.2	0.439	.0139
	0.917	29.0	30.0	58.0	34.1	88.0	0.564	.0178
Belle Fourche	0.322	10.19	8.9	83.2	9.7	92.1	0.332	.0105
	0.628	19.87	18.1	73.7	19.7	91.8	0.391	.0124
	0.917	29.0	29.1	61.9	32.0	91.0	0.513	.0162
Polkville	0.322	10.19	12.4	90.4	12.0	102.8	0.426	.0135
	0.628	19.87	22.6	80.0	22.0	102.6	0.450	.0142
	0.917	29.0	33.7	68.5	33.0	102.2	0.536	.0170
Otay	0.322	10.19	12.5	109.0	10.3	121.5	0.356	.0113
	0.628	19.87	25.7	95.3	21.2	121.0	0.429	.0136
	0.917	29.0	40.5	80.5	33.5	121.0	0.549	.0173

[1] Sources listed in Table 1.
[2] Sodium adsorption ratio = $(Na)/(Ca)^{1/2}$ where ( ) is the concentration in mmole/liter.
[3] Exchangeable sodium percentage.
[4] Cation-exchange capacity.
[5] Gapon selectivity coefficient.
[6] K'_G is Gapon's constant expressed in mmole/liter. $K'_G = K_G/31.62$.

ly by the fraction of exchangeable Na. (2) The affinity of the clays for K increased with a decrease in the fraction of K in the exchanged phase. Such a phenomenon was observed also in the K-Ca-exchange isotherm (Table 2). As the fraction of exchangeable K decreased, sites with greater affinity for K remained saturated with K, and the selectivity coefficient for K increased. (3) An increase in charge density of the clay increased the affinity of the smectites for K (Table 4). The regression coefficient for this relation (Table 3) is high (r = .990) and is similar to those for K-Ca isotherms. The ratios between the Gapon constants of the smectites and that of Wyoming montmorillonite are 1.0, 1.05, 1.50, and 2.67 for K-Ca exchange on the Wyoming, Belle Fourche, Polkville, and Otay smectites, respectively. These ratios for K-Na exchange are 1.0, 1.09, 1.63, and 2.84 for the same clays, respectively. The effect of charge density on the affinity of the clays for K is similar in both K-Ca and K-Na ion pairs.

From the data listed in Table 5, the following effects of charge density on Na-Ca selectivity coefficients are suggested: (1) In Table 5, Gapon's constants are presented in two manners. If the concentration of the cations in the solution is given in mole/liter, K_G was calculated from Eq. (5). If the concentration is given in mmole/liter, the ionic ratio in the solution is the sodium adsorption ratio (SAR), and the values of Gapon's constant so calculated (K'_G) may be compared to the values in the literature on saline soils (see, e.g., U.S. Salinity Laboratory Staff, 1954). The charge density on the smectites had no effect on the selectivity coefficient; the average values of K_G and K'_G for the four smectites are 0.446 and 0.0141, respectively. The value of K'_G is similar to the values reported in the literature (U.S. Salinity Laboratory Staff, 1954). (2) Gapon's constant decreased as the fraction of exchangeable Ca increased at the Ca-end of the exchange isotherm. Similar observations were made by van Bladel *et al.* (1972) who concluded that the most significant feature about Na-Ca exchange on montmorillonite was the "more pronounced selectivity of the clay for Ca^{2+} ions at the Ca-rich end isotherms." Keren (1979) and Shainberg *et al.* (1980) attributed the increased affinity of montmorillonite to Ca^{2+} at the Ca-end of the exchange isotherm to tactoid formation and the difficulty of Na to penetrate in between the platelets which are dominated by Ca ions. (4) The value of K_G for Na-Ca exchange can also be estimated from Gapon's experimental values for K-Ca- and Na-K-exchange equilibria as follows:

$$K^K_{Ca}/K^K_{Na} = K^{Na}_{Ca}. \quad (8)$$

These Gapon constant ratios are presented on the bottom line of Table 3. As expected, the values obtained from the direct experimental measurement of Na-Ca equilibrium (Table 5) are similar to that calculated from the Ca-K- and Na-K-exchange isotherms. The Gapon constants for Na-Ca exchange as determined by both methods were independent of the charge density on the smectites.

The selectivity of reference smectites (with negative charge due to cationic substitution in the octahedral layer) for K increased with an increase in charge density. The effect of charge density was similar in both Na-K- and Ca-K-exchange isotherms. The charge density on the smectites had no effect on the Na-Ca-exchange isotherm.

The effect of charge density on the selectivity of smectites for K in K-Ca and K-Na exchange may be

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correlated and explained by the effect of charge density and hydration energy of the adsorbed cations on swelling of montmorillonite and vermiculite (Norrish, 1954). K-vermiculite, having a CEC of 150 meq/100g (cmole(+)/kg) does not swell in water, whereas two molecular layers of H_2O penetrate between the platelets of Na-, Mg-, and Ca-vermiculite, and Li-vermiculite may swell to an infinite thickness. Conversely, Na- and Li-montmorillonite swell to an infinite thickness in H_2O, K-montmorillonite may swell similarly (depending on the experimental conditions), and Ca- and Mg-montmorillonites swell only slightly (only three molecular layers of H_2O penetrate in between the platelets).

Swelling of the 2:1 clays depends on the interparticle forces. The forces of attraction between two clay platelets are the van der Waals and electrostatic forces (Norrish, 1954). For a small gap between the crystal sheets, Norrish (1954) considered the electrostatic energy of attraction between the interlayer ions and the montmorillonite platelets as a compromise between a point charge relationship, where $E_a = qve/2dD$, and a condenser relationship where $E_a = 2q^2d/D$, where q is the surface charge density, 2d is the distance between the platelets, ve is the charge on the cation, and D is the dielectric constant of water. Forces of repulsion are the osmotic forces as predicted by the diffuse double-layer theory and the "hydration" forces (Murray and Quirk, 1984; Shainberg and Kemper, 1966). The magnitude of the hydration forces depends on the electric field strength at the ion surface [(ion valence)^2/ionic radius].

The hydration energy of adsorbed Na is enough to overcome the electrostatic and van der Waals attraction forces between montmorillonite platelets, and swelling to an infinite thickness is possible. The hydration energy of adsorbed K is hardly enough to overcome the attraction between Wyoming montmorillonite platelets, and the degree of swelling depends on the experimental conditions (e.g., drying and wetting cycle, Norrish, 1954). As the charge density on the clay increases, the attraction energies predominate and the clay does not swell (e.g., vermiculite). Because the effect of charge density on the attraction forces is continuous, the swelling of K-smectites should diminish as the charge density increases with the collapse of K-platelets, the affinity of the clay for exchangeable K should increase.

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