Clays and Clay Minerals, Vol. 47, No. 2, 174–180, 1999.

CATION EXCHANGE CAPACITY OF KAOLINITE

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Abstract—Experimental cation exchange capacities (CEC) of kaolinites were determined and compared to theoretical calculations of CEC. The comparison reveals that the exchangeable cations occur mostly on the edges and on the basal (OH) surfaces of the mineral. It also shows that permanent negative charge from isomorphous substitution of Al^{3+} for Si^{4+} is insignificant. The CEC of kaolinite strongly depends on the particle size (both thickness and diameter in the (00*l* plane) and pH value. Particle size is more important than crystallinity in affecting kaolinite CEC. This study shows that the hydroxyls on the exposed basal surfaces may be ionizable in aqueous solutions. The amount of negative charge on the edges and the exposed basal hydroxyls depends on pH and other ion concentrations. A higher pH value gives rise to more negative charges, which lead to a higher CEC value. This study indicates that charge from broken edges and exposed OH planes rather than charge from Al/Si substitution determines the kaolinite CEC, even at zero point charge. A high CEC in some kaolinites is found to be due to smectite layers on the surface of the kaolinite crystals.

Key Words—Cation Exchange Capacity, Edges, Exposed (OH) Planes, Kaolinite, Substitution, Surface Charge.

INTRODUCTION

Clay minerals have the property of absorbing certain ions and retaining them in an exchangeable state. Except for smectites and vermiculites, exchangeable ions are held on external surfaces of the mineral, and the exchange reaction does not affect its structure. Vastly more information is available regarding cation exchange than anion exchange. In clay minerals the most common exchangeable cations, in order of usual relative abundance, are Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, Na^+ (Grim, 1968). It is commonly believed that cation exchange occurs due to *the broken bonds* around the crystal edges, *the substitutions* within the lattice, and *the hydrogen of exposed surface hydroxyls* that may be exchanged. The clay minerals are not the only components having CEC. All minerals of extremely small particle size have a small CEC as a result of broken bonds around their edges. This capacity increases as the particle size decreases, but even at the smallest size in which non-clay minerals occur associated with clays, the exchange capacity due to broken bonds is relatively insignificant (Grim, 1968).

Kaolinite has a heterogeneous surface charge. The basal siloxane surfaces of kaolinite are believed by many (van Olphen, 1977; McBride, 1976; Rand and Melton, 1977; Williams and Williams, 1978) to carry a constant structural charge due to the isomorphous substitution of Si^{4+} by Al^{3+}, whereas the charge on the edges is due to the protonation/deprotonation of exposed hydroxyl groups and therefore depends on the solution pH. McBride (1989) proposed that isomorphous substitution in kaolinite generates about 0.01 mol Kg^{-1} of permanent charge but gave no details. The attribution of surface charge in kaolinites to isomorphous substitution is called the Constant Basal Surface Charge model (Zhou and Gunter, 1992). Bolland *et al.*, (1976) concluded that most of the negative surface charge on kaolinite is pH independent and is likely to be due to isomorphous substitution.

Grim (1968) concluded that the surface negative charge of kaolinite is derived mainly from broken bonds around the edges and from exposed basal hydroxyls. Unlike broken bonds, the hydrogen of exposed hydroxyls is an integral part of the structure and may be replaced by an exchangeable cation. However, Grim (1968) also suspected that such hydrogens would probably be relatively tightly held compared with those associated with broken bonds and hence, in the main, not be replaceable. He suggested that exchange capacity from exposed hydroxyls would be important for kaolinite and halloysite because of the presence of the sheet of hydroxyls on one side of the basal crystal or cleavage surface. In a number of isotopically labelled ion-exchange experiments, Ferris and Jepson (1975) found that cation uptake by kaolinite depends upon the cation chosen, the electrolyte concentration, and the solution pH. They concluded that a structural charge did not exist on the basal surface of their samples. A nuclear magnetic resonance (NMR) study of Cs-133 exchange on kaolinite by Kim *et al.*, (1996) implied that basal surfaces are important adsorption sites along with edge sites and expandable sites.

The controversy over whether isomorphous substitutions contribute significantly to kaolinite CEC has

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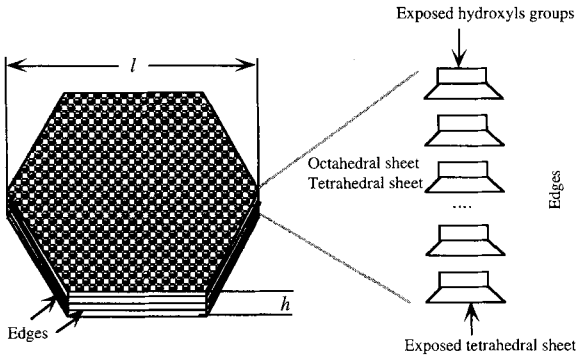


Figure 1. A simplified model for a kaolinite crystal showing possible exchangeable sites on the edges, the surface of the basal hydroxyls plane, and the basal surface of the tetrahedral sheet. l = diameter along the [100] direction; h = thickness perpendicular to (001).

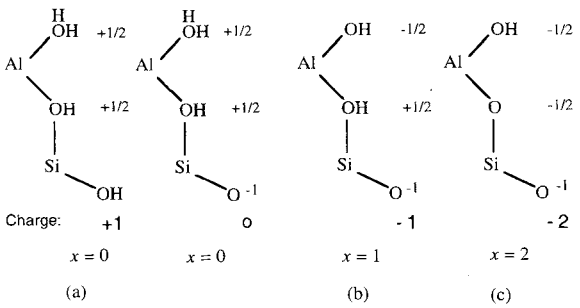


Figure 2. Hydrogen attached to oxygen at the edge faces of kaolinite in aqueous solution that is (a) acid, (b) neutral, and (c) strongly alkaline. x is the unit negative charge per one 1 : 1 layer, used in the calculation of CEC from the edges.

continued for some time. This paper tries to clarify the causes of kaolinite CEC and to determine the nature of kaolinite surface charge. To do so, the theoretical CEC of platy kaolinite was calculated through a structural approach.

THEORETICAL CEC

We assume that the origins of kaolinite CEC are broken bonds at crystal edges (*i.e.*, {110} and {010} planes), exposed hydroxyls on an octahedral cover sheet on one side of a kaolinite crystal (as illustrated in Figure 1), and isomorphous substitutions of Si by Al in the surface tetrahedral sheet or all tetrahedral sheets within the crystal lattice. This section aims to calculate CEC from these different origins. For the convenience of discussion, CEC of edges is referred to as CEC_e, CEC of surface basal hydroxyls as CEC_b, and CEC of isomorphous substitutions from one basal tetrahedral sheet as CEC_s. Although CEC is commonly measured in milliequivalents per 100 grams (Grim, 1968), throughout this paper CEC is expressed in mol Kg^{-1}.

The unit cell parameters of ideal kaolinite ($Al_4[Si_4O_{10}](OH)_8$) used here were modified from Bailey (1984) by assuming $\alpha = \gamma = 90°$; a = 0.5139 nm, b = 0.8932 nm, c = 0.7371 nm, β = 104.8°, Z = 1, which corresponds to a calculated density (d) of 2.62 $\times 10^{-24}$ (Kg nm^{-3}).

For an ideal single crystal as illustrated in Figure 1, where l is defined as the diameter along the [100] direction, h is the thickness along the [001] direction, then

$$\text{basal surface area} = 3(3^{1/2})/8 \times l^2,$$

$$\text{all edges area} = 3lh,$$

$$\text{total surface area} = 3lh + 3(3^{1/2})/4 \times l^2,$$

$$\text{edge area \% (over total surface area)} = h/(h + (3^{1/2})/4 \times l) \times 100,$$

$$\text{volume} = 3(3^{1/2})/8 \times l^2h,$$

$$\text{weight (Kg)} = \text{volume} \times \text{density} = 3(3^{1/2})/8 \times l^2h \times d,$$

$$\text{specific total surface area} = \text{total surface area/weight} = 8/(3^{1/2}ld) + 2/(hd),$$

$$\text{specific basal surface area} = 2/(hd),$$

$$\text{specific edge area} = 8/(3^{1/2}ld),$$

$$\text{total 1:1 layers per one crystal} = h/(c \times \sin 104.8°),$$

$$\text{total crystal numbers (n) per 1 Kg} = 1/\text{weight}.$$

Based on the above, it is clear that the specific basal-surface area depends on the crystal thickness, whereas the specific edge-surface area depends on the crystal diameter.

For the edge CEC, assume a variable, x, which stands for unit negative charge per one 1 : 1 layer and varies from 0 to 2 (see Figure 2 for explanation), then

$$\text{number of negative charge per one 1:1 layer} = x[l/(2a) + 0.5] \times 6,$$

$$\text{number of negative charge per one crystal} = h/(c \times \sin 104.8°) \times x[l/(2a) + 0.5] \times 6.$$

Therefore,

$$CEC_e = \mathbf{n}/(6.022045 \times 10^{23}) \times h/(c \times \sin 104.8°) \times x[l/(2a) + 0.5] \times 6 \approx (x/l) \times [8/3^{1/2}/(d \times 6.022045 \times 10^{23} \times ac \times \sin 104.8°)].$$

If the unit for size, l, is nm, then $CEC_e \approx 7.99(x/l)$, which is evaluated in Figure 3.

Assume that y out of six OH (per unit cell) on the basal surface hydroxyl plane lost H^+ and became negatively charged, then

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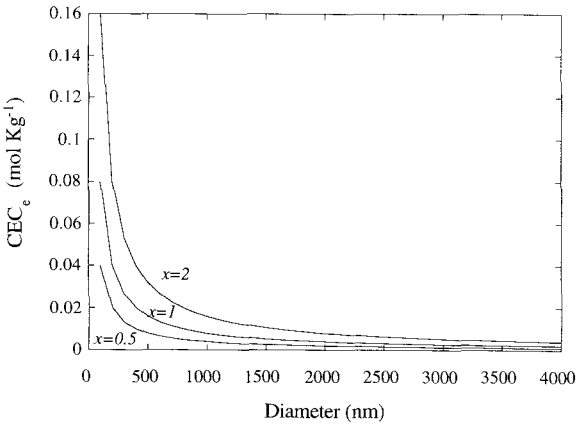


Figure 3. Edge CEC versus plate diameter, calculated as $7.99(x/l)$. x = number of unit negative charge per one 1 : 1 layer.

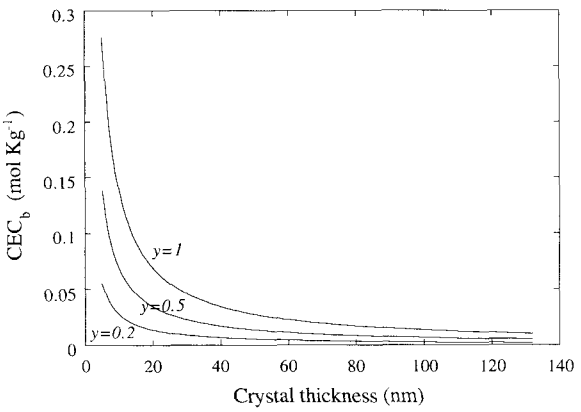


Figure 4. Basal OH CEC versus crystal thickness, calculated as $1.381\ (y/h)$. y = number of OH^- on basal OH plane per unit cell which are replaced by O^{2-}.

number of negative charges per one crystal

$$= y \times 3(3^{1/2})/8 \times l^2/(ab),$$

$$CEC_b = [\mathbf{n}/(6.022045 \times 10^{23})] \times y \times 3(3^{1/2})/8 \times l^2/(ab)$$

$$= (y/h)/(abd \times 6.022045 \times 10^{23}).$$

Therefore, $CEC_b \approx 1.381(y/h)$, where the crystal thickness, h, has nm as its unit (see Figure 4).

To assess the CEC of isomorphous substitution, assume a variable, z, which stands for tetrahedral Al per unit cell (*i.e.*, one out of $4/z$ Si of the tetrahedral sheet replaced by Al) and gives rise to a negative charge, then, the number of negative charge per one tetrahedral sheet $= z \times 3(3^{1/2})/8 \times l^2/(ab)$,

$$CEC_s = [\mathbf{n}/(6.022045 \times 10^{23})] \times z \times 3(3^{1/2})/8 \times l^2/(ab)$$

$$= (z/h)/(abd \times 6.022045 \times 10^{23}),$$

where CEC_s is only from substitution in the basal surface tetrahedral sheet. If the unit for thickness, h, is nm, then $CEC_s \approx 1.381(z/h)$, which is presented in Figure 5.

If all substitutions within the lattice contributed to the permanent CEC, the CEC of all substitutions = $CEC_s \times [h/c \sin(104.8°)]$ or the CEC of all substitutions $= z/(abcd \times \sin(104.8°) \times (6.022045 \times 10^{23})$. Therefore, CEC of all substitutions is about $1.938z$, which is independent of crystal size.

Based on the above calculation, the edge CEC has a positive linear relation with the specific edge area, whereas the exposed basal hydroxyl CEC and basal substitution CEC have a positive linear relation with the specific basal surface area.

EXPERIMENTAL CEC

The kaolin samples selected for CEC measurement were recovered in eastern Australia, from southern Victoria to northern Queensland, and from New Zealand. Sample information is shown in Table 1. The kaolinite samples were from a wide range of sources and origins, studied in detail by Ma (1996).

Various methods have been developed for measuring CEC of clay minerals (for review, see Grim, 1968; Bain and Smith, 1987). It is widely accepted that CECs should be measured at neutral pH since the CEC values are strongly affected by pH. In this study, the method for CEC measurement was modified from the procedure developed at the CSIRO, Division of Soils (Churchman *et al.*, 1994). Clay fractions from each sample were separated, and approximately 0.1 g deposited onto a filter paper and washed ten times with deionized water using vacuum filtration. The exchangeable cations were then replaced by Ba using a

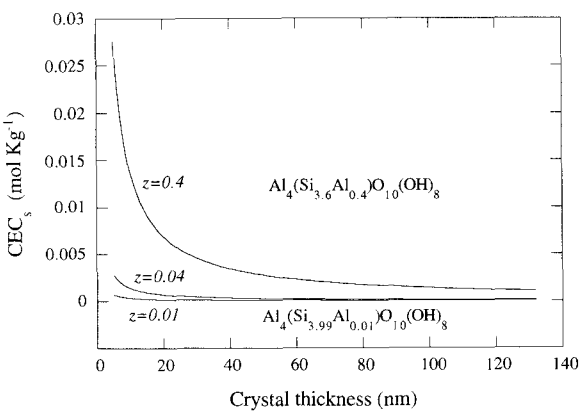


Figure 5. Surface substitution CEC versus crystal thickness, calculated as $1.381(z/h)$. z = number of ^{IV}Al replacing Si per unit cell.

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Table 1. Kaolinite samples studied.

Location	Source	Age of clay	Sample no.
Weathered *in situ*			
Pittong, Vic.	Granite	Tertiary?	PONG2, PONG3, PONG4 PONG5, PONG6, PONG7
Lal-Lal, Vic.	Granite	Tertiary?	LAL1, LAL3
Bexhill, NSW	Basalt	Jurassic?	BEX3, TAT
Wodside, SA	Schist	Tertiary?	WOODSIDE
Weipa, Qld	Sediments	Tertiary	ST, NT, PF C1175, C1875, C1925, G1500
Transported origin			
Bunyan, NSW	Basalt	Tertiary	B804
Swan Bay, NSW	Felsic volcanics	Tertiary?	SB7
Tarong, Qld	Basalt	Jurassic?	TARONG1, TARONG2, TARONG3
Cooyar, Old	Basalt?	Tertiary	COOYAR1, COOYAR2, COOYAR3
Hydrothermal origin			
Pierce's Creek, Qld.	Granite	Tertiary?	PRC
Wairakei, NZ	Felsic volcanics	Quaternary	GV38, GV57
Kiri Kiri, NZ	Volcanics	Quaternary?	KIRI
Unknown origin			
Mt Morgan			MT MORGAN

(from Ma 1996).

1 M $BaCl_2$ solution passed through the sample three times. Each specimen was then washed with deionized water at least ten times and dried at 60°C. The Ba content in the fraction was measured by X-ray fluorescence (XRF) to determine the CEC. Table 2 lists CEC values for clay fractions of kaolin samples analyzed by the XRF method.

As shown in Table 2 and Figure 6, the CEC values of kaolinite increase as the particle size (mean diameter and thickness) decreases. For comparison with the experimental CEC, the theoretical CEC of the edges, surface basal hydroxyls, and substitutions in the surface tetrahedral sheets were calculated for primary kaolinite fractions (*i.e.,* the pure kaolinites formed *in situ*) (see Table 3). Assumptions made in the calculations were that $x = 1$ (edge charge), $y = 1$ (surface charge), and z values were as derived from their chemical compositions. (The basis used to select $x = 1$ is the neutral pH for CEC measurement.) The mean thickness (h) of kaolinite crystals for each fraction was obtained from their X-ray diffraction (XRD) (001) peak using the Scherrer equation, and the mean diameter (equivalent spherical diameter or e.s.d., l) of the (001) plane was estimated from the particle size analysis. It is accepted that e.s.d. values of particle size are related to the diameters rather than to the thickness of platy clay minerals (Brown and Brindley, 1984). Although the assumptions might vary considerably, the theoretical CEC shows a close correlation with the experimental CEC (Table 3). This implies that diameter and thickness play an important role in cation exchange behaviour of kaolinites. The CEC of substitutions (*i.e.,* CEC_s) can only be to 5% of the total theoretical CEC (Table 3), which indicates that the CEC_s is relatively insignificant.

The experimental results show that the CEC of highly crystalline kaolinites seems to be lower than that of poorly crystalline (transported) kaolinites. For instance, it is apparent that the CEC of well ordered kaolinites from weathered granite in the pallid zone at Pittong ranges from 0.028 to 0.050 mol Kg^{-1}, whereas the CEC of poorly ordered kaolinites of secondary origin at Swan Bay is 0.16–0.34 mol Kg^{-1}. However, the high CEC of kaolinite at Swan Bay was mainly attributed to its extreme thinness (about 15 nm along the [001] direction). It is evident that particle size is more important than crystallinity (*i.e.,* degree of structure ordering) in affecting kaolinite CEC.

High CEC values in kaolinite samples from G1500 (Weipa) and B804 (Bunyan) are partially attributable to smectite and interstratified kaolinite/smectite impurities (Ma, 1996). High-resolution transmission electron microscopy study showed that one or two smectite layers occur on the surface of some kaolinite particles in the two samples.

The CEC of halloysite is generally higher than that of kaolinite, as listed in Table 2. Grim (1968) showed that halloysite $2H_2O$ (7-Å) and halloysite $4H_2O$ (10-Å) have a CEC of 0.05–0.1, and 0.4–0.5 mol Kg^{-1}, respectively. Because halloysite usually occurs with a tubular morphology, it is suspected that some exchangeable cations reside inside the tubes and cause a slightly higher CEC. In the case of an ideal platy morphology, the CEC of 7-Å halloysite is theoretically similar to that of platy kaolinite. However, there is a lack of experimental CEC data for different halloysites.

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Table 2. Experimental CEC of kaolin samples by the XRF method and the crystal thickness estimated from the XRD peak width.

Sample no.	Clay fraction (nm)	Thickness (nm)	CEC (mol Kg $^{-1}$)
Kaolinite			
PONG2	<2000	58	0.034
PONG3	<2000	66	0.050
PONG4	<2000	154	0.028
PONG5	<2000	96	0.032
PONG6	<2000	56	0.048
PONG7	<2000	81	0.028
PONG7	500–1000	59	0.034
LAL1	<2000	192	0.034
LAL3	<2000	92	0.034
SB7	<2000	17	0.162
PRC	<2000	44	0.200
GV38	1000–2000	74	0.056
GV38	500–1000	48	0.056
GV38	200–500	43	0.060
GV57	500–1000	18	0.100
COOYAR1	<2000	144	0.056
COOYAR2	<2000	19	0.138
COOYAR3	<2000	6?	0.040
BEX3	1000–2000	13?	0.052
BEX3	500–1000	8?	0.058
BEX3	200–500	8?	0.072
TAT	<2000	32	0.118
TARONG2	<2000	9?	0.124
TARONG3	<2000	38	0.108
ST	<2000	38	0.046
NT	<2000	36	0.050
PF	<2000	41	0.052
C1175	1000–2000	32	0.054
C1175	500–1000	35	0.056
C1875	1000–2000	54	0.038
C1875	500–1000	44	0.044
C1875	200–500	39	0.050
C1925	1000–2000	54	0.038
C1925	500–1000	42	0.044
G1500[1]	1000–2000	43	0.244
B804[1]	<2000	17	0.228
Halloysite			
TARONG1	1000–2000		0.208
KIRI	<2000		0.142
WOODSIDE	<2000		0.454
MT MORGAN	<2000		0.170

[1] Containing smectite layers.

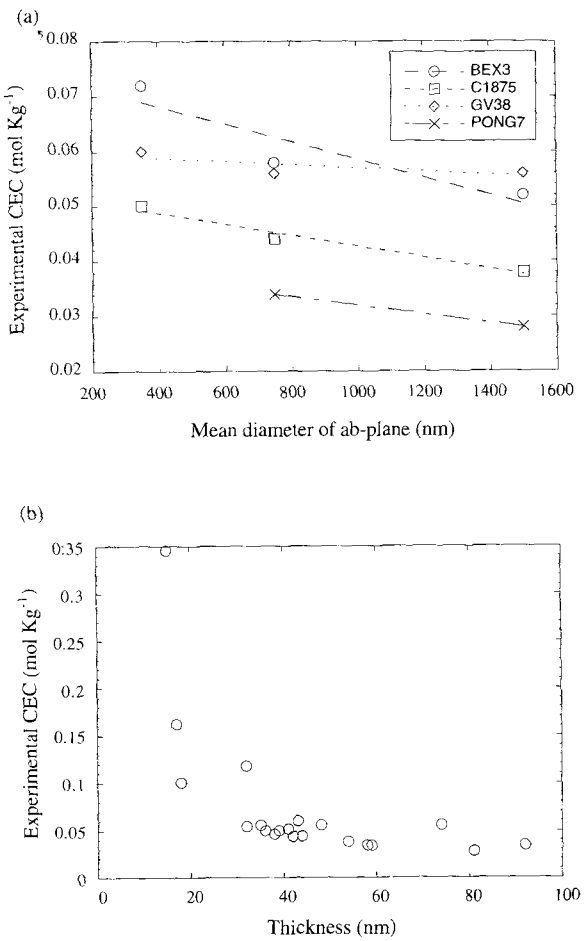


Figure 6. (a) Relation between experimental CEC and kaolinite plate diameter. (b) Relation between experimental CEC and crystal thickness.

DISCUSSION

Origins of kaolinite CEC

Schofield and Samson (1953) showed that only one silicon out of 400 needs to be replaced by aluminum to reach a CEC of 0.02 mol Kg^{-1} for kaolinite. Because such low levels of isomorphous substitution can not be detected by chemical analyses, isomorphous substitution can not be eliminated as a possible cause for CEC of low charge kaolinite. However, they gave no detail on how to reach this result. If all isomorphous substitutions within the kaolinite tetrahedral sheets contribute negative charges, according to the calculations above, the permanent CEC should be 0.019 mol Kg^{-1} if only one out of 400 Si is replaced by Al. Therefore, it is very likely that Schofield and Samson (1953) drew their conclusion by assuming all isomorphous substitutions within the crystal lattice give rise to the negative charges on the surfaces of kaolin crystals and contribute to the CEC. According to the principle of local charge balance, charge differences inside a crystal are not likely to be compensated far from their source, *i.e.,* at the surface. Since kaolinite has no interlayer region, it is not possible to introduce an exchange ion to the structure, except conceivably an extra proton. No structural evidence for such a charge balance position has ever been presented. Because in reality the exchange sites are only available around the surface of the kaolinite crystal, it appears that only substitutions of Si in the surface tetrahedral sheet can contribute to the permanent CEC. One substitution per 400 Si (*i.e.,* $z = 0.01$) in the surface tetrahedral sheet yields an insignificant CEC (see Figure 5). However, if as many as one out of eight Si of the

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Table 3. Comparison of theoretical CEC with experimental CEC and the crystal size.

Sample no.	Clay fraction (nm)	Diameter: l (nm)	Thickness: h (nm)	CEC(e) $x = 1$	CEC(b) $y = 1$	CEC(s)	Theoretical CEC[1] (mol Kg^{-1})	Experimental CEC (mol Kg^{-1})	CEC(e) $x = 2$	CEC(b)[2] Calculated	CEC(b)[3] (%)
PONG7	<2000	1200	81	0.007	0.017	0.001	0.025	0.028	0.013	0.014	49
PONG7	500–1000	750	59	0.011	0.023	0.001	0.035	0.034	0.021	0.011	33
GV57	500–1000	750	18	0.011	0.077	0.003	0.090	0.100	0.021	0.076	76
ST	<2000	1000	38	0.008	0.036	0.001	0.046	0.046	0.016	0.029	62
NT	<2000	1000	36	0.008	0.038	0.002	0.048	0.050	0.016	0.032	65
PF	<2000	1000	41	0.008	0.034	0.001	0.043	0.052	0.016	0.035	67
C1175	1000–2000	1500	32	0.005	0.043	0.002	0.050	0.054	0.011	0.042	77
C1175	500–1000	750	35	0.011	0.039	0.002	0.052	0.056	0.021	0.033	59
C1875	1000–2000	1500	54	0.005	0.026	0.001	0.032	0.038	0.011	0.026	69
C1875	500–1000	750	44	0.011	0.031	0.001	0.043	0.044	0.021	0.021	49
C1875	200–500	400	39	0.020	0.035	0.001	0.057	0.050	0.040	0.009	17
C1925	1000–2000	1500	54	0.005	0.026	0.001	0.032	0.038	0.011	0.026	69
C1925	500–1000	750	42	0.011	0.033	0.001	0.045	0.044	0.021	0.021	49

[1] Theoretical CEC = CEC(e)(x = 1) + CEC(b)(y = 1) + CEC(s).
[2] Calculated CEC(b) = Experimental CEC − CEC(e)(x = 2) − CEC(s).
[3] CEC(b)% = Calculated CEC(b)/Experimental CEC × 100.

surface tetrahedral sheet is replaced by an Al (*i.e.*, this unit has a formula of $Al_4(Si_{3.5}Al_{0.5})O_{10}(OH)_8$), the CEC of the surface basal tetrahedral sheet would be 0.014 mol Kg^{-1} for a kaolinite crystal with a thickness of 50 nm. Most natural kaolinites have bulk tetrahedral Al values around 0.04 with a range between 0.0–0.2 in the formula, *i.e.*, $Al_4(Si_{4\sim3.8}Al_{0\sim0.2})O_{10}(OH)_8$. The permanent CEC of kaolinite of composition $Al_4(Si_{3.96}Al_{0.04})O_{10}(OH)_8$ is <0.0028 mol Kg^{-1} when crystal thicknesses are >20 nm.

The CEC arising from all substitutions in kaolinite is independent of particle size in the above calculations. This conclusion may be applied to other clay minerals. In the case of smectite, the CEC from substitutions in the crystal structure contributes to about 80% of the total CEC, but here the exchangeable sites occur also within the interlayers throughout each crystal. Therefore, the CEC of smectite is much less affected by particle size. This explains why the experimental CEC of smectite is independent of particle sizes (Grim, 1968).

This structural approach to assess theoretical CEC has clarified the causes of exchange capacity for kaolinite, and provided information for evaluating the experimental CEC and the nature of its surface charge. These calculations suggest that ion exchange reactions take place on heterogeneous -SiOH and -AlOH sites but many fewer exchange reactions take place on the surface tetrahedral plane. They do not support the simple model of isomorphous substitution charges plus basic edge sites so often assumed (*e.g.*, Bolland *et al.*, 1976). The calculated data show no evidence for any structural cation exchange capacity. As for the pH dependent CEC, the CEC of the edges increases with a decrease in the crystal diameter of the (001) plane, whereas the proportion of the surface CEC contributed by the basal surface hydroxyls increases with a decrease in crystal thickness along the [001] direction. The calculated CEC (CEC_e + CEC_b) for a nominal 1000 nm kaolinite crystal with an aspect ratio of 1:10 is 0.022 mol Kg^{-1} when $x = 1$ and $y = 1$, which falls in the range of reported CECs. This is satisfactory theoretical evidence for the view that the exchange capacity of unground kaolinite is proportional to the area of edge faces.

pH control on CEC

It is well known that the negative charge caused by substitutions within the lattice structure is permanent and pH independent, whereas the charges on the edges and the exposed hydroxyls surface depend upon pH. The effect of pH on the CEC of kaolinite is well documented (*e.g.*, Ferris and Jepson, 1975); higher pH leads to a higher CEC value. In practice, the pH effect can be minimized by leaching or washing the sample with enough deionized water to bring it to a near neutral condition. Although the CEC of edges and the basal surface hydroxyl plane is strongly pH-dependent (*i.e.*, pH controls the values of x and y), concentration of an exchange cation strongly influences the pH effect during CEC measurement. For example, in the case of edge CEC, assuming A^+ is the index cation, the following reactions take place:

$$\text{Si-OH} = \text{Si-O}^- + \text{H}^+,$$

$$\text{Si-O}^- + \text{A}^+ = \text{Si-O-A},$$

thus,

$$\text{Si-OH} + \text{A}^+ = \text{Si-O-A} + \text{H}^+.$$

An increase in the $[A^+]$ concentration will push the exchange reaction towards the right and decrease Si-OH on the broken edges, which causes more absorption of cation A and gives rise to a higher edge CEC.

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When [OH^-] concentration increases, negative charges are developed at the edges according to the reaction, Si-OH + OH^- = Si-O^- + H_2O. The same applies to Al-OH at edges and exposed basal surfaces. Therefore, under acidic conditions, the CEC of edges and basal surface hydroxyl planes can still contribute most to the total CEC, whereas the total CEC is lower since some exchangeable sites are occupied by hydrogen. Hence, cation exchange sites on the edges of kaolinite crystals and other phyllosilicate plates can not simply be considered to be completely inactive in the acidic range of pH. In other words, the kaolinite CEC measured under strongly acidic conditions may not derive from substitutions, but rather from broken edges and possible exposed (OH) planes.

Nature of the surface charge

Sposito (1984) indicated that the exposed basal OH layer contributes to ion exchange reactions on kaolinite. Wieland and Stumm (1992) showed that successive surface protonation at the gibbsite layer and the edge surface can account for the pH-dependent surface charge of kaolinite in acidic aqueous solutions. It is apparent that the functional OH groups at the gibbsite and edge surfaces are able to complex metal ions (Schindler and Stumm, 1987).

Based on the consideration of surface charge density, Zhou and Gunter (1992) noted that the ionization of edges alone can not explain the magnitude of the changes in the CEC with pH. Thus, they concluded that the basal surface must also contribute to these charges. The charges on the basal surfaces are always negative but the magnitude is pH-dependent. This result implies that the basal faces of kaolinite are ionizable in aqueous solutions. Their conclusion is in agreement with this study. Comparison between theoretical and experimental CEC clearly shows the importance of the exposed basal hydroxyls' contribution to the total CEC. As shown in Table 3, assuming that all edge sites contribute to CEC (*i.e.*, $x = 2$), the basal OH surface comprises a crucial and significant part of the total CEC. Apparently, the number of hydroxyls which lose H^+ and become negatively charged is controlled by solution pH. Higher pH values give rise to more negative charges.

SUMMARY

Provided there are no smectite layers present, kaolinite CEC is almost entirely caused by surface charge; structural substitution is minor, generally contributing <5% of the total CEC. Determinations of particle size and CEC may be used to estimate the presence of the included smectite.

ACKNOWLEDGMENTS

We thank D. Laird, P. Komadel and P. Schiffman for their constructive reviews on the manuscript, G. R. Rossman and W. H. Hudnall for improving the quality of the writing. GRR also helped with the use of computer facilities at the Caltech Mineralogy Lab. This project was supported by Comalco Aluminum Ltd. and also funded partially by the Australian Research Council.

REFERENCES

Bailey, S.W. (1984) Structures of layer silicates. In *Crystal Structures of Clay Minerals and Their X-ray Identification,* G.W. Brindley and G. Brown, eds., Mineralogical Society, London, 1–124.

Bain, D.C. and Smith, B.F.L. (1987) Chemical analysis. In *A Handbook of Determinative Methods in Clay Mineralogy,* M.J. Wilson, ed., Blackie, Glasgow, 301–320.

Bolland, M.D.A., Posner, A.M., and Quirk, J.P. (1976) Surface charge on kaolinites in aqueous suspension. *Australian Journal of Soil Research,* **14,** 197–216.

Brown, G. and Brindley, G.W. (1984) X-ray diffraction procedure for clay mineral identification. In *Crystal Structures of Clay Minerals and Their X-ray Identification,* G.W. Brindley and G. Brown, eds., Mineralogical Society, London, 305–360.

Churchman, G.W., Slade, P.G., Self, P.G., and Janik, L.J. (1994) Nature of interstratified kaolin-smectites in some Australian soils. *Australian Journal of Soil Research,* **32,** 805–822.

Ferris, A.P. and Jepson, W.B. (1975) The exchange capacities of kaolinite and the preparation of homoionic clays. *Journal of Colloid Interface Science,* **51,** 245–259.

Grim, R.E. (1968) *Clay Mineralogy.* McGraw-Hill, New York, 596 pp.

Kim, Y., Kirkpatrick, R.J., and Cygan, R.T. (1996) Cs-133 NMR study of cesium of the surfaces of kaolinite and illite. *Geochimica et Cosmochimica Acta,* **60,** 4059–4074.

Ma, C. (1996) The ultra-structure of kaolin. Ph.D. thesis, Australian National University, Canberra, Australia, 343 pp.

McBride, M.B. (1976) Origin and position of exchange sites in kaolinite: As ESR study. *Clays and Clay Minerals,* **24,** 88–92.

McBride, M.B. (1989) Surface chemistry of soil minerals. In *Minerals in Soil Environments (2nd edition),* J.B. Dixon and S.B. Weed, eds., Soil Science Society of America, Madison, Wisconsin, 35–88.

Rand, B. and Melton, I.E. (1977) Particle interactions in aqueous kaolinite suspensions, I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions. *Journal of Colloid Interface Science,* **60,** 308–320.

Schindler, P.W. and Stumm, W. (1987) The surface chemistry of oxides, hydroxides, and oxide minerals. In *Aquatic Surface Chemistry,* W. Stumm, ed., Wiley Interscience, New York, 83–110.

Schofield, R.K. and Samson, H.R. (1953) The deflocculation of kaolinite suspensions and the accompanying change over from positive to negative chloride adsorption. *Clay Minerals Bulletin,* **2,** 45–51.

Sposito, G. (1984) *The Surface Chemistry of Soils.* Oxford University Press, New York, 227 pp.

van Olphen, H. (1977) *Clay Colloid Chemistry, 2nd edition.* John Wiley & Sons, New York, 318 pp.

Wieland, E. and Stumm, W. (1992) Dissolution kinetics of kaolinite in acidic aqueous solution at 25°C. *Geochimica et Cosmochimica Acta,* **56,** 3339–3355.

Williams, D.J.A. and Williams, K.P. (1978) Electrophoresis and zeta potential of kaolinite. *Journal of Colloid Interface Science,* **65,** 79–87.

Zhou, Z. and Gunter, W.D. (1992) The nature of the surface charge of kaolinite. *Clays and Clay Minerals,* **40,** 365–368.

(Received 8 June 1997; accepted 25 June 1998; Ms. 97-073)

https://doi.org/10.1346/CCMN.1999.0470207 Published online by Cambridge University Press