REDUCTION OF THE CATION-EXCHANGE CAPACITY OF MONTMORILLONITE BY TAKE-UP OF HYDROXY-Al POLYMERS[1]

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Abstract—The cation-exchange capacity (CEC) of Na-Al- and Ca-Al-montmorillonite after neutralization with NaOH or Ca(OH)$_2$ was studied at three Al levels: 10, 25, and 50% of the CEC. Hydroxy-Al polymers were effective in reducing the CEC of Na-montmorillonite (by more than 46%), the exact effectiveness being dependent on the hydroxy-Al content. The hydroxy-Al polymers were less effective in reducing the CEC of Ca-montmorillonite (less than 26%). The CEC reduction was equal to or larger than the amount of the untitrated Al. The electrostatic charges of the clay which were blocked by the hydroxy-Al polymers were compensated for by both the positive charge of the hydroxy-Al polymers and the trapped cations on the clay surfaces. These cations remained on the clay even after extensive washing with 0.1 M KCl.

Key Words—Cation-exchange capacity, Hydroxy-Al polymer, Interlayer, Montmorillonite, Smectite.

INTRODUCTION

Aluminum is common in soils as a weathering product of soil-forming minerals; it also occurs as coatings on clay minerals (Rich, 1968), where it influences the physicochemical properties of the minerals (Keren, 1979). A reduction in cation-exchange capacity (CEC) following the formation of Al-interlayers has been observed by several investigators (Shen and Rich, 1962; Barnhisel and Rich, 1963; Tullock and Roth, 1975; Keren *et al.*, 1977; Keren, 1980). The extent and mechanism by which such hydroxy-Al interlayers reduce the CEC of montmorillonite were studied by Keren *et al.* (1977) and Keren (1980) who found that the addition of 5.33 mole AlCl$_3$/kg clay in suspension, followed by titration with NaOH, resulted in a CEC reduction of 60% at pH 7.5.

Barnhisel and Rich (1963) and Turner and Brydon (1967) also found that hydroxy-Al interlayers, prepared at OH/Al mole ratios of 2.25–3.0 and ~5.33 mole Al/kg clay, initially decreased the CEC of montmorillonite, but after aging, the original CEC was regained. These results contradict those of Meyers and Ahlrichs (1973), who found that the CEC of the clay decreased with increasing degree of interlayer formation, even after 4 months of aging.

These disparate observations may be attributed to the variation in experimental procedure and conditions (Keren *et al.*, 1977; Keren, 1980), OH/Al mole ratios (Shen and Rich, 1962), or amounts of Al/kg of clay (Coleman *et al.*, 1964). In the above studies Al was

added to the suspensions at a rate of either 2.67 or 5.33 mole/kg clay. The rate of 5.33 mole Al/kg clay was selected to provide sufficient precipitate to cover the clay surface, assuming that (1) the specific surface area of the clay was 0.76 km^2/kg; (2) the clay platelets were parallel to each other; (3) the hydroxy-Al precipitate was uniformly distributed on the surfaces; and (4) the hydroxy-Al precipitate had a structure similar to gibbsite.

It is of interest to study the effect of hydroxy-Al and exchangeable Na and Ca ions on the CEC of montmorillonite at an aluminum content lower than the CEC. This range is encountered in many soils; for example, a loamy sand from Netanya, Israel, has been found in this laboratory to contain ~10% free oxides (on a clay basis).

The present study was conducted to clarify the extent to which hydroxy-Al interlayers, at contents less than the CEC, reduce the CEC of montmorillonite, and to study the effect that the exchangeable cation species (i.e., Na vs. Ca) has on this reduction.

MATERIALS AND METHODS

Clay preparation

The clay-size fraction of Wyoming montmorillonite (API No. 25) was obtained by allowing larger fractions to settle out of a suspension and then decanting the suspension. Na-clay was prepared by saturating the colloidal size fraction with 1 N NaCl solutions. This treatment was repeated three times. The clay was then washed with distilled water and separated in a high-speed centrifuge until the equilibrium solution was free of chloride. Chloride was presumed to be absent when the supernatant liquid tested negative with AgNO$_3$.

534

Table 1. OH/Al mole ratio at pH 7.5 for various titrated Na-Al-montmorillonite and Ca-Al-montmorillonite mixtures.

| System | Ion composition | | | Amount of added Al (mole) | Amount of added OH[1] (mole) | OH/Al mole ratio | Neutral-ization (%) |
	Na (%)	Ca (%)	Al (%)				
1	90	—	10	14	40	2.85	95
2	75	—	25	36	104	2.89	96
3	50	—	50	72	199	2.76	92
4	—	90	10	15	38	2.71	90
5	—	75	25	36	98	2.72	91
5	—	50	50	72	202	2.80	93

[1] NaOH and $Ca(OH)_2$ were used for Na and Ca systems, respectively.

Table 2. Light transmittance ($\lambda = 500$ nm) of suspended Na-Al- and Ca-Al-montmorillonite at a concentration of 0.05% (w/v).

| Al content (%) | Light transmittance | |
	Na-mont. (%)	Ca-mont. (%)
0	69	20
10	59	20
25	55	18
50	51	17
100	45	—

The salt-free clay was freeze-dried and stored in a desiccator over P_2O_5. Ca- and Al-montmorillonite were prepared by saturating the Na-clay with 1 N $CaCl_2$ or $AlCl_3$ solutions. After three saturation treatments, the clay was washed with distilled water and separated in a high-speed centrifuge until the equilibrium solution was free of chloride.

Hydroxy-Al interlayer preparation

The bi-ionic Na-clay + Al-clay or Ca-clay + Al-clay mixtures having Al contents of 10, 25, and 50% of the exchangeable ions in the clay were prepared by suspending Na-clay or Ca-clay with Al-clay in distilled water in appropriate amounts. The suspensions were then stirred for about 2 hr until redistribution of the cations in the exchange complex was complete (Shainberg and Kaiserman, 1969). Suspensions (25 ml) containing 0.5 g clay were stirred continuously, and hydroxy-Al precipitates were formed by adding NaOH or $Ca(OH)_2$ solution at the rate of 0.025 mmole OH^-/min, using a syringe pump (Sage Instruments Model 355), to a pH of 7.5 (Keren et al., 1977). This rate was chosen to maximize CEC reduction (Keren, 1980). Following the titration, the volume was adjusted to 50 ml, and the mixture was shaken continuously for an additional 18 hr. These samples were prepared to study the effect of hydroxy-Al interlayers on CEC reduction, and they were not allowed to dry.

Cation-exchange capacity determination

The CEC of the samples was determined by ^{22}Na analysis using a Packard Instrument Co. 5,000 Series Auto-Gamma Spectrometer system. The CEC of both the clay and the hydroxy-Al clay complexes was determined by washing with ^{22}Na-labeled 0.1 M NaCl solution having a known count per min and determining the ^{22}Na remaining on the clay. The CEC was based on the 110°C dry weight of the clay and did not include the CEC of the hydroxy-Al precipitate, which is negligible (Keren et al., 1977).

pH measurements

The pH of the suspensions were determined by glass-calomel combined electrodes using an El-Hama digital pH meter model PBS 710.

Light transmittance measurements

Optical properties were used to estimate the size of the clay-hydroxy-Al particles in suspension (Shainberg and Otoh, 1968). Light transmittance was determined using a variant Techtron UV-VIS spectrophotometer model 635. The transmittance of the suspensions (0.05% clay) was measured at a wavelength of 500 nm (the length of the light pass was 1 cm).

RESULTS AND DISCUSSION

The OH/Al mole ratios of the various titrated montmorillonite systems at pH 7.5 are given in Table 1. The results indicate that at this pH the OH/Al mole ratios of all systems ranged between 2.71 and 2.89. These values are close to those found by Frink and Sawhney (1967) and Keren et al. (1977). Frink and Sawhney (1967) suggested that the deviation between the observed ratio of 2.8 (the ratio obtained at the inflection point) and the value of 3.0 which might be expected, is probably due to a replacement of OH^- by Cl^- in the precipitate. Turner and Ross (1969), however, moreover reported that Cl^- replacement of OH^- decreased rapidly after ~80% neutralization and was essentially zero at 100% neutralization. Inasmuch as no Cl^- or other anions (except OH^-) were present in the clay suspensions, a neutralization fraction of <1 indicates that part of the negative charge of the clay was compensated by Al ions. Barnhisel and Rich (1963) and Hsu (1968) also suggested that Al^{3+} is the only major exchangeable Al species on the basis of partially neutralized Al-treated clay systems. For example, when 10% and 50% of the CEC of Ca-montmorillonite were saturated by Al ions, the amount of untitrated Al was 10 and 30 mmole/kg, respectively (Tables 1 and 3).

It is evident that the degree of neutralization for the Na systems was higher than that for the Ca systems,

Table 3. Na-saturation and ^{22}Na adsorption (counts/min) on montmorillonite-hydroxy-Al mixtures at pH 7.5 following successive saturation and extraction treatments.

System	Fraction of adsorbed ion[1] (%)			A[3]			B	C
	Na	Ca	Al	^{22}Na (cpm/sample)	Adsorbed Na (mmole/kg)	CEC reduction (%)	^{22}Na (cpm/sample)	Adsorbed Na (mmole/kg)
Na-clay				2530 ± 212	914 ± 76		6	—
Ca-clay				2412 ± 121	871 ± 44		70	—
Al-clay[2]				389 ± 3	872 ± 11		0	—
Clay-hydroxy-Al	90	0	10	1371 ± 56	495 ± 21	46	0	442 ± 45
Clay-hydroxy-Al	75	0	25	1337 ± 167	483 ± 60	47	0	462 ± 54
Clay-hydroxy-Al	50	0	50	1296 ± 118	468 ± 43	49	2	435 ± 36
Clay-hydroxy-Al	0	90	10	2198 ± 56	791 ± 20	9	17	781 ± 12
Clay-hydroxy-Al	0	75	25	2175 ± 21	786 ± 7	10	0	801 ± 15
Clay-hydroxy-Al	0	50	50	1791 ± 27	647 ± 10	26	2	675 ± 10

[1] The fraction of adsorbed ions before titration with OH⁻ took place.
[2] Five washes with ^{22}Na-labeled 1 M NaCl at pH 3.5 plus five ethanol washes.
[3] A = five washes with ^{22}Na labeled 0.1 M NaCl plus five ethanol washes; B = five washes with 0.1 M KCl solution; C = five washes with ^{22}Na-labeled 0.1 M NaCl plus five ethanol washes.

probably due to differences in the clay particle size. The light transmittance of Na-Al- and Ca-Al-montmorillonite suspensions before hydroxy-Al was precipitated at the various Al contents is given in Table 2. The results indicate that the average particle size of the clay in the presence of Ca ions was greater than that in the presence of Na ions. The results suggest that the number of platelets in an average tactoid in the Ca form was much higher than that existing in the Na form, even when Al ions were present. Therefore, the hydroxyl ions movement between the platelets was possibly limited by the stronger negative electric field of the larger particles. Thus, the fraction of the untitrated Al^{3+} between the clay platelets in the Ca systems was greater than that in the Na systems. The larger particles and the smaller percentage of neutralization of Al in the Ca-Al-montmorillonite at the highest Al level (50% Al) supports this hypothesis.

The CEC and Na exchangeability for the clays before and after hydroxy-Al precipitation are given in Table 3. Although the CEC of the clay alone was independent of the adsorbed cation, the CEC of the clay-hydroxy-Al mixture was dependent on the initial composition of the exchangeable cations. The CEC of Na-montmorillonite-hydroxy-Al mixtures was 495, 483, and 468 mmole/kg for the systems containing Al at levels of 10, 25, and 50% of the CEC, respectively. Thus, the CEC reduction was ~46, 47, and 49%, respectively, of the value obtained for the Na-montmorillonite alone. These results indicate that the hydroxy-Al polymers which developed *in situ* during the titration process effectively reduced the CEC of Na-montmorillonite. This reduction was found for a wide range of Al content: from 0.1 (present study) to 17 times the CEC (Keren *et al.,* 1977); however, the degree of reduction in CEC depends on the Al content. For the same clay, final pH, and titration rate, the CEC reduction was 71% at an Al content of 5.33 mole/kg (Keren, 1980)

vs. 46% at an Al content about 100 times smaller (0.03 mole Al/kg) (Table 3). Despite the large difference in the Al content, only a relatively small change was noted in the CEC, indicating that only a small amount of Al-hydroxy polymers was responsible for CEC reduction. Thus, this strong effect appears to have been due to precipitation of hydroxy-Al polymers on the planar surfaces of the single platelets. These polymers may have strongly adsorbed on the clay surface as a monolayer, interacting with another platelet free of hydroxy-Al polymers to form a tactoid in which a significant part of the adsorbed Na was trapped and became nonexchangeable (see below).

The results (Table 3) indicate also that the hydroxy-Al polymers were less effective in the reduction of the CEC of Ca-montmorillonite systems (<26%) than of the CEC of Na-montmorillonite systems (>46%). This difference may be explained by the difference in the arrangement of the clay platelets as suggested by the light transmittance measurements (Table 2). Because of the limited movement of the hydroxyl ions between the platelets (due to a stronger negative electric field in the larger particles), the amount of hydroxy-Al precipitation between the platelets was smaller than that in the Na systems; hence, the CEC reduction was smaller.

Contrary to the small reduction in CEC of the Ca-system, noted here, Keren *et al.* (1977) found that CEC reduction for Sr-montmorillonite was similar to that for Na-montmorillonite. This difference in behavior is probably due to the differences in the amount of Al which was present in the system. Whereas the Al content was less than the CEC in systems studied here, the Al level was about 16 times higher than the CEC in the Sr-clay system. Thus, at this large amount of Al, the clay was almost completely saturated by Al ions regardless of the initial adsorbed cation; hence, the reduction in CEC (Keren *et al.,* 1977). At Al levels

lower than the CEC, however, the complementary ions had a significant impact on the CEC of the clay after hydroxy-Al precipitation.

It is evident that the CEC reduction in all the Na systems and in the Ca system with the highest level of Al is larger than the amount of the untitrated Al (Table 1). Because electrical neutrality must exist, the blocked electrostatic charge of the clay must have been compensated for by both the positive charges of the hydroxy-Al polymers and Al, Ca, and Na cations trapped on the clay surfaces by the hydroxy-Al polymers. Introducing ^{22}Na into the Na-montmorillonite suspension prior to titration (and not after the titration as stated in Table 3) resulted in the entrapment of ^{22}Na ions after hydroxy-Al precipitation. The count per minute of 50 mg clay was 615 ± 40 after five washes with 0.1 M KCl, and not zero, as found in the systems where ^{22}Na was added after precipitation had taken place (Table 3). Keren et al. (1977) observed, however, no trapped ^{22}Na in the clay system after the addition of Al, as is to be expected, because $AlCl_3$ was added at a high rate (5.33 mole/kg) to the ^{22}Na-labeled Na-clay prior to adding NaOH. As a result, most of the adsorbed Na was replaced by Al. Consequently, the clay was Al-saturated prior to the subsequent addition of NaOH and precipitation of hydroxy-Al.

All adsorbed ^{22}Na in the montmorillonite-hydroxy-Al mixtures (which remain after CEC determination, column A, Table 3) was removed by washing with 0.1 M KCl (column B, Table 3), showing that the adsorbed Na on the exposed surfaces was exchangeable. Moreover, after these washings, most of the blockage of the exchange sites remained (column C, Table 3), indicating that the interaction between the hydroxy-Al precipitate and the clay platelets was relatively stable. This stability can be explained as follows: The isoelectric point of noncrystalline $Al(OH)_3$ is 7.3–7.7 (Gayer et al., 1958; Parks, 1965). Although the pH of the bulk solution phase was 7.5, that at the clay surface was probably lower. The surface acidity of montmorillonite appeared to be 2–4 pH units lower than the suspension pH (Hartley and Roe, 1940; Bailey et al., 1968). Thus, the Al polymers that were adsorbed on the montmorillonite surface probably had a net positive charge despite the pH of 7.5 of the suspension. In addition, the dissociation constants likely changed appreciably when the Al polymers resided at the clay mineral surface due to the force fields emanating from the surface. This change in the dissociation constant would be reflected in the magnitude of the net positive charge of adsorbed Al polymers.

CONCLUSIONS

(1) The CEC of montmorillonite at pH 7.5 was reduced due to hydroxy-Al precipitation at low levels of Al (10–50% of CEC).

(2) Due to hydroxy-Al precipitation, an exchangeable ion effect (Na^+ vs. Ca^{2+}) took place on CEC reduction in montmorillonite.

(3) Because CEC reduction was found to be higher than the charge of the untitrated Al, other cations (i.e., Na^+ or Ca^{2+}) must have been trapped on the montmorillonite by the hydroxy-Al polymers.

The CEC of soils which are exposed to rainfall may be reduced due to clay dissolution and hydroxy-Al interlayer formation. This interlayer phase may change both the chemical and physical properties of soils, such as ion exchangeability (Keren, 1979), clay dispersion, and soil permeability.

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