Calcium-Magnesium Exchange Selectivity of Wyoming Montmorillonite in Chloride, Sulfate and Perchlorate Solutions

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ABSTRACT

The need to consider $CaCl^+$ and $MgCl^+$ complexes in Ca–Mg exchange reactions on montmorillonite was evaluated by examining cation selectivity in various anion backgrounds. The Ca–Mg exchange isotherms on SWy-1 Wyoming bentonite were determined in 0.0125 M SO_4, 0.025, 0.050, and 0.100 M Cl and 0.03 M perchlorate background. Calculated selectivity values for the reaction $Ca^{2+} + MgX = Mg^{2+} + CaX$ were $K_v = 1.15$, 1.11 and 1.10 for the SO_4, Cl and perchlorate media, respectively. There was no trend in K_v with exchangeable Ca with any anion or with ionic strength in Cl media. The Ca preference in SO_4 and perchlorate media indicates that montmorillonite preference for Ca is not an artifact of complexation in Cl media. These K_v values are also consistent with earlier published Ca–Mg selectivity of the same clay in perchlorate media. The $CaCl^+$ and $MgCl^+$ complexes comprised an insignificant amount of the exchangeable cations.

P REDICTION of the effect of irrigation water on soil solution composition is dependent on the cation exchange process and thus the selectivity that a soil complex has for a particular ion. The exchange reactions involving Na–Ca–Mg have been studied extensively in bulk soils and soil clays as well as in relatively pure specimen clays. From all these investigations it is apparent that the exchange reactions characterized for specimen clays cannot yet be used to predict exchange behavior in soil clays. Solution chemistry models thus require that soil cation-exchange constants be measured for the individual soils and under the chemical conditions to be simulated. The site specificity of exchange constants is one of the obstacles to generalization of predictive soil water models.

Poor prediction of cation exchange constants in soils is due to several factors. Clays may not behave as simple mixtures, as evidenced by the inability to predict exchange constants of a mixture from those of the pure clays (Krishnamoorthy and Overstreet, 1950). Organic matter and oxides also have exchange capacities and their exchange constants are usually much different from those of clays. Samples of the same clay mineral from different locations also have different exchange constant values, due in part, to variation in structural composition

The possibility that ion pairs are important species on the exchange complex has been discussed by several researchers (Bower and Truog, 1940; Babcock et al., 1959). Recently, Sposito et al. (1983a,b), concluded that $CaCl^+$ and $MgCl^+$ are important in montmorillonite exchange in Cl media. They noted that almost all exchange experiments with specimen clays

have been conducted in Cl background solutions. Sposito et al. (1983a), estimated that for Na–Ca exchange in their Cl media experiments, up to half of the exchangeable Ca was in the form $CaCl^+$ and that for Na–Mg exchange up to about 30% of the exchangeable Mg was in the form $MgCl^+$. If these ion pairs are adsorbed, then Ca–Mg exchange in a Cl background is actually a quarternary system (or even a quinternary system if H^+ competition is considered).

Sposito et al. (1983b), further hypothesized that the reported preference of montmorillonite for Ca over Mg was due to the use of Cl. The increase in adsorbed charge with increasing exchangeable Ca or Mg (when the counter ion was Cl), was considered an artifact of attributing all adsorbed Ca to the species Ca^{2+}. This hypothesis was supported by the equal preference of montmorillonite for Ca and Mg in the presence of a perchlorate (ClO_4) background (which is assumed not to form complexes), reported by Sposito et al. (1983b).

The present study was initiated to examine Mg–Ca exchange in SO_4 and ClO_4 (perchlorate) media and Mg–Ca exchange in Cl media under different ionic strengths. Our objective was to evaluate the importance of Ca and Mg chloride complexes in Ca and Mg exchange reactions and the applicability of selectivity values determined with one anion to other anion systems. If the preference for Ca over Mg in the Cl system is due to the preference of $CaCl^+$ over $MgCl^+$ then Ca and Mg should have equal preference in the SO_4 and ClO_4 media. Additionally, Ca preference in Cl media should increase with increasing ionic strength as the percent Ca complexed and the activity ratio $CaCl^+/Ca^{2+}$ increases. These predictions have important implications for saline soils and especially for the reclamation of sodic soils by using Ca salts.

MATERIALS AND METHODS

The Na–montmorillonite, SWy-1, (Crook County, WY) was obtained from the Clay Mineral Society Source Clay Repository. This SWy-1 bentonite was also used by Sposito et al. (1983a,b) in their studies of Ca–Mg, Na–Ca and Na–Mg exchange. In 0.25 L tared bottles, 32.0 g of clay were reacted with 0.200 L of 1 M NaCl. The bottles were shaken for 15 min then centrifuged for 10 min at 3400 $\times$ g and 25 °C. The supernatant was decanted and the procedure repeated. Each bottle was subsequently reacted with 0.05 M NaCl and treated in a similar manner. The clay was next mixed with 20 L of 0.02 M NaCl and left standing for 16 h. The <2-μm size fraction was decanted, centrifuged and dried for 36 h at 60 °C.

A subsample of the prepared clay was Mg saturated and equilibrated with glycerol at 30% humidity. A prepared oriented slide gave x-ray diffraction basal reflections in agreement with published data for Wyoming montmorillonite (Brown, 1972). We detected no other minerals except a trace of quartz in our prepared SWy-1 clay. Montmorillonite standards were spiked with 0 to 10% vermiculite by weight, Mg saturated and equilibrated with glycerol at 30% humidity. Based on the estimated detection limit of 0.5% we consider that SWy-1 contains < 0.5% vermiculite.

Mixed Ca–Mg solutions (0.0300 L) were added to Oak Ridge centrifuge tubes containing 0.300 g of prepared clay. The clays were reacted at various Ca–Mg ratios, first with 1.0 M solutions. Suspensions were placed on a shaker for 2 h, centrifuged at 16 300 $\times$ g for 20 min at 25 °C and the supernatant discarded. This process was repeated. The clays were next reacted with solutions with the same Ca–Mg ratios at 0.025 moles$_c$ L^{-1} (either Cl or SO$_4$). Suspensions were placed on a shaker for 2 h, centrifuged at 16 300 $\times$ g for 20 min at 25 °C and the supernatant discarded. After two more rinses with solutions of the same composition, the third equilibration was 16 h at 23 °C. The suspensions were centrifuged and the supernatants collected for determination of Ca, Mg and Cl or SO$_4$. The bottles were reweighed to determine the amount of clay and solution remaining. Next the samples were extracted three times with 1.0 M ammonium acetate. The supernatants of each sample were composited after centrifugation and made up to fixed volume for analysis of Ca, Mg, and Cl or SO$_4$. The pH values were all between 6.0 and 6.6. Three replicate clay samples were reacted for each solution composition. The Ca and Mg were analyzed by inductively coupled plasma using standards prepared in the background acetate, Cl, SO$_4$ or ClO$_4$ media. The exchangeable cations were determined by subtracting the excess cations present in the residual carryover solution from the total extracted cations. This correction was based on the quantity of Cl or SO$_4$ found in the acetate extract. Similar experiments to those described above were conducted with 0.0500 and 0.100 M Ca–Mg Cl solutions and with 0.03 M ClO$_4$ solutions.

RESULTS AND DISCUSSION

Table 1 lists the exchangeable quantities and Ca and Mg solution concentrations for the reactions in SO$_4$ media. The total adsorbed metal charge is given as

$$Q = \sum_{i=1}^{n} q_i \qquad [1]$$

where q_i equals the surface excess (in moles of charge per kilogram of clay) of a metal cation species. In SO$_4$ media Q was 0.835 mol$_c$ kg^{-1} with a standard deviation of 0.022 and a SE of 0.0065. The mean value of Q for the reactions in Cl media, listed in Table 2, was 0.828 with a standard deviation of 0.021 and a SE of 0.0063. There was no statistically significant difference between the apparent adsorbed metal charge in the Cl as compared to the SO$_4$ solutions (at the 5% or even 50% confidence level). The Ca–Mg SO$_4$ solutions did not contain charged ion pairs and thus the apparent and actual adsorbed metal charge should be equal. If Cl ion pairs were important for exchange, Q would be

predicted to be greater in the Cl as compared to SO$_4$ media. The larger Q values reported by Sposito et al. (1983a) as compared to this study appear consistent with the finer particle size of their clay fraction. Talibudeen and Goulding (1983), observed larger CEC values for the smaller, as compared to larger size clay fraction of Wyoming bentonite. They attributed the CEC difference to a greater percentage of fully expanding layers in the finer clay fraction.

A further test of the idea that the Wyoming bentonite preference for Ca over Mg in Cl solutions is due to preferential adsorption of CaCl$^+$ was made by examining the change in Q with changing exchanger composition. A change in Q is a necessary but not sufficient indicator of CaCl$^+$ preference. If CaCl$^+$ is preferred over MgCl$^+$ on the exchanger, then there should be an increase in Q as exchangeable Ca increases. The Q values in Table 2 showed no significant trend (at the 5% level) of increasing Q with increasing exchangeable Ca. As expected, there was also no trend of increasing Q with increasing exchangeable Ca in the SO$_4$ solutions. The data shown in Table 3 for higher ionic strength do, however, show a trend of increasing Q with increasing exchangeable Ca. The trend in the 0.050 M Cl solutions was not significant (at the 5% level) but the trend in Q for the 0.100 M Cl solution was significant (at the 1% level). Possible reasons for increasing Q (other than MCl$^+$) including displacement of H on the variable charge component of the CEC, will be discussed later.

The evidence for substantial ion pair adsorption based on apparent differences in CEC is ambiguous. Jensen and Babcock (1973), using Cl solutions, found an increase in Q with increasing Ca saturation in K–Ca exchange on Yolo loam soil, however; they found no increase in Q with increasing Mg in K–Mg reactions or increasing Ca in Mg–Ca reactions. Some of

Table 2. Ca–Mg exchange on Wyoming bentonite in 0.025 M Cl solution.

Ca	Mg	q_{Ca}	q_{Mg}	Q
mmol L^{-1}		mmol kg^{-1}		
0.005	12.6	8.80	828	837
1.25	11.3	102	746	848
2.46	9.67	198	635	833
3.74	8.64	267	561	828
4.82	7.34	353	499	852
6.24	5.98	434	389	823
7.40	4.78	505	297	802
8.82	3.34	584	224	808
9.75	2.34	656	148	804
11.2	1.20	737	75	812
12.3	0.00	844	14.9	859

Table 3. Ca–Mg exchange on Wyoming bentonite in 0.050 M and 0.100M Cl solution.

Ca	Mg	Cl	q_{Ca}	q_{Mg}	Q
mmol L^{-1}			mmol kg^{-1}		
5.20	23.5	50	138	561	699
10.3	17.9	50	281	443	724
15.7	11.6	50	472	314	786
20.8	5.93	50	613	166	779
10.3	38.7	100	167	537	704
20.6	29.4	100	315	396	711
31.2	19.4	100	474	257	731
42.2	9.80	100	619	125	744

Table 1. Ca–Mg exchange on Wyoming bentonite in 0.0125 M SO$_4$ solution.

Ca	Mg	q_{Ca}	q_{Mg}	Q
mmol L^{-1}		mmol$_c$ kg^{-1}		
0.0083	12.87	11.1	856	867
1.44	11.33	106	752	858
2.85	9.91	198	641	839
4.17	8.72	282	557	839
5.45	7.56	369	473	842
6.79	6.20	437	377	814
8.03	4.92	526	308	834
9.46	3.68	580	212	792
10.08	2.39	683	146	829
12.26	1.29	753	69.5	823
13.17	<0.0005	836	000	836

these differences may be due to heterogeneous sites. Organic matter is known to exhibit Ca-specific sites, so that its presence would result in increases in Q with increasing Ca. For these reasons it is preferable to examine only the data for pure clays. Even in pure clays, however, exchange capacity has been shown to consist of several distinct sites (Talibudeen and Goulding, 1983), which makes interpretation of isotherms difficult.

Jensen (1973) examined K–Ca exchange on Clarsol bentonite and considered that Q was constant. Maes and Cremers (1977) found a 7 and 10% increase in Q for the Ca as compared to Na-saturated Otay and Camp Berteau bentonite, respectively. Their observation was based on Na- and Ca-saturated clay which underwent dialysis. This process results in hydrolysis of the exchanger cation (Shainberg, 1973; Frenkel and Suarez, 1977). Van Bladel and Menzel (1969), also found increasing Q with increasing divalent cation saturation for Na–Sr exchange, however, the trend with increasing ionic strength was reversed. Maes et al. (1975) found 5 to 10% increases in Q when Ni, Cu, Zn, and Co as compared to Na were the exchange end members. This result was explained as due to preferential adsorption of divalent ions on the pH dependent sites, estimated by Maes et al. (1975) to be 28% of the total sites at pH 5.8. This value may be too large, since there is often reasonable correspondence between measured Q and theoretical Q values based on isomorphous substitution. Alternative explanations include cation hydrolysis at low pH, which would likely not affect di-divalent selectivity, as well as the adsorption of metal hydroxide complexes. These trace metals, unlike the alkali and alkaline earth metals, form strong hydroxide complexes which could partake in exchange.

The Ca–Mg exchange isotherms for montmorillonite in Cl and SO$_4$ solutions at 0.025 mol$_c$ L^{-1} are shown in Fig. 1. These values are directly comparable since they were all at an ionic strength of 0.037, calculated using the program GEOCHEM (Sposito and Mattigod, 1980). There were no apparent differences in Ca–Mg exchange in the SO$_4$ as compared to Cl media.
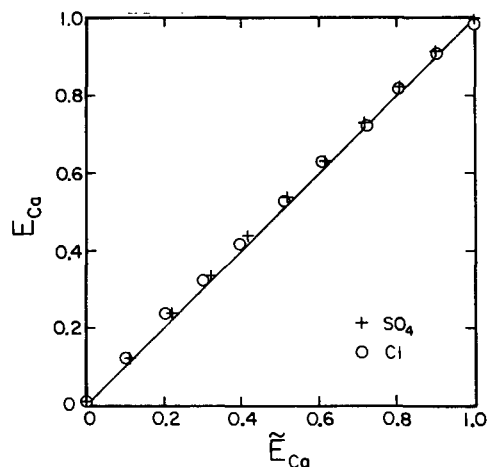
Also shown in Fig. 1, as the solid line, is the thermodynamic nonpreference isotherm. In both media there was a slight Ca preference on the exchanger. This Ca preference is consistent with the published data for Ca-Mg exchange in Cl media. The Ca–Mg exchange isotherms in Cl media at three different ionic strengths, given in Fig. 2, can be represented by a single line.

Vanselow selectivity coefficients were calculated from the exchange data in Tables 1 and 2. Where

$$K_v = \frac{X_{Ca}}{X_{Na}} \cdot \frac{a_{Mg}^{2+}}{a_{Ca}^{2+}} \qquad [2]$$

and X_{Ca} is the mole fraction of Ca on the exchanger. Solution activities of Ca^{2+} ($a_{Ca^{2+}}$) and Mg^{2+} ($a_{Mg^{2+}}$) were calculated using the Davies equation, the free metal concentrations and ionic strength values obtained from the speciation program GEOCHEM (Sposito and Mattigod, 1980). Use of the Debye-Huckel equation yields lower activity coefficients for Ca as compared to Mg, thus greater Ca selectivity over Mg on the exchanger. For the purposes of this analysis, we assumed that CaSO$_4$ and MgSO$_4$ ion pairs do not participate in exchange. The calculated solution concentrations of CaCl$^+$ and MgCl$^+$ were 2.4% and 2.0% of the total Ca and Mg concentrations in solution, respectively.

The selectivity coefficient values shown in Fig. 3 indicate that there is no apparent difference between Ca–Mg exchange in Cl as compared to SO$_4$ media. These results indicate that CaCl$^+$ and MgCl$^+$ either have equal exchange affinity, or insignificant amounts of these species adsorb on Wyoming bentonite. Since there was no trend in K_v values with increasing E_{Ca} (not significant at 5% level) we were able to compare the mean values in the Cl, SO$_4$, and ClO$_4$ media. The mean K_v values and standard deviations were 1.11 ± 0.09 for Cl media. 1.15 ± 0.04 for SO$_4$ media and 1.10 ± 0.04 for ClO$_4$ media.

Based on these data, we conclude the following: (i) There is no statistical difference in K_v for Ca–Mg exchange in Cl, SO$_4$ and ClO$_4$ media (not significant at 5% level), and (ii) there is a significant preference for Ca over Mg in SO$_4$, Cl and ClO$_4$ media. Further sup-

Fig. 1. Ca–Mg exchange isotherms on Wyoming bentonite in 0.025 mol$_c$ L^{-1} Cl and SO$_4$ media. These solutions are at comparable ionic strength (μ = 0.037). $E_{Ca} = q_{Ca}{}^{2+}/Q$ and $\tilde{E}_{Ca} = 2$ Ca mol L^{-1}/ sum mol$_c$ L^{-1}.
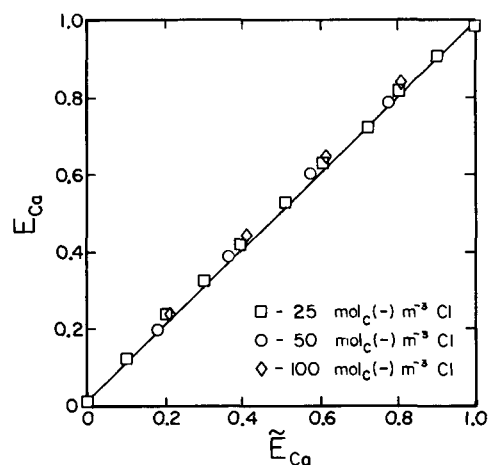

Fig. 2. Ca–Mg exchange isotherms on Wyoming bentonite in 0.025, 0.050, and 0.100 M Cl media. $E_{Ca} = q_{Ca}{}^{2+}/Q$ and $\tilde{E}_{Ca} = 2$ Ca mol L^{-1}/sum mol$_c$ L^{-1}.

porting information is provided by the equilibrations at higher ionic strength. There was no significant difference (at 5% level) in K_v with ionic strength (Fig. 4), despite an increase in the percentage of the metals present as Cl complexes (6.2 and 5.0% of solution Ca and Mg, respectively).

The Ca–Mg exchange data obtained in this study can also be compared to $K_v = 1.0 \pm 0.2$ obtained by Sposito et al. (1983b), also on SWy-1 Wyoming bentonite, in ClO_4 media. They concluded that there was no preference of Ca over Mg, however their data are not inconsistent with the Ca preference found in the present study. There was no significant difference (at the 5% level) between their K_v in ClO_4 media and the K_v determined for Cl, ClO_4, or SO_4 media in this study. The Ca preference found in the present study is also consistent with the results of earlier studies (see Table 4). Gheyi and Van Bladel (1975), considered this Ca preference due to the smaller equivalent volume of the hydrated Ca as compared to Mg ion. This concept has applicability over a wide spectrum of homovalent exchange reactions and is manifested in the lyotropic series. For soil clays the divalent cation ion preference is generally in the order Ba > Sr > Ca > Mg, consistent with increasing preference with decreasing hydrated radius and decreasing polarizing power (Talibudeen, 1981). Krishnamoorthy and Overstreet (1950) reported the same order for Utah bentonite.

The mean K_v value for our data is slightly lower than the average K_v of 1.28 ± 0.24 calculated from the values compiled in Table 4. Several authors used the Debye-Huckel equation for activity coefficients, thus their K_v values are larger than if the Davies equation had been used. Previously published values could not be corrected to obtain a consistent data set because the method of activity calculation or raw data was not always provided by the authors. Variations in selectivity can also result from different preparation methods which may introduce hysteresis into the exchange reaction (Tabikh et al., 1960). Other significant factors affecting selectivity include the surface charge density, location of the charge deficiency in the silicate struc-
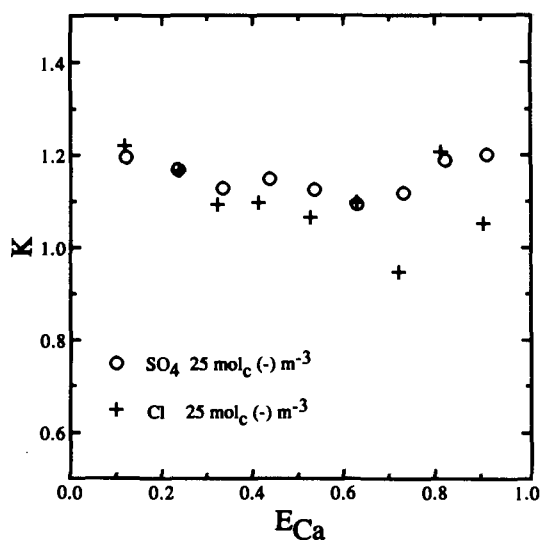
Table 4. Ca–Mg Selectivity coefficient on montmorillonite.

Clay	Anion	Concentration	K, mean	SD	Source
Wyoming bentonite SWy-1	ClO_4	0.05 M	1.0	± 0.2	Sposito et al., 1938b
Camp Berteau	Cl	—	1.38	± 0.13	Gheyi and Van Bladel, 1975
Wyoming bentonite	Cl	0.01 M	1.05	0.08	Clark, 1966
Wyoming bentonite (API no. 26)	Cl	0.1, 0.06 M	1.47	—	Levy and Shainberg, 1972
Otay Mesa, CA	Cl	0.04 M	1.31	± 0.06	Hunsaker and Pratt, 1971
Wyoming bentonite, Colony	Cl	—	1.65	—	Tabikh et al., 1960
Utal bentonite	Cl		1.09		Krishnamoorthy and Overstreet, 1950

ture, and contamination of the clay by organic matter and calcite.

The surface charge density and location of the clay charge deficiency affect the selectivity of exchange reactions. Increases in charge density produce increases in selectivity. Maes and Cremers (1979), for example, noted that the preference of Na over Li, K over Na, Rb over Na, and Cs over Na were all greater for Chambers ($Q = 1.200$ mol_ckg^{-1}) than for Wyoming bentonite ($Q = 0.850$ mol_ckg^{-1}). This effect can be attributed to increased selectivity with increasing charge density, since both specimens contain about 25% tetrahedral charge. The selectivity sequence for monovalent ions on montmorillonite listed above follows the order expected from hydration energies, i.e., the surface is selective for the cation with the smallest hydration energy. Maes and Cremers (1979) also observed this increasing selectivity of Cs over Na with increasing charge for octahedrally substituted montmorillonites. Their data also showed less preference for Cs at the same surface charge density, for partially tetrahedrally substituted vs. octahedrally substituted montmorillonites. It follows that Ca should be pre-
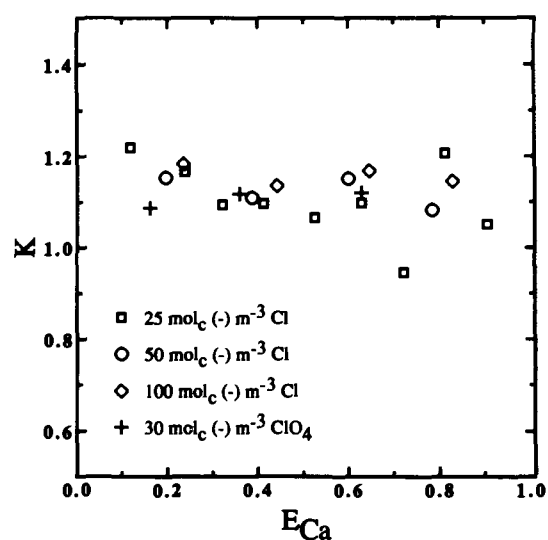

Fig. 3. Ca–Mg exchange constant (K_v) for Wyoming bentonite in 0.025 mol_c L^{-1} Cl and SO_4 media.

Fig. 4. Ca–Mg exchange constant (K_v) for Wyoming bentonite in 0.025, 0.050, 0.100 M Cl and 0.03 M ClO_4 media.

ferred over Mg (based on hydration energies or Lewis acid softness) and that the preference should decrease with decreasing surface charge density and increasing tetrahedral substitution. Using the composition data of Weaver and Pollard (1973), Sposito et al. (1983a), estimated that one-third of the exchange capacity of SWy-1 montmorillonite is due to tetrahedral substitution. Based on the above reasoning and the relatively low surface charge density of SWy-1 montmorillonite most montmorillonites should show a greater preference for Ca over Mg than the SWy-1 used in this study. Indeed, consistent with this reasoning, the K_v values in Table 4 are slightly greater than those found in the present study.

Additional literature data are available to test the hypothesis of measurable $CaCl^+$ and $MgCl^+$ adsorption and equal Ca–Mg selectivity on montmorillonite. Levy et al. (1983), examined the effect of exchangeable Na on Ca–Mg selectivity on Wyoming bentonite. They reported no difference in selectivity between the binary Ca–Mg system and the ternary Na–Ca–Mg system (at 27% exchangeable Na). Since the introduction of Na also resulted in an increase in Cl, the $a_{CaCl^+}/a_{Ca^{2+}}$ and $a_{MgCl^+}/a_{Mg^{2+}}$ ratios were increased. Using the program GEOCHEM (Sposito and Mattigod, 1980) we calculated that the Ca and Mg complexed as $CaCl^+$ and $MgCl^+$ increased from about 3.5 and 2.7% in a Ca–Mg–Cl solution to 9 and 11% respectively, in the Ca–Mg–Na–Cl solutions. Despite increased availability of $CaCl^+$ for adsorption no increase in Ca preference was observed.

Since the published Ca–Mg exchange selectivity in ClO_4 media is not in conflict with the Ca preference reported in this study for Cl, SO_4 and ClO_4 media, the evidence for $CaCl^+$ and $MgCl^+$ exchange stems from the change in Q in Ca–Na and Mg–Na exchange experiments in Cl and ClO_4 media (Sposito et al., 1983a).

The statistical significance of the differences between the $CaCl^+$ and $MgCl^+$ exchange isotherms shown by Sposito et al. (1983a) cannot be determined and thus the differences in K_v (Sposito et al., 1983b) cannot be analyzed. The reported values were based on "smooth curves as functions of the charge fraction" rather than the experimental data (Sposito et al.,
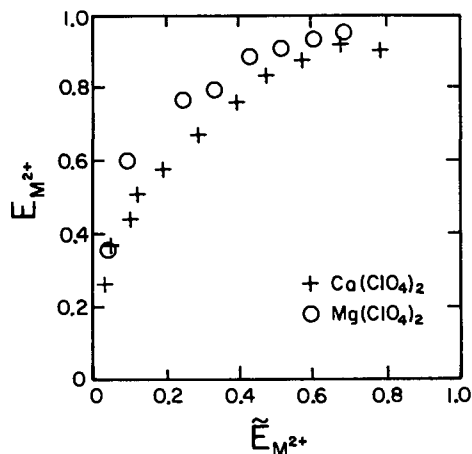
1983a). The Ca–Na and Mg–Na exchange isotherms shown in Fig. 5 for ClO_4 media are calculated from the raw data in Tables 2 and 3 of Sposito et al. (1983a). These data clearly show that Mg preference over Na was greater than Ca over Na in ClO_4 media. In contrast, the exchange isotherms for Ca–Na and Mg–Na in Cl media shown in Fig. 6 (calculated from the raw data in Tables 4 and 5 of Sposito et al., 1983a), indicate equal Ca and Mg preference. This does not support their hypothesis which should predict the following (i) Ca and Mg equally preferred over Na in the ClO_4 media and (ii) Ca preferred over Na more than Mg is over Na in the Cl media.

We also recalculated the apparent exchange isotherms for $CaCl^+$ and $MgCl^+$ using the exchanger data and Na^+ solution concentrations in Tables 4 and 5, and the Ca^{2+}, $CaCl^+$, Mg^+, and $MgCl^+$ concentrations in Tables 6 and 7, of Sposito et al. (1983a). Figure 7 is thus directly comparable to Fig. 1 of Sposito et al. (1983a) except that they used the smoothed Q and q_{Na} values and we used the calculated values from their data. To calculate exchangeable ion pairs we used their
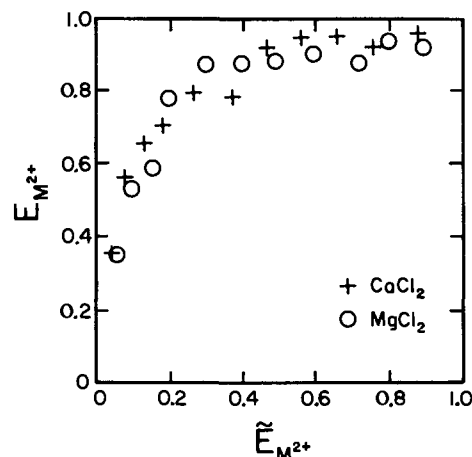

Fig. 6. Ca–Na and Mg–Na exchange isotherms on Wyoming bentonite in Cl media (calculated from data in Sposito et al., 1983a, Tables 4 and 5).
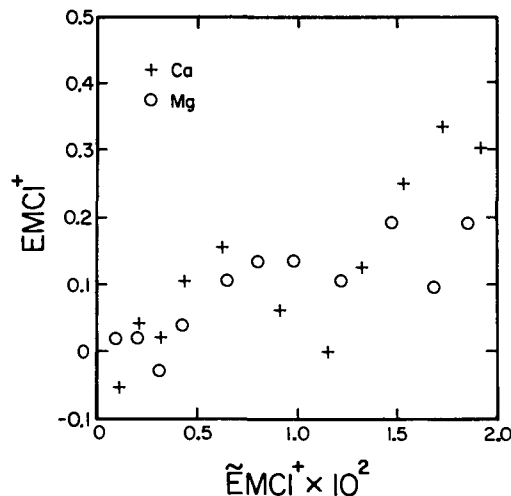

Fig. 7. $CaCl^+$–Ca^{2+}–Na and $MgCl^+$–Mg^{2+}–Na exchange isotherms on Wyoming bentonite in 0.050 M Cl media (calculated from data in Sposito et al., 1983a, Tables 4, 5, 6 and 7). Data were calculated assuming increases in Q were the result of MCl^+ absorption.

Fig. 5. Ca–Na and Mg–Na exchange isotherms on Wyoming bentonite in ClO_4 media (calculated from data in Sposito et al., 1983a, Tables 2 and 3).

values of Q_0 and their assumption that values of Q greater than Q_0 were the result of adsorbed MCl^+. Figure 7 demonstrates that the apparent isotherm for $CaCl^+$ was not significantly different than that for $MgCl^+$. The data shown in Fig. 7 was fit to linear and 2nd- and 3rd-order polynomial models. In all instances there were no significant differences (at the 5 or 10% levels) between the data sets, thus the apparent exchange affinity of $CaCl^+$ and $MgCl^+$ appear similar in these experiments.

CONCLUSIONS

Determination of Ca–Mg exchange isotherms on SW_y-1 Wyoming bentonite does not confirm the hypotheses that Ca^{2+} and Mg^{2+} have equal preference and that apparent Ca preference in Cl media is due to preferential adsorption of $CaCl^+$ over $MgCl^+$. The following observations were made: (i) CEC values were the same in Cl and SO_4 media indicating no detectable MCl^+ complexes on the exchanger, (ii) There was no trend of increasing CEC with increasing Ca for either the 0.025 mol_c L^{-1} (ionic strength 0.037) Cl or SO_4 systems; (iii) There was no trend of increasing CEC with increasing ionic strength in Cl media despite the increase in proportions of Ca and Mg complexed as $CaCl^+$ and $MgCl^+$, (iv) Ca selectivity over Mg was established in Cl, SO_4 and ClO_4 media; (v) The K_v exchange constants of 1.11, 1.15 and 1.10 determined in Cl, SO_4 and ClO_4 media respectively, were not significantly different from each other, or from the published constant for Ca–Mg exchange in ClO_4 media.

The relatively low Ca preference over Mg exhibited by SW_y-1 montmorillonite as compared to other montmorillonites may be due to its relatively low CEC and relatively high tetrahedral site charge. The K_v values for Ca–Mg exchange obtained in this study are applicable for varying ionic strength and anion composition.

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