

Calcium and Sulfate Retention by Two Oxisols of the Brazilian Cerrado

E. Marcano-Martinez and M. B. McBride

ABSTRACT

The ability of two representative oxisols from the Cerrado region of Brazil to adsorb Ca^{2+} and SO_4^{2-} , when in their natural acidic state, was determined by using dissolved CaCl_2 , K_2SO_4 , and CaSO_4 salts as adsorbates. Calcium adsorption from CaCl_2 and CaSO_4 was nearly linearly dependent on the equilibrium Ca^{2+} concentration, and was most successfully fitted to a Freundlich equation. Conversely, sulfate adsorption from K_2SO_4 and CaSO_4 was curvilinearly dependent on equilibrium SO_4^{2-} concentration, conforming more closely to Langmuir adsorption behavior. Calcium adsorption was explained by nonspecific electrostatic attraction to soil clays, and did not appear to be adsorbed to any significant degree by the native organic matter. Sulfate adsorption was attributed at least in part to a ligand exchange mechanism, resulting in a measured increase in the negative charge of the soil surfaces. Simultaneous adsorption of Ca^{2+} and SO_4^{2-} from CaSO_4 solutions caused an enhancement in retention of both ions at higher concentrations, despite undersaturation with respect to gypsum precipitation. A mechanism of CaSO_4 ion pair adsorption on mineral surfaces is proposed in which the presence of one ion facilitates adsorption of the other.

SURFACE CHARGE in variable-charge soils is altered by adsorption of anions with high affinities for the surface, such as phosphate, sulfate, and silicate (Mott, 1981), as well as by selectively adsorbed cations such as Ca, Ba, Zn, and Cu (Breeuwsma and Lyklema, 1973; Huang and Stumm, 1973; Parfitt, 1980). Phosphate adsorption has received the most attention in the study of anion adsorption by soils and effects on surface charge. Sulfate adsorption by acid soils has also been studied extensively (Chao et al. 1962; Couto et al. 1979; Gebhardt and Coleman, 1974; Harward and Reisenauer, 1966; Johnson et al., 1979; Singh, 1984a,b,c), although the effect of sulfate adsorption on surface charge properties has not received much attention. Some workers considered sulfate to adsorb electrostatically (Marsh et al., 1987; Mott, 1981); others postulated that sulfate coordinates to surfaces of oxides by a ligand exchange mechanism (Parfitt and Smart, 1978; Rajan, 1978), altering the point of zero charge (PZC) of the oxide. Rajan (1978, 1979) reported a decrease in the PZC of both hydrous alumina and allophane after adsorption of sulfate. On the other hand, Breeuwsma and Lyklema (1973) reported the PZC of hematite to increase after sulfate adsorption.

Couto et al. (1979) showed evidence that SO_4^{2-} adsorption increased the retention of cations in two Oxisols and an Alfisol. Similar results have been observed by Hue et al. (1985) and Zhang et al. (1987). As a result of the ligand exchange mechanism of adsorption, SO_4^{2-} retention is usually accompanied by a rise in pH of the soil solution due to the release of OH^- groups from the surface (Couto et al., 1979; Mott,

1981). This higher pH in itself increases the ability of the soil to retain cations because of the pH-dependent charge of Oxisols (Bowden et al., 1980).

The adsorption of Ca^{2+} is believed to create positive charge on oxides (Kinniburgh, 1983), but the magnitude of this charge, detectable as an increase in anion retention, has not been reported. In addition, there is very little information on the adsorption behavior of this ion in variable-charge soils. Most of the studies involving Ca^{2+} adsorption have been limited to Ca-K (or another monovalent cation) or Ca-Mg exchange reactions, on layer silicates (Galindo and Bingham, 1977; Goulding and Talibudeen, 1980; Hunsaker and Pratt, 1971; Hutcheon, 1966).

The study of the behavior of Ca^{2+} and SO_4^{2-} in soils is of agricultural importance because of their major role as plant nutrients. In Oxisols, the amount of Ca^{2+} available to plants is usually low and tends to decrease with depth; values of less than 0.1 cmol_c/kg are not uncommon below a depth of 15 to 30 cm (Reeve and Sumner, 1972; Ritchey et al., 1982). Sulfate is deficient in some tropical soils; the SO_4^{2-} already present might not be readily available to plants because of strong adsorption (Fox, 1980). The application of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has been recommended to overcome the problems of Ca^{2+} deficiency in the lower horizons of acid soils (Gillman and Sumner, 1987; Ritchey et al., 1980). The greater mobility in soils of gypsum compared with lime makes gypsum a better source of Ca^{2+} for the subsoil.

The objective of this study was to compare the behavior of Ca^{2+} and SO_4^{2-} in two representative soils of the Brazilian Cerrado when applied individually as CaCl_2 and K_2SO_4 , to behavior when applied together as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. For this reason, adsorption isotherms were measured using solutions of CaCl_2 , K_2SO_4 , and CaSO_4 as adsorbates. It was initially assumed that both K^+ and Cl^- were indifferent ions and did not significantly affect the specific adsorption of either Ca^{2+} or SO_4^{2-} . The effect of the adsorption of these ions on the development of surface positive or negative charge was determined by measuring differences in retention of anions and cations after Ca and sulfate adsorption.

MATERIALS AND METHODS

Soil Characteristics

The soils used in this study were the Dark Red Acrustox A and B horizons (DRA and DRB) and the Red Yellow Acrustox A and B Horizons (RYA and RYB) from Brazil. These soils have been described in detail elsewhere (Macedo and Bryant, 1987) and relevant soil chemical data are available in a separate paper (Marcano-Martinez and McBride, in review). Because *Soil Taxonomy* does not distinguish these soils, the nomenclature of the Brazilian classification, based upon soil color, is used in this paper.

Calcium Adsorption Isotherms

Two grams of soil were suspended in centrifuge tubes in 20 mL of 0.01 M KCl with a Ca^{2+} concentration of 0, 0.05,

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0.1, 0.15, 0.2, 0.25, 1.0, 1.5, 2.0, 2.5, and 3.0 mM as CaCl_2 . The treatments were replicated four times. These were shaken continuously for a predetermined equilibrium time of 1 h. At the end of the hour, samples were centrifuged and the supernatants collected for measurement of pH, Ca^{2+} , K^+ , Cl^- , and Al^{3+} . Next, the adsorbed Ca^{2+} and Cl^- were displaced by washing the soil four times with 20 mL of 0.25 M $\text{Mg}(\text{NO}_3)_2$, and the supernatants collected in 100-mL volumetric flasks; after making up to volume, the displaced Ca^{2+} and Cl^- were measured. The adsorbed ions were calculated after correcting for the KCl solution entrained in the soil volume. Calcium was determined by atomic absorption and Cl^- with a chloride electrode.

Sulfate Adsorption Isotherms

Two grams of soil were equilibrated with 20 mL of 0.01 M KCl with a SO_4^{2-} concentration of 0, 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, and 3.0 mM as K_2SO_4 in triplicated treatments. Two drops of toluene were added to each sample to suppress microbial growth. The samples were shaken intermittently for a predetermined equilibrium time of 24 h. After equilibration, the samples were centrifuged and the supernatants collected for determination of pH, SO_4^{2-} , K^+ , and Cl^- . The adsorbed K^+ was extracted by washing the soil four times with 0.1 M NH_4NO_3 , and collecting the supernatants after each wash in 100-mL flasks. Adsorbed sulfate was estimated from the amount initially present in the equilibrium solution minus the concentration found after equilibration. Sulfate was determined with a Dionex 2000i ion chromatograph (Dionex Corp., Sunnyvale, CA) with the AS3 column using an eluting solution of 0.003 M NaHCO_3 + 0.003 M Na_2CO_3 .

Simultaneous Ca^{2+} and SO_4^{2-} Adsorption

The concurrent adsorption of Ca^{2+} and SO_4^{2-} was studied by a similar procedure to Ca^{2+} and SO_4^{2-} adsorption. The levels of CaSO_4 dissolved in solution were 0, 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, and 3.0 mM in triplicate. Equilibration time was 24 h, after which time samples were centrifuged, and SO_4^{2-} and Ca^{2+} analyzed in the supernatants. The samples were then extracted with 0.25 M $\text{Mg}(\text{NO}_3)_2$ to displace and measure the adsorbed Ca^{2+} and K^+ .

RESULTS AND DISCUSSION

Calcium Adsorption

A kinetic study assessed the minimum required equilibration time for Ca^{2+} adsorption. A concentration of 0.5 mM CaCl_2 was added to the four soils in a 0.01 M KCl background. The change in Ca^{2+} concentration in solution, as well as pH, was measured after 5 min, 35 min, 1 h, 2 h and 3.5 h.

Adsorption of Ca^{2+} occurred quickly; Ca^{2+} concentration was constant 5 min after adding Ca^{2+} to the soil. Adsorption did not change the pH, suggesting that Ca^{2+} was adsorbing on sites previously occupied by K^+ . Negligible quantities of Al^{3+} were exchanged into solution by Ca^{2+} adsorption. Thereafter, an equilibration time of 1 h was selected for the CaCl_2 sorption studies as a matter of convenience.

The isotherms for Ca^{2+} adsorption from CaCl_2 were slightly curvilinear for all four soils as demonstrated in Fig. 1 for the Dark Red Soils. The isotherms for the Red Yellow soils (not shown) are similar to those for the Dark Red soils. There was little difference in adsorption between the A and B horizons of either soil. The nearly linear isotherms illustrated in Fig. 1

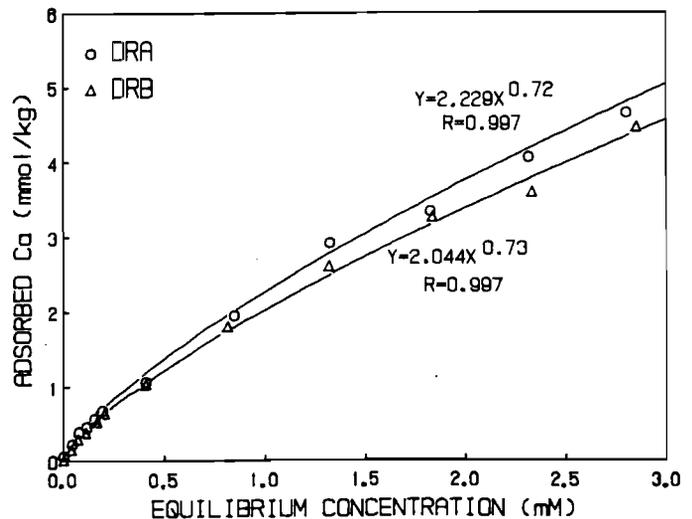


Fig. 1. Calcium adsorption isotherms (CaCl_2) for the Dark Red A (DRA) and B (DRB) horizons. Solid lines in this and subsequent figures represent the fitted equations.

have also been reported for Ca^{2+} and K^+ adsorption in other highly weathered soils (Fox, 1974, 1982).

The maximum amount of Ca^{2+} adsorbed under the experimental conditions and the proportion of the total cation exchange capacity (CEC) that this value represents (on an equivalent basis) are shown in Table 1. Assuming that the Ca^{2+} ion is acting as an exchangeable cation, the maximum adsorption obtained experimentally represents between 57 and 94% of the exchange sites. The fact that Ca^{2+} adsorption is not limited by available sites could explain the linear nature of the isotherms. In fact, when these adsorption data are compared with data for Ca^{2+} - K^+ ion exchange on permanent charge clays at similar ionic strength (Hutcheon, 1966), the selectivity for Ca^{2+} is not substantially different. In other words, the preference for Ca^{2+} , despite the presence of 0.01 M K^+ , can be explained by the concentration-valency effect of ion exchange theory.

Because of the difference in organic matter content between the A and B horizons, higher adsorption of Ca^{2+} was expected but not observed in DRA and RYA. Larger amounts of Al^{3+} and Fe^{3+} were organically complexed in these upper horizons (Marcano-Martinez and McBride, in review) possibly blocking exchange sites, and suppressing Ca^{2+} adsorption. This would explain the lack of difference between DRA and DRB, but not the similar behavior of RYA and RYB, because the CEC measured in the last two soils differed significantly.

Table 1. Comparison of the maximum Ca^{2+} retention and the CEC of the soils.

Soil	CEC† (mmol/kg)	Maximum Ca^{2+} sorption (mmol/kg)	% of total CEC
DRA	11.9 ± 0.8*	9.3 ± 0.03*	78.5%
DRB	13.4 ± 0.9	8.9 ± 0.2	66.2
RYA	15.7 ± 1.3	9.0 ± 0.1	57.0
RYB	9.2 ± 0.4	8.7 ± 0.1	94.3

* 95% confidence interval.

† Data from Marcano-Martinez and McBride, in press.

Numerous equations (including linear, quadratic, Langmuir, Freundlich, Tempkin and Gunary) were fit to the adsorption data by nonlinear regression analysis. The Freundlich and quadratic equations fit the Ca adsorption data most satisfactorily, with comparable R^2 and residual sum of squares (RSS) values. Consequently, the Freundlich was selected to describe adsorption because of its simplicity. The best-fit Freundlich equations are plotted in Fig. 1 for the Dark Red soils. The coefficients of these equations for all the soils are reported in Table 2.

Adsorption of Ca^{2+} and other metals on pure Fe and Al oxides results in the release of H^+ to solution with the surface becoming more positive (Huang and Stumm, 1973; Kinniburgh, 1983; Kinniburgh et al., 1975). In the present experiments Ca^{2+} adsorption did not decrease pH, i.e., displacement of protons by Ca^{2+} . This implies that Ca^{2+} was displacing exchangeable K^+ formed in the 0.01 M KCl medium. It is likely that these sites were on kaolinite because adsorption of Ca^{2+} on oxides is unlikely to be significant at the low native pH values of these soils (Kinniburgh and Jackson, 1982). Adsorption of Ca^{2+} occurred at a pH of 4.2 to 4.3 in the A horizons, and 4.7 to 4.8 in the B horizons.

The positive charge of the surface, measured by Cl^- retention, was not greatly affected by the adsorption of Ca^{2+} . In the four soil materials, Cl^- retention was nearly constant up to a Ca^{2+} concentration of 1 mM; at higher levels, Cl^- adsorption was higher but did not increase in proportion to increases in Ca^{2+} . The mean values of Cl^- retention at Ca^{2+} concentrations < 1 mM were 1.12, 3.81, 1.06, and 3.89 mmol/kg for DRA, DRB, RYA, and RYB respectively. For Ca^{2+} concentrations > 1 mM, Cl^- adsorption averaged 1.76, 3.85, 3.25, and 5.96 for these same soil materials. Higher Cl^- retention in the B horizons may reflect the lower organic matter, and greater number of positively charged oxide surface sites. These sites are involved in ligand exchange with functional groups of organic matter, reducing surface positive charge (Parfitt, 1978).

The increased Cl^- adsorption at high Ca^{2+} levels could be due to an increase in surface charge upon Ca^{2+} adsorption on oxides (Huang and Stumm, 1973).

Table 2. Freundlich function parameters ($Y = AX^B$) used to describe Ca^{2+} and SO_4^{2-} adsorption isotherms, and 95% confidence limits.

Horizon	Adsorbed Ion†	Parameter	
		A	B
DRA	Ca(Cl)	2.23 ± 0.05	0.72 ± 0.03
	Ca(SO ₄)	2.99 ± 0.15	1.03 ± 0.06
	SO ₄ (K)	3.50 ± 0.17	0.25 ± 0.04
DRB	SO ₄ (Ca)	5.65 ± 0.23	0.35 ± 0.04
	Ca (Cl)	2.04 ± 0.05	0.73 ± 0.03
	Ca(SO ₄)	ND	ND
RYA	SO ₄ (K)	4.86 ± 0.24	0.26 ± 0.04
	SO ₄ (Ca)	ND	ND
	Ca (Cl)	1.96 ± 0.05	0.87 ± 0.03
RYB	Ca(SO ₄)	2.69 ± 0.18	1.08 ± 0.08
	SO ₄ (K)	3.14 ± 0.16	0.23 ± 0.04
	SO ₄ (Ca)	4.57 ± 0.25	0.45 ± 0.06
RYB	Ca(Cl)	1.92 ± 0.05	0.81 ± 0.03
	Ca(SO ₄)	ND	ND
	SO ₄ (K)	3.93 ± 0.22	0.17 ± 0.03
	SO ₄ (Ca)	ND	ND

† Brackets denote the counterion associated with the adsorbing ion. ND = these adsorption data were not collected.

This mechanism should have been apparent at lower Ca^{2+} levels, however, requiring the displacement of protons from the oxide surface. Alternatively, adsorption of the ion pair CaCl^+ would have been significant at the highest CaCl_2 levels. Although the concentration of CaCl^+ in the aqueous phase would be very low even at the highest CaCl_2 additions ($\sim 2 \times 10^{-6}$ M), this ion pair may be preferentially adsorbed at clay surfaces. Selective adsorption of CaCl^+ or MgCl^+ complexes by smectites has been documented (Sposito et al., 1983). However, the simplest explanation of at least part of this Cl^- adsorption is the substantially increased Cl^- concentrations at the highest CaCl_2 levels, which could effect greater retention on positive charge sites.

Sulfate Adsorption

The reaction rate for sulfate adsorption was slower than for Ca. This is shown in Fig. 2 as a reduction in SO_4^{2-} concentration with time after mixing the soils with 0.5 mM K_2SO_4 . An equilibration time of 24 h was chosen for both K_2SO_4 and CaSO_4 adsorption studies based on these data.

Unlike Ca^{2+} , sulfate adsorption followed a high affinity isotherm, as seen in Fig. 3 for the Dark Red soil material. The Red Yellow soil materials produced similar isotherms (not shown). The B horizons had significantly higher adsorption than the A horizons. Both horizons of the Dark Red Acrustox adsorbed significantly higher amounts of SO_4^{2-} than the corresponding Red Yellow horizons; this effect was more noticeable in the B horizons.

The differences in SO_4^{2-} adsorption between the A and B horizons are probably an effect of organic matter content, since neither pH nor free Fe oxides can be related to these differences. Similar results have been reported previously (Bornemisza and Llanos, 1967; Couto et al., 1979; Johnson and Todd, 1983; Singh, 1984b). Organic anions in the A-horizons may compete with SO_4^{2-} for positively charged sites (Parfitt, 1978). The higher adsorption of sulfate in the Dark Red soil materials is probably attributable to the greater amount of Fe oxides in these soils compared to the

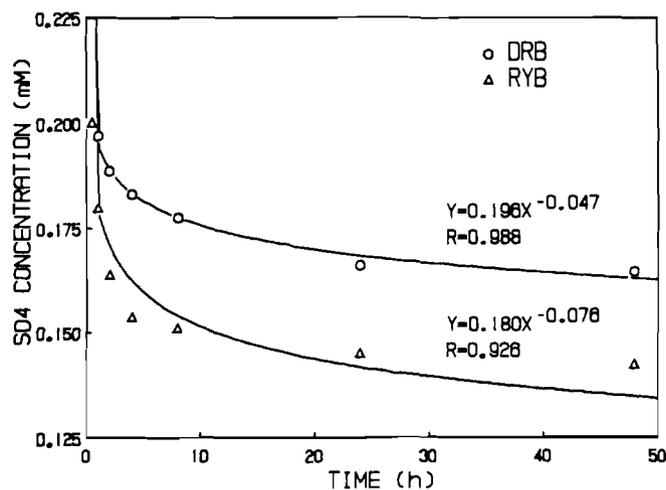


Fig. 2. Reduction of sulfate concentration with time in B horizon materials.

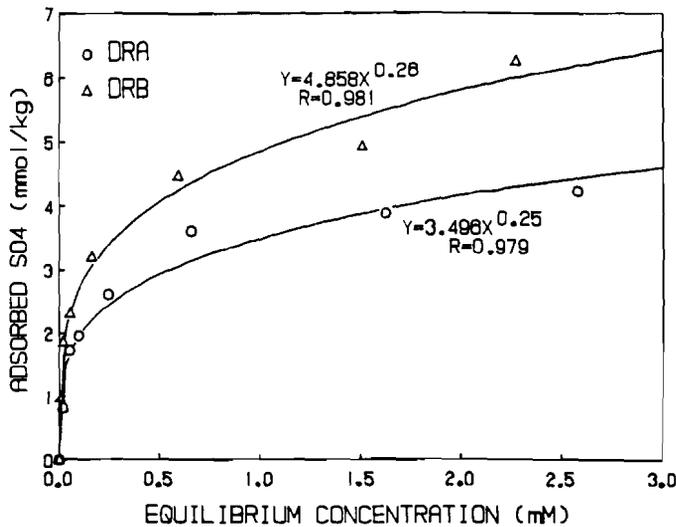


Fig. 3. Sulfate adsorption isotherms (K_2SO_4) in the Dark Red Acrustox (DRA).

Red Yellow soils (Marcano-Martinez and McBride, in review).

Adsorption isotherms for SO_4^{2-} tended toward a plateau or maximum adsorption, as seen in Fig. 3. As was done for the Ca isotherms, various equations (including the Langmuir) were tested by nonlinear regression analysis, to describe these data. The Freundlich equation was selected to describe SO_4^{2-} adsorption because of its good fit, simplicity, and superior residual plots (not shown). The plotted functions are shown in Fig. 3 for the Dark Red soil materials. The estimated coefficients, A and B, for all the soils are given in Table 2. Coefficient A differs significantly among the soil horizons, and is greatest for the B horizons. This coefficient relates to the affinity of the soil for SO_4^{2-} and is larger in the horizons of the Dark Red soil than the corresponding horizons in the Red Yellow soil. The B coefficient did not differ significantly from one horizon to the other within each soil profile.

The Freundlich equation has generally been able to describe SO_4^{2-} retention more successfully than the Langmuir equation because of the lack of a clear adsorption maximum (Chao et al., 1962; Bornemisza and Llano, 1967; Singh, 1984a; Weaver et al., 1985). However, the Langmuir equation has also been used to describe SO_4^{2-} retention in some soils (Kamprath et al., 1956; Couto et al., 1979; Hasan et al., 1970).

In all soil materials except RYB, the adsorption maxima obtained experimentally exceeded the AEC of the soils as determined by Cl^- adsorption (Marcano-Martinez and McBride, in review). This super-equivalent adsorption of sulfate has been reported previously (Rajan, 1979; Marsh et al., 1987), implying that SO_4^{2-} is adsorbed in preference to Cl^- . Even if the adsorption mechanism were simple electrostatic attraction, measurements of AEC with sulfate salts would give higher estimates than measurements with Cl^- or NO_3^- salts, (Van Raij and Peech, 1972; Morais et al., 1976). On the other hand, a specific adsorption mechanism (ligand exchange), could explain the preferential adsorption of SO_4^{2-} as well as the rise in pH and the increased K^+ retention (to be discussed) associated with SO_4^{2-} adsorption.

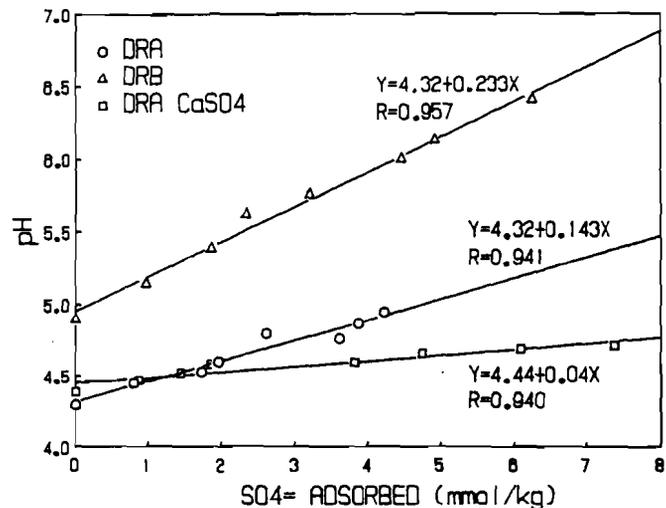
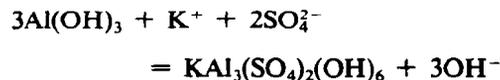


Fig. 4. Effect of the adsorption of sulfate from K_2SO_4 and $CaSO_4$ on soil pH in the Dark Red Acrustox (DRA).

Adsorption of K_2SO_4 increased the pH of the soil suspension almost linearly as shown in Fig. 4 for the Dark Red soil material. Similar results were obtained for the Red Yellow Soil (not shown). The calculated linear regression lines (significant at the 99% confidence level) are also depicted in Fig. 4.

An increase of the solution pH when SO_4^{2-} is adsorbed occurs in pure oxides (Parfitt and Smart, 1978; Rajan, 1978), clays (Rajan, 1979; Rao and Sridharan, 1984) and soils (Bornemisza and Llanos, 1967; Couto et al., 1979; Zhang et al., 1987). The higher pH could be due to a ligand exchange mechanism where SO_4^{2-} enters into direct coordination with the Fe or Al ion of the oxide surface as OH^- groups are displaced from the surface. Alternatively, precipitation of alunite $Al_4(OH)_{10}SO_4$, or basaluminite $KAl_3(OH)_6(SO_4)_2$ could raise the pH. Formation of these minerals at the expense of gibbsite results in the release of OH^- ions into solution according to the following reactions (Adams and Rawajfih, 1977; Lindsay, 1979)



In the present study, all solutions were undersaturated with respect to basaluminite, although alunite precipitation may have been possible at the highest SO_4^{2-} additions.

Adsorption of SO_4^{2-} increased the CEC (exchangeable $K^+ + 3Al^{3+}$) of the DRB, RYA, and RYB soil materials plotted in Fig. 5. Estimation of cation adsorption in DRA was not possible due to a very large experimental error for this particular measurement. The increases in CEC were not significantly different for the various soil materials and the calculated overall regression line gave a slope of 1.27 mmol/mmol SO_4^{2-} . Increases in CEC upon SO_4^{2-} adsorption have been reported previously in soils (Couto et al., 1979; Hue et al., 1985; Zhang et al., 1987) and allophane (Rajan, 1979). No effect on cation retention has been observed in kaolinite and alumina (Rajan, 1978; Rao and Sridharan, 1984), however. Creation of negative

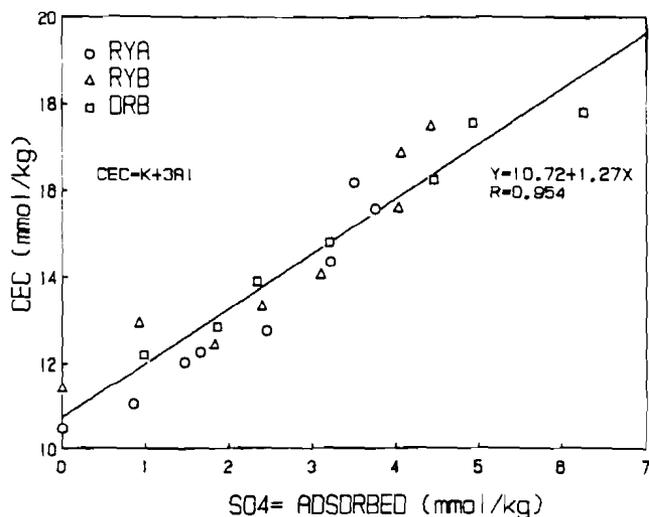


Fig. 5. Effect of the adsorption of sulfate from K_2SO_4 on the cation exchange capacity (CEC) of the soil materials.

charge upon SO_4^{2-} adsorption can be due to monodentate or bidentate complex formation at the surface.

The higher pH resulting from SO_4^{2-} adsorption can also increase the CEC of the soil, a consequence of the pH dependence of the soils' negative charge (Marcano-Martinez and McBride, in review). For DRB and RYB, the increase in pH alone is enough to generate some negative charge. For DRA and RYA, the change in pH from the lowest to the highest level of adsorbed SO_4^{2-} was not enough to increase the CEC significantly, so the higher CEC observed in these soil materials must have arisen largely from the SO_4^{2-} ligand exchange reaction.

Simultaneous Ca^{2+} and SO_4^{2-} Adsorption

Concurrent Ca^{2+} and SO_4^{2-} adsorption was measured for the A horizons only. As was found for adsorption of Ca^{2+} and SO_4^{2-} independently, the Ca^{2+} adsorption isotherm was almost linear while SO_4^{2-} adsorption more closely resembled a Langmuir type of isotherm. When compared with adsorption from $CaCl_2$ and K_2SO_4 solutions, adsorption from $CaSO_4$ above an equilibrium concentration of 0.5 mM caused greater retention of both Ca^{2+} and SO_4^{2-} (Fig. 6 and 7).

The adsorption data were fitted to a Freundlich equation, with calculated coefficients and the plotted functions shown in Table 2 and Fig. 6 and 7. In all cases, the coefficients obtained for Ca^{2+} and SO_4^{2-} adsorption from $CaSO_4$ were significantly higher than those obtained previously. In the case of Ca^{2+} adsorption, the B coefficients were not significantly different from unity; that is, the adsorption isotherms were described by straight lines with slopes equal to the coefficient A.

The higher Ca^{2+} retention in the presence of SO_4^{2-} might be explained by the increase in negative charge created by specific adsorption of SO_4^{2-} ions (see Fig. 5). However, the increased SO_4^{2-} retention in the presence of Ca^{2+} cannot be similarly explained by adsorption of Ca^{2+} , because this cation alone did not generate significant positive charge at the surface. It appears that an alternate mechanism of sorption is necessary to explain Ca^{2+} and SO_4^{2-} adsorption at the higher levels of addition.

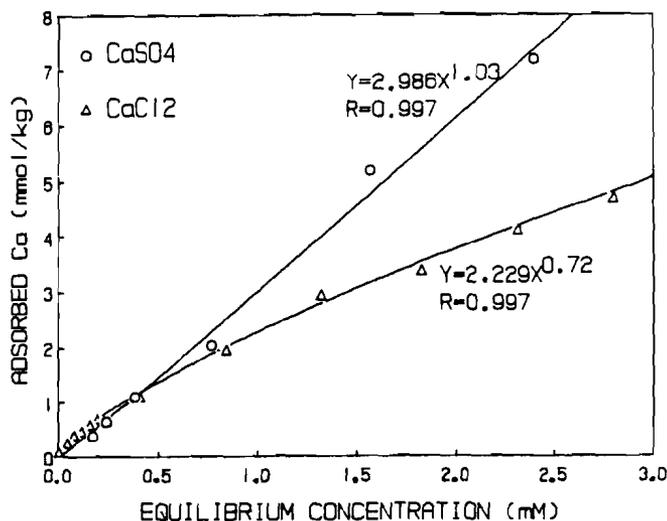


Fig. 6. Comparison of Ca^{2+} adsorption from $CaCl_2$ and $CaSO_4$ by the Dark Red A horizon (DRA) material.

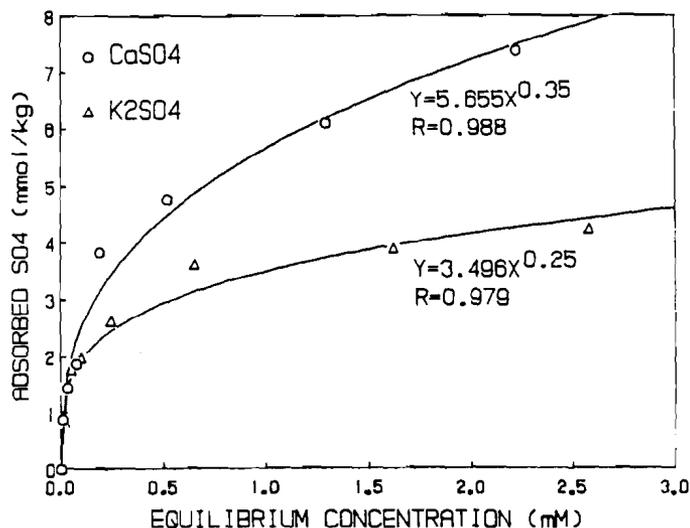


Fig. 7. Comparison of SO_4^{2-} adsorption from K_2SO_4 and $CaSO_4$ by the Dark Red A horizon (DRA) material.

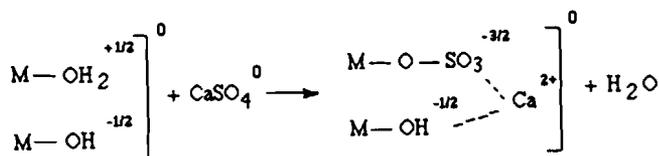
It is tempting to suggest that the higher adsorption of both Ca^{2+} and SO_4^{2-} at the highest $CaSO_4$ concentrations is simply gypsum precipitation, but the highest level of $CaSO_4$ was selected to avoid exceeding the solubility product of gypsum.

The presence of Ca^{2+} has been reported previously to increase the retention of SO_4^{2-} by acid soils (Barrow, 1972; Chao et al., 1963; Marsh et al., 1987) and of PO_4^{3-} by goethite (Barrow et al., 1980), gibbsite (Helyar et al., 1976), and soils (Smillie et al., 1987; Ryden et al., 1977; Ryden and Syers, 1976). These observations suggest a mechanism involving the formation of a surface complex between SO_4^{2-} and Ca^{2+} , or, equivalently, adsorption of the solution complex, $CaSO_4^0$. A surface complex with phosphate and certain divalent cations of particular ionic size was proposed by Helyar et al. (1976) to explain greater phosphate retention by gibbsite in the presence of Ca^{2+} , Cd^{2+} , and Sr^{2+} and not with Mg^{2+} , Zn^{2+} , Na^+ , K^+ . This proposed complex involves the coordination of one Ca^{2+} atom to two adsorbed PO_4^{3-} groups, reducing the repulsive force

between two adjacent phosphate groups and enhancing further adsorption.

In the present study, a CaSO_4 concentration greater than 1 mM produced excess adsorption of SO_4^{2-} (attributable to the Ca- SO_4 interaction) that was essentially equal to excess adsorption of Ca^{2+} (Fig. 6 and 7). For example, in DRA, SO_4^{2-} tended to adsorb in proportionately greater amounts than Ca^{2+} at low CaSO_4 concentrations, but in equal mole quantities at high concentrations. These observations suggest that the two ions are adsorbing cooperatively only at higher concentrations, probably as an ion pair. Above 1 mM, the CaSO_4^0 complex represented a significant fraction of the total Ca^{2+} and SO_4^{2-} in solution, based upon chemical speciation calculations for the solution phase using MINEQL (Westall et al., 1976).

A reasonable reaction, then, would involve a 1:1 sulfate-calcium complex, with one O ligand of the SO_4^{2-} bonded to an oxide surface



This reaction, although similar to the adsorption of SO_4^{2-} from K_2SO_4 , is favored because of the closer approach of Ca^{2+} to the SO_4^{2-} ion compared to K^+ . This mechanism of adsorption can reduce the electrical charge developed by SO_4^{2-} adsorption, thus favoring greater adsorption.

Physical adsorption of CaSO_4^0 ion pairs on non-reactive mineral surfaces could also account for equimolar excess adsorption of Ca^{2+} and SO_4^{2-} , but such a process would be difficult to distinguish experimentally from the above reaction in which SO_4^{2-} is chemisorbed.

Increased pH which accompanied CaSO_4 adsorption was notably smaller than that which accompanied adsorption of K_2SO_4 (Fig. 4). This observation provides further evidence for chemisorption of

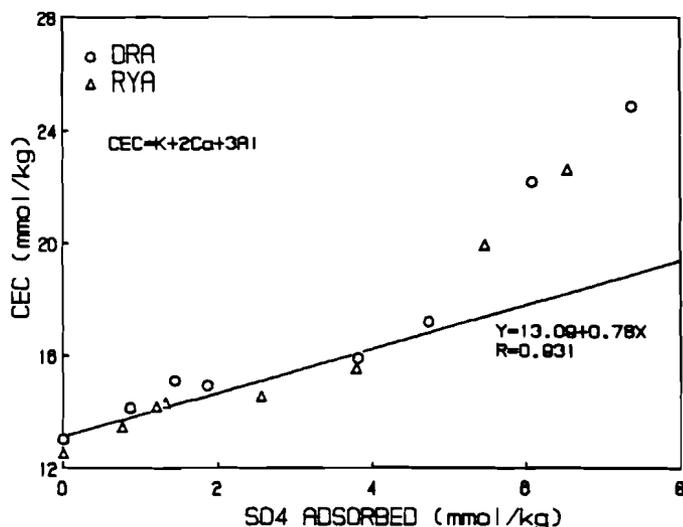


Fig. 8. Effect of the adsorption of sulfate from CaSO_4 on the cation exchange capacity of DRA and RYA. (Regression line does not include the highest CaSO_4 treatment levels.)

CaSO_4^0 ion pairs on oxides, or physical adsorption of CaSO_4^0 on nonreactive surfaces of the soil. Neither of these reactions should displace OH^- into solution to the extent that chemisorption of SO_4^{2-} alone does.

The apparent CEC (exchangeable $\text{K}^+ + \text{Ca}^{2+} + \text{Al}^{3+}$) was increased by the adsorption of CaSO_4 (Fig. 8). The two highest CaSO_4 levels produced an abrupt increase in the CEC because of the higher Ca^{2+} retention in these treatments. These same two levels generated the highest CaSO_4 adsorption (Fig. 6). Apparently, excess Ca^{2+} adsorbed in the presence of SO_4^{2-} is exchangeable. Most of the increase in CEC was attributable to negative charge created by SO_4^{2-} adsorption, because the CaSO_4 treatment had relatively little effect on soil pH.

CONCLUSIONS

Surface charge of Oxisols is affected by the adsorption of SO_4^{2-} . This ion adsorbs on the surfaces of highly weathered soil materials by a ligand exchange mechanism that releases OH^- and increases cation retention by such soils. In contrast, adsorption of Ca^{2+} from CaCl_2 does not significantly affect surface charge nor solution pH, suggesting that this ion adsorbed electrostatically, presumably on kaolinite surfaces.

While Ca^{2+} adsorption is almost linearly dependent on Ca^{2+} concentration, SO_4^{2-} adsorption tends to approach a maximum which is beyond the experimental range of SO_4^{2-} additions. Retention of both ions conforms to the Freundlich equation, although SO_4^{2-} adsorption is also described adequately by a Langmuir function.

When Ca^{2+} and SO_4^{2-} are applied together as a solution of CaSO_4 , adsorption of each ion is enhanced as compared with adsorption from CaCl_2 and K_2SO_4 , respectively. A simple precipitation reaction is ruled out by the fact that the soil solutions were undersaturated with respect to gypsum and other likely solid phases. A possible explanation is based on the cooperative adsorption of Ca^{2+} and SO_4^{2-} as an ion pair, a process which minimizes the development of negative charge on oxide surfaces resulting from SO_4^{2-} chemisorption. Thus, further adsorption of SO_4^{2-} is facilitated by Ca^{2+} adsorption. This excess of adsorbed Ca^{2+} is exchangeable, increasing the CEC of these soils.

The similarity in behavior of the Red Yellow and Dark Red soil materials with respect to Ca^{2+} and SO_4^{2-} adsorption can be attributed to their similar mineralogies and surface areas (Marcano-Martinez and McBride, in review). The inability of organic matter in the A horizons of these naturally acid soils to retain Ca^{2+} is evidently a result of the effective blockage of organic functional groups by Al^{3+} and Fe^{3+} ; that is, the native organic matter is inactive in cation exchange reactions because of association with these metals in the form of monomeric cations or oxide particles.

In summary, initial adsorption of SO_4^{2-} from CaSO_4 appears to be independent of Ca^{2+} adsorption, possibly occurring predominantly by bidentate bonding at positively charged sites and minimizing the creation of surface negative charge. Initial SO_4^{2-} adsorp-

tion is accompanied by relatively little Ca^{2+} adsorption. At higher SO_4^{2-} adsorption levels, the weaker monodentate bonding mechanism may be operative, creating significant negative charge on oxides. The presence of Ca^{2+} assists this mechanism since co-adsorbed Ca^{2+} can efficiently compensate the surface negative charge by forming an ion pair with SO_4^{2-} . Consequently, adsorption at high CaSO_4 concentrations is characterised by equimolar retention of Ca^{2+} and SO_4^{2-} in the soil.

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