

EFFECT OF SELECTIVE DISSOLUTION ON CHARGE AND SURFACE PROPERTIES OF AN ACID SOIL CLAY

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Abstract—To evaluate the importance of oxides to the surface chemistry of acid mineral soils, clay fractions were separated from a surface and subsurface horizon of an Inceptisol representative of many of the acid soils of the Southern Tier of New York state. Portions of the clays were treated to remove selectively noncrystalline and microcrystalline Fe and Al oxides (acid ammonium oxalate extraction), total free iron oxides (dithionite reduction in buffered citrate solution), and organic matter (hypochlorite oxidation). Charge and ion-adsorption characteristics of the treated and untreated clays were investigated by means of Ca²⁺- and Cl⁻-exchange capacities, potentiometric titrations, and electrophoretic mobility (zeta potential) measurements of the CaCl₂-treated clays.

Based upon surface area and anion- and cation-exchange measurements, the Fe and Al oxides or oxide-organic matter complexes were found to contribute a large part of the surface area and pH-dependent charge of these clays. Oxide removal increased the cation-exchange capacity (CEC) and virtually eliminated the anion-exchange capacity (AEC) at pH 3 and 5.5 while shifting the positive zeta potential (ZPC) of the B-horizon clay toward negative values. Organic matter oxidation increased the AEC at pH 3 and the CEC at pH 5.5 and markedly shifted the ZPCs of both A- and B-horizon clays toward more positive values, probably by the removal of adsorbed organics from oxide surfaces. Estimates of the ZPCs of the clays varied among the three methods used, Ca²⁺- and Cl⁻-exchange capacities giving the lowest, and electrophoresis giving the highest values.

Key Words—Anion exchange, Cation exchange, Electrophoresis, Inceptisol, Soil clay, Surface charge, Zeta potential.

INTRODUCTION

The relatively young acid soils of the northeastern United States tend to contain moderately inactive layer silicate minerals, such as illites, chlorites, and kaolinite. Due to the paucity of basic cations, these minerals commonly have exchange complexes dominated by aluminum and aluminum-hydroxy species, with the result that the apparent exchange capacity of these minerals is pH-dependent, despite the permanent charge of the layer silicates. Fe and Al oxides and hydroxides, microcrystalline silicates, and organic matter can also contribute to pH-dependent charge. Curtin and Smillie (1979) concluded that a significant portion of the pH-dependent charge of Irish soils was inorganic in origin, inasmuch as the removal of oxide and noncrystalline material by selective dissolution dramatically reduced the pH-dependent charge. This fraction may be small in terms of weight, but it is likely to have a high surface area and may be highly reactive, either alone or as a complex with organic matter, especially with respect to anion and trace metal sorption.

The purpose of the present study was to characterize some acid soil clays with respect to charge and exchange properties and to determine the influence of the selective removal of various inorganic and organic fractions on these properties. Charge properties were examined using potentiometric titrations, ion exchange, and electrophoretic mobility.

MATERIALS AND METHODS

The soil from which the clays were extracted is a fragiochrept silt loam from Mt. Pleasant, New York. A surface A horizon (0–15 cm) with pH 4.7 (1:2 distilled water) and 5.2% organic matter and a cambic B horizon (20–30 cm) with pH 5.2 and 1.6% organic matter were collected from an uncultivated, unlimed area. Both horizons contain about 15% clay-size material of which the dominant mineral, as determined by X-ray powder diffraction (XRD) of the dithionite-treated clays, is illite. Kaolinite, chlorite, and vermiculite were also detected by XRD.

To separate the clay fractions, field-moist soils were saturated with NaCl and dispersed by sonification. The <2- μ m fraction was separated by repeated dispersion and centrifugation. The clays were flocculated by the addition of CaCl₂ and then washed repeatedly with distilled water and ethanol to remove excess salt. The clays were then air-dried and stored. The pH of the resultant clays when resuspended in distilled water was 4.8 for the surface (A) clay and 5.0 for the subsurface (B) clay.

Noncrystalline and microcrystalline oxides were extracted with 0.2 M ammonium oxalate titrated to pH 3 with oxalic acid (McKeague and Day, 1966). The clays were extracted in 3-g batches by shaking for 4 hr with 150 ml of oxalate solution in a dark room. Dithionite reduction in citrate solution buffered with sodium bicarbonate (CBD) extracted free iron oxides from the clay (Mehra and Jackson, 1960). The reduction was

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carried out on 2-g quantities at 80°C after adding 60 ml of citrate-bicarbonate solution and 0.5 g of sodium dithionite. The process was repeated until the iron oxides appeared to have been removed as evidenced by the light grey color of the clays. Organic matter in the clays was oxidized with bleach (5.25% hypochlorite solution) adjusted to pH 9.5 with concentrated HCl. Fifty milliliters of this solution was reacted with 5 g of clay for 15 min in a boiling water bath. After centrifugation the supernatant solution was poured off and the process repeated four more times. Samples of the solutions from each of these extraction procedures were reserved for elemental analysis. After each treatment the clays were washed, resaturated with CaCl₂, washed free of excess salt, and air-dried.

Smaller portions of the untreated clays were also extracted with 0.1 M sodium pyrophosphate and with cold 5% sodium carbonate to estimate organically bound Fe and Al (McKeague *et al.*, 1971), and non-crystalline Al oxides (Follett *et al.*, 1965), respectively.

Extracted Fe and Mn were measured by atomic absorption spectroscopy using appropriate matrices for standard solutions. Al was measured colorimetrically using 8-hydroxyquinoline (Bloom *et al.*, 1978). Si was measured colorimetrically by the molybdate complex method described by Weaver *et al.* (1968) which was designed specifically for CBD extracts. Phosphate was also measured as the blue molybdate complex using SnCl₂ as the reductant.

CECs and AECs by Ca²⁺ and Cl⁻ adsorption were determined at pH 3 and 5.5. Samples were washed twice with 0.05 M CaCl₂, allowing 15 min equilibration time for each wash, then five times with 0.001 M CaCl₂ solutions at the appropriate pH. After the last centrifugation, tubes were weighed to determine the amount of occluded CaCl₂. Sorbed and occluded CaCl₂ was displaced by five washes with 0.05 M MgNO₃. Calcium was measured by flame emission spectroscopy and chloride by potentiometric titration with AgNO₃.

Potentiometric titrations to find the pH of zero salt effect (PZSE) were carried out by the continuous titration method of Laverdiere and Weaver (1977), using 0.2 g of clay in 50 ml of 0.01, 0.1, or 1.0 M NaCl. Whereas direct comparison of these titration results with those of ion adsorption and electrophoretic mobility would have required the use of CaCl₂, the latter salt is not considered an indifferent electrolyte for ZPC measurements.

Electrophoretic mobilities were measured at pH 3.5 to 8 using a Riddick Zeta Meter. The clays were suspended in CaCl₂ solution at the appropriate pH and allowed to equilibrate for 3 days. pH was adjusted daily and just before measurement of the electrophoretic mobility (if necessary), and the volume adjusted to give a CaCl₂ concentration of 5×10^{-4} M. Ca was used as the saturating cation and CaCl₂ as the ionic medium, a choice justified by the dominance of Ca²⁺ as the

exchangeable cation in the soils under study. Mobilities were taken as the average of 10 measurements.

Clay surface areas were measured by a three point B.E.T. isotherm for N₂ sorption at liquid nitrogen temperature on a Quantasorb sorptometer.

RESULTS AND DISCUSSION

Table 1 gives the concentrations of elements extracted by the various treatments. As expected, the major element extracted by the oxalate and CBD treatments was Fe, and more was extracted by the CBD than the oxalate treatment. These results are logical because the CBD treatment does not distinguish the highly hydrated and microcrystalline Fe minerals from the more crystalline Fe oxides (Schwertmann and Taylor, 1977). Almost 100% of the Fe of well-crystallized hematite and goethite is dissolved by CBD treatment (Mehra and Jackson, 1960); Schwertmann (1973), however, found that an ammonium oxalate extraction in darkness removed only X-ray-amorphous oxides. The difference in the amount of Fe extracted by these two treatments is not great, indicating that most of the Fe in these clays is in reactive microcrystalline forms. Further evidence that two different kinds of Fe were dissolved by the oxalate and CBD treatment was provided by electron spin resonance (ESR) spectra of the clays (Figure 1). The broad "ferromagnetic resonance" which is generally attributable to Fe minerals was only slightly affected by the oxalate treatment and virtually eliminated by the CBD treatments. The resonance observed is probably not attributable to magnetite because oxalate is more efficient in extracting magnetite than CBD (Rhoton *et al.*, 1981). As Figure 1 reveals, the ferromagnetic signal intensity was greatly enhanced in a magnetic separate from the B-horizon clay. Another feature of the ferromagnetic signal was its anisotropy, detected by orienting A horizon clay films (untreated) in the magnetic field of the ESR spectrometer. The orientation-dependence of the low-field component of the signal is demonstrated in Figure 2, suggesting that Fe oxide particles or coatings are associated with the aligned layer silicate surfaces.

The change in surface area of the clays after the various treatments (Table 2) also demonstrates the microcrystallinity of the material removed by the oxalate and CBD treatments. Surface areas calculated for the dissolved minerals based on weight loss due to the treatments agree well with surface areas of oxides from several different soil types studied by Gallez *et al.* (1976) and Greenland *et al.* (1968), who estimated surface areas both by surface-area reduction following dithionite treatment (100–400 m²/g) and from electron micrographs of the untreated soils (150–300 m²/g). One possible error in the assumption that all of the loss in surface area upon chemical treatment could be attributed to the dissolved oxides is the likely improved efficiency of stacking of layer silicate plates, reducing

Table 1. Elements extracted from acid soil clays by selective dissolutions.

Treatment	Fe (mg/g)	Al (mg/g)	Mn (mg/g)	Si (mg/g)	P (mg/g)	Weight loss (%)
Oxalate:						
A horizon	38	11	0.57	0.16	0.15	15
B horizon	51	10	0.48	0.35	0.98	17
A after NaOCl	46	16	1.1	1.6	2.7	—
B after NaOCl	53	17	1.0	1.1	2.7	—
CBD:						
A horizon	45	13	0.90	0.48	—	18
B horizon	56	8.9	0.60	1.0	—	20
A after NaOCl	60	17	1.2	3.5	2.8	—
B after NaOCl	63	19	1.0	3.3	2.4	—
Pyrophosphate:						
A horizon	9.8	6.5	—	—	—	7.5
B horizon	10	3.4	—	—	—	5.0
Na₂CO₃:						
A horizon	0	12	0	0.09	0.99	—
B horizon	0	6.1	0	0.10	1.1	—
NaOCl:						
A horizon	~0.03	~0.03	~0.03	~0.01	—	6.6
B horizon	~0.02	~0.20	~0.01	<0.01	—	3.3

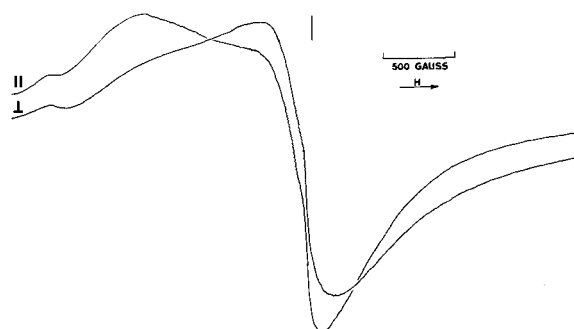
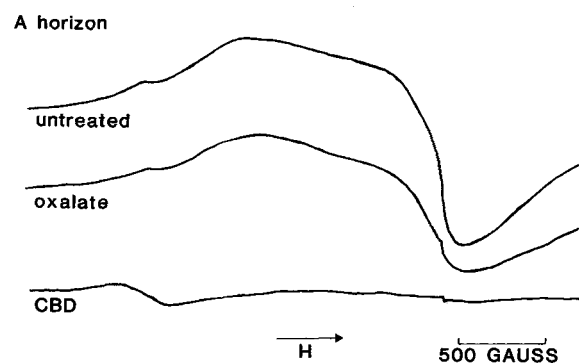


Figure 2. The electron spin resonance spectrum of a self-supporting A-horizon clay film (untreated) oriented parallel (||) and perpendicular (⊥) to the magnetic field.

the surface area contributed by the layer silicates after oxide removal.

The increases in surface area and extractable Fe and Al (Table 1) following organic matter oxidation suggest that Fe and Al oxides were either formed or exposed by the oxidation. The procedure also may have re-

Figure 1. Room temperature electron spin resonance spectra of air-dry A-horizon and B-horizon clays, untreated, acid oxalate-treated, and CBD-treated. The spectrum of the clay separated magnetically from the B-horizon is also shown. A small marker indicates the $g = 2.0023$ position.

Table 2. Surface areas of soil clays.

Treatment	A clay (m ² /g)	B clay (m ² /g)
Untreated	37.1	71.0
Oxalate	11.9	28.8
CBD	15.8	25.0
NaOCl	58.3	78.0
Calculated for oxalate-soluble minerals	206	251
Calculated for CBD-soluble minerals	128	255

moved materials that cement particles together, of which organic matter as well as Al and Si are likely components.

As for most soils, the CBD treatment extracted more Al than the oxalate treatment for the A horizon clay. The opposite, however, was true for the B horizon, a result commonly reported for spodic horizons (McKeague and Day, 1966; McKeague *et al.*, 1971; Giovanni and Sequi, 1976). In as much as oxalate and citrate can also extract Fe and Al complexed by organic matter (Schnitzer and Skinner, 1964), an extraction with pyrophosphate was carried out to estimate the amount of Fe in this fraction (the extractant is not specific for organic matter-complexed Al) (McKeague *et al.*, 1971; Wada and Higashi, 1976). The extraction probably overestimates the organically complexed Fe because organo-mineral complexes are also susceptible to pyrophosphate dissolution (Schnitzer and Skinner, 1964; Higashi *et al.*, 1981).

Cold 5% sodium carbonate is a specific extractant for noncrystalline aluminum oxides and noncrystalline aluminosilicates. The amounts of Al extracted by the carbonate are not greatly different from those extracted with oxalate and CBD, suggesting that the latter two treatments extracted most of the Al from the noncrystalline clay components.

The exchange capacities for Ca²⁺ and Cl⁻ are presented in Table 3. These capacities were calculated on the basis of the untreated clay weight and represent the average of duplicate measurements. The lower CEC values for the clays at pH 3 can be attributed in part to increased Al³⁺ solubility and competition for ex-

change sites at this low pH. The increased CEC and decreased AEC with the removal of oxides, as seen here, was demonstrated previously by Sumner (1964), Follett *et al.* (1965), Greenland (1975), Shuman (1976) and Curtin and Smillie (1979). These changes following oxide dissolution can be explained by a positive charge on Fe and Al oxides and hydroxy-polymers below pH 6 which neutralizes some of the negative charge of the layer silicate clays. Herrera and Peech (1970) found that as little as 1%, 2.5%, and 3% iron-hydroxy polymers reversed the charge of kaolinite, illite, and montmorillonite, respectively.

In the few studies where some CEC increase was reported after oxide dissolution, the soils had been pretreated with peroxide to remove organic matter (Krishna Murthi *et al.*, 1976; Shuman, 1976). As seen in Table 3, organic matter oxidation tended to increase the CEC of the clays. This additional charge was highly pH-dependent and may have been due to exposure or alteration of metal oxide surfaces formerly complexed by organic matter (Moshi *et al.*, 1974). In particular, peroxide generates oxalate which readily chemisorbs on oxides to create negative surface charge.

The AEC at pH 3 (Table 3) also increased considerably with organic matter oxidation, thus putting the pH of zero net charge (ZPC) somewhere between 3 and 5.5 for these systems, whereas for the untreated clays it was at pH 3. For both clays, the ZPC could not be estimated after the treatments to remove Fe and Al oxide because of the high permanent negative charge of the layer silicate clays.

Figures 3 and 4 show potentiometric titration curves of the two untreated clays. These types of curves are commonly used to determine the ZPCs of minerals and soils, corresponding to the crossover point of the three curves (Gast, 1977). Duplicate runs for each titration curve gave virtually identical curves; however, no unique crossover point was found for either the A or B horizon clay. In the A horizon, the crossover points were at lower pH than in the B horizon clay. This sort of behavior was reported for the titration curves of spodosols (Laverdiere and Weaver, 1977) and of an aluminum peat (Bloom, 1979). All of the crossover points are at pH values above those at which Ca²⁺-exchange capacity was equal to the Cl⁻-exchange

Table 3. Cation- and anion-exchange capacity of soil clays.¹

Treatment	pH 3				pH 5.5			
	A horizon		B horizon		A horizon		B horizon	
	CEC	AEC	CEC	AEC	CEC	AEC	CEC	AEC
Untreated	1.6	1.4	2.2	2.1	13.1	0.9	7.9	0.1
Oxalate	12.2	0.6	9.3	0.2	18.3	0.0	10.2	0.0
CBD	10.7	0.1	10.3	0.0	17.3	0.0	15.0	0.0
NaOCl	1.7	13.0	3.4	10.0	25.3	0.9	18.1	0.3

¹ Units of meq/100 g, estimated error limits of ±0.2 meq/100 g.

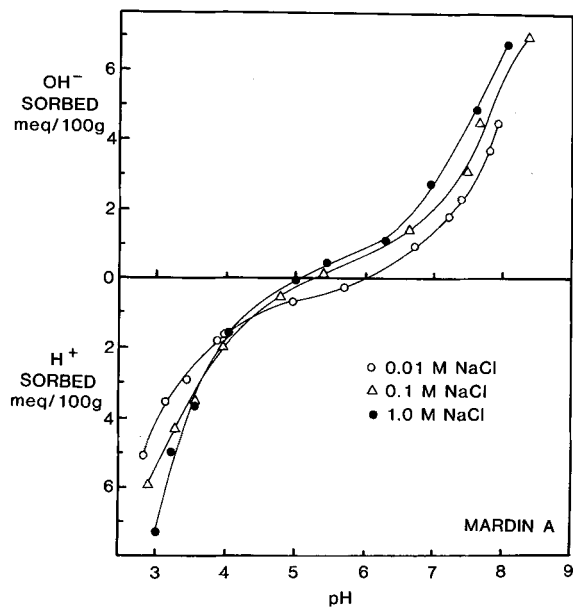


Figure 3. Potentiometric titration curves of the untreated Mardin A-horizon clay.

capacity; this difference between the crossover pH and the pH of ZPC has been noted by several authors (Galvez *et al.*, 1976; Parker *et al.*, 1979; Gillman and Uehara, 1980). The difference may be attributed to the specific sorption of Ca^{2+} in the CEC measurements or simply to a greater ability of Ca ions to displace sorbed Al species. Unstable minerals may also dissolve and consume protons without changing the surface charge of

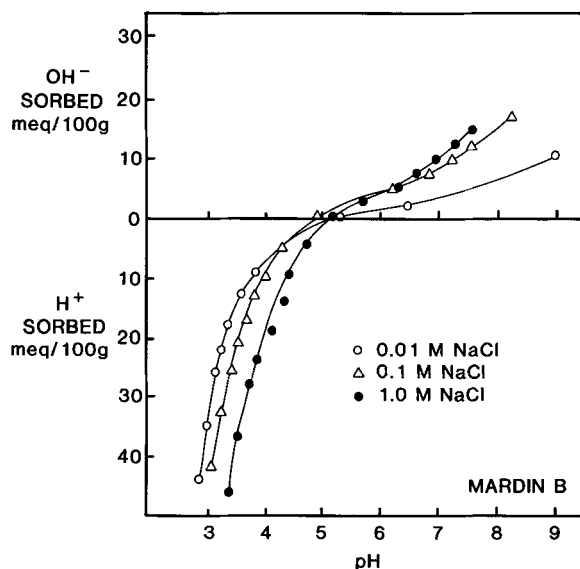


Figure 4. Potentiometric titration curves of the untreated Mardin B-horizon clay.

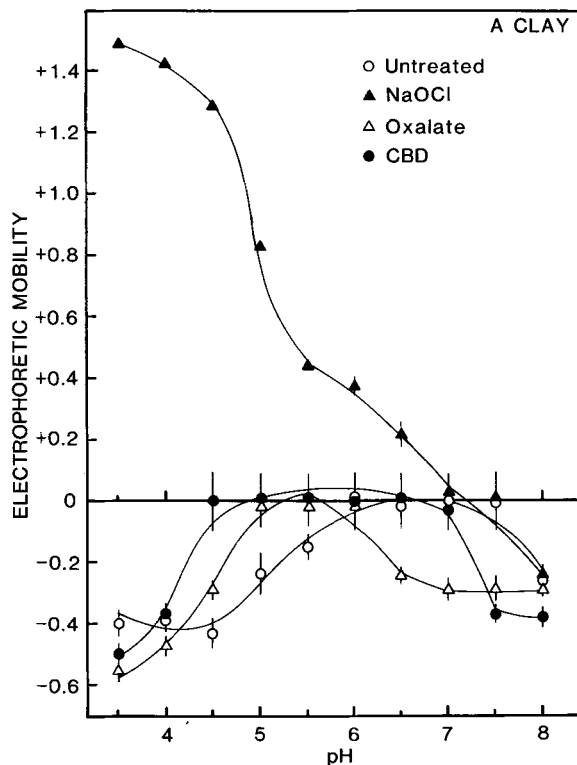


Figure 5. Electrophoretic mobility measurement (units of $\mu\text{m-cm sec}^{-1}\text{volt}^{-1}$) as a function of suspension pH for the untreated and treated Mardin A-horizon clay.

the minerals in the system (Parker *et al.*, 1979; Bloom, 1979).

The phenomenon of a non-unique crossover of potentiometric titration curves was predicted by Pyman *et al.* (1979) based on the electric double layer model developed by Bowden *et al.* (1977), and by Sposito (1981) based on the law of conservation of charge and concepts of coordination chemistry. Both models predict a non-unique crossover if one of the ions in the electrolyte is specifically sorbed, but the use of NaCl in the present study rules out an explanation based upon specific adsorption. The small amount of Ca^{2+} added with the clay should shift the crossover point to a higher pH than the ZPC, but Al^{3+} and Al-hydroxy species may be responsible for the three different crossover points. Increasing NaCl concentrations may have altered the surface by displacing Al, thereby changing the relative affinity of the clays for H^+ and OH^- . This exchange process may have prevented a single point of zero salt effect from being defined in this layer silicate-oxide system.

Electrophoretic mobility measurements at various pHs provide yet another estimate of ZPCs (Figures 5 and 6). It should be noted that, except for the hypochlorite treated clays, these mobilities are fairly low

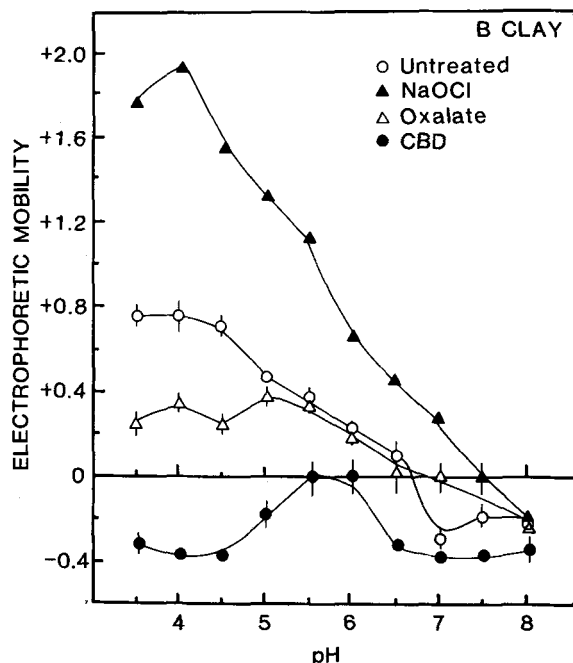


Figure 6. Electrophoretic mobility measurements (units of $\mu\text{m-cm sec}^{-1}\text{volt}^{-1}$) as a function of suspension pH for the untreated and treated Mardin B-horizon clay.

compared to those of kaolinites (Street and Buchanan, 1956; Buchanan and Oppenheim, 1972; Lorenz, 1969), smectites and illites (Harter, 1977; Herrera and Peech, 1970; Swartzen-Allen and Matejevic, 1975), and Al and Fe oxides (Matejevic *et al.*, 1973). In the negative mobility region (movement towards the positive pole), the low mobilities probably arise from surface adsorption of the divalent Ca ion in the suspension, and in the positive mobility region, low mobilities are expected because of the negatively charged minerals and organics. The lines on the data points or the size of the points in Figure 5 and 6 represent one standard deviation; this range is fairly large due to the inhomogeneity of the clays, and, at low mobilities, to the difficulties of following slowly moving particles. The points at zero mobility have especially large uncertainties because some particles were moving in either direction in these systems. Despite these problems, the movement of particles was surprisingly uniform at most pHs considering the different types of colloids present, which suggests that the oxides, clay minerals, and organic matter were intimately associated and moving as individual units under these conditions.

The A horizon clay had negative or zero electrophoretic mobility over the entire pH range studied, whereas the B horizon had positive mobility (was positively charged at the shear plane) below pH 6.7. The large difference here is presumably caused by the stabilizing influence of organic matter because the oxi-

dation of organic matter led to substantial positive mobility in the A horizon clay and a more than doubling of the positive mobility of the B clay.

Considering the mineralogy of the clay fractions studied, the electrophoretic mobilities of the untreated, oxalate- and CBD-treated clays should have been negative over the entire pH range, but as the pH of the A-horizon clay was adjusted from 3.5 to 5.5 the negative charge of the particles appeared to diminish to zero (Figure 5). Because the surface charge became more negative at higher pH (Table 3), the lowered mobility must reflect a change in counter-ion distribution. Possibly, the organic matter complexed Ca^{2+} in the pH range 5.5–7 in such a way that all surface charge was balanced within the shear plane. Because the B horizon clay had considerably less organic matter and higher surface area, the effect was less evident in this clay.

CONCLUSIONS

The Fe and Al oxides in these acid soils are in a highly reactive hydrated state and make up a large part of the surface area of the clay fraction. They account for most of the pH-dependent charge and are apparently able to block permanent negative charge sites at low pH. Some evidence was found that the oxides exist, at least partially, in intimate association with the layer silicate clays as coating or particles.

Electrophoretic mobility measurements revealed a positive zeta potential for the B-horizon clay possibly due to specific adsorption of Ca^{2+} by oxide surfaces and a negative zeta potential for the A-horizon generated by organics. The negative potential was eliminated by adjusting the pH to 5.5–7.0, a possible result of strong Ca^{2+} complexation of negatively charged organic functional groups in this pH range.

The ZPCs of the clays as estimated by CaCl_2 exchange and electrophoretic mobility experiments were low and high, respectively, probably due to the specific adsorption of Ca^{2+} . Potentiometric titration curves determined in three different concentrations of NaCl gave estimates of ZPC between those for the other two methods; however, the three curves had no unique crossover point.

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Резюме—Фракции глин сепарировались из почвенных и подпочвенных ярусов характерных для большинства кислотных почв Южного Яруса в Штате Нью-Йорк, для оценки значения окисей в химии поверхностей почв, содержащих кислотные минералы. Порции глин обрабатывались для селективного отделения некристаллических и микрокристаллических окисей Fe и Al (экстракция при использовании щавелевокислого аммония), всех свободных окисей железа (редуцирование дитионитом в содержащем буфер растворе цитрата), и органической материи (окисление гипохлоритом). Зарядо- и ионо-адсорбционные характеристики обработанных и необработанных глин исследовались путем изменений Ca^{2+} - и Cl^- -обменных способностей, потенциометрического титрования и электрофорезной подвижности (потенциал зета) на глинах, обработанных CaCl_2 .

На основании измерений площади поверхности и анионо- и катионо-обмена, окиси Fe и Al или комплексы окисей с органической материей вносили большой вклад в величину площади поверхности и pH-зависимый заряд этих глин. Удаление окиси увеличивало катионо-обменную способность (КОС) и фактически исключало анионо-обменную способность (АОС) при pH = 3 и 5,5, в то время, как положительный потенциал зета (ПЗ) глины из яруса В перемещался в сторону отрицательных величин. Окисление органической материи увеличивало АОС при pH = 3 и КОС при pH = 5,5 и значительно перемещало величины ПЗ глин из обоих, А- и В-ярусов к более положительным значениям, вероятно, путем удаления адсорбированных органических веществ с поверхности окисей. Оценки величин ПЗ глин были различны при использовании этих трех методов; Ca^{2+} - и Cl^- -обменные способности давали наиболее низкие величины, а электрофорез—наибольшие величины. [E.G.]

Resümee—Um die Bedeutung von Oxiden für die Oberflächenchemie von sauren Mineralböden abzuschätzen, wurden die Tonfraktionen von einem Oberflächenhorizont und einem Unterbodenhorizont eines Inceptisols abgetrennt, der für viele saure Böden von Southern Tier, New York Staat, repräsentative ist. Teile der Tone wurden behandelt, um nichtkristalline und mikrokristalline Fe- and Al-Oxide (mittels saurer Ammoniumoxalat-Extraktion), die gesamten freien Eisenoxide (mittels Reduktion durch Dithionit in gepufferten Citratlösungen) und organische Substanzen (mittels Oxidation durch Hypochlorit) selektiv zu entfernen. Ladungs- und Ionenadsorptions-Charakteristika der behandelten und unbehandelten Tone wurden mittels Ca^{2+} - und Cl^- -Austauschkapazitätssmessungen, potentiometrischen Titrationen und elektrophoretischen Beweglichkeitsmessungen (Zeta-Potential) der CaCl_2 -behandelten Tone untersucht.

Aufgrund von Oberflächen- und Anionen- sowie Kationenaustauschmessungen zeigte sich, daß Fe- und Al-Oxide sowie Komplexe aus Oxiden und organischen Substanzen einen großen Anteil der Oberfläche und der pH-abhängigen Ladung dieser Tone ausmachen. Senn die Oxide entfernt wurden, nahm die Kationenaustauschkapazität (CEC) zu und wurde die Anionenaustauschkapazität (AEC) bei pH 3 und 5,5 praktisch zerstört, während das positive Zeta-Potential (ZPC) des B-Horizonttons gegen negative Werte verschoben wird. Die Oxidation organischer Substanzen vergrößert die AEC bei pH 3 und die CEC bei pH 5,5. Außerdem verschiebt sie die ZPCs sowohl des A- als auch des B-Horizonttons in Richtung höherer Werte, was wahrscheinlich auf dem Entfernen von adsorbierten organischen Substanzen von den Oxidoberflächen beruht. Die Schätzwerte der ZPCs der Tone variiert zwischen den drei verwendeten Methoden, wobei Ca^{2+} - und Cl^- -Austauschkapazität die niedrigsten und Elektrophorese die höchsten Werte ergibt. [U.W.]

Résumé—Pour évaluer l'importance d'oxides à la chimie de surface de sols minéraux acides, des fractions d'argile ont été séparées d'un horizon de surface et souterrain d'un représentant d'un Inceptisol d'un des nombreux sols acides de l'état de New York. On a traité des portions des argiles pour enlever sélectivement les oxides Fe et Al non-cristallins et microcristallins (extraction d'oxalate d'ammonium acide), les oxides à fer totalement libre (réduction dithionite dans une solution citrate tempérée) et la matière organique (oxidation hypochlorite). Les caractéristiques d'adsorption de charge et d'ions des argiles traités et non-traités ont été investiguées au moyen des capacités d'échange de Ca^{2+} et Cl^- , des titrations potentiométriques, et des mesures de mobilité électrophorétiques (potentiel zeta) des argiles traités au CaCl_2 .

Basé sur l'aire de surface et sur des mesures d'échange d'anions et de cations, on a trouvé que les oxides Fe et Al ou les complexes oxide-matière organique contribuaient une grande partie de l'aire de surface et de la charge dépendante du pH de ces argiles. L'enlèvement de l'oxide a augmenté la capacité d'échange de cations (CEC) et a de fait éliminé la capacité d'échange d'anions (AEC) aux pH 3 et 5,5, tandis que le potentiel zeta positif (ZPC) de l'argile de l'horizon B a été déplacé vers les valeurs négatives. L'oxidation par matière organique a augmenté l'AEC au pH 3 et la CEC au pH 5,5, et a déplacé de manière marquée les ZPCs des argiles des horizons A et B vers des valeurs plus positives, sans doute par l'enlèvement de la matière organique adsorbée des surfaces oxides. Les estimations des ZPCs des argiles étaient variées parmi les trois méthodes utilisées, les capacités d'échange de Ca^{2+} et de Cl^- donnant les valeurs les plus basses, et l'électrophorèse donnant les plus élevées. [D. J.]