INORGANIC pH DEPENDENT CATION EXCHANGE CHARGE OF SOILS

by

V. V. VOLK and M. L. JACKSON

University of Wisconsin, Madison, Wisconsin

ABSTRACT

Sodium hydroxide titration curves were determined on H resin treated montmorillonite, untreated acid and neutral soils of different origins and on the same soils with an H resin treatment. The acid montmorillonite titration curve reveals four buffer ranges corresponding to hydronium ions (range I), monomeric trivalent aluminum ions Range II), and two pH dependent charge ranges. Untreated acid soils contained pH dependent buffer zones governed jointly by the organic fraction, the soil pH, the presence of monomeric trivalent aluminum, and the exchange blocking mechanisms of other cations. Following an H resin treatment, soils containing less than 2 per cent of organic matter exhibited a clearly defined third buffer range (Range III) from pH 5.5 to 7.6. The inflection points are masked in the pH dependent buffer range in soils containing more than 2 per cent organic matter. The presence of added aluminum increased the pH dependent charge in an acidified montmorillonite while added ferric iron slightly decreased it. The natural acid weathering processes in soils result in some blocking of pH dependent charge as in Dodge soil of Wisconsin (KCl pH 4.5). When greater acidity develops, a large pH dependent charge results, as in Coolville soil in Ohio (KCl pH 4.0), and the lime requirement of the soil thus increases greatly.

INTRODUCTION

THE pH dependent charge or variable exchange charge of soils refers to the weak acid portion of the cation exchange capacity from which protons are released as a function of rise in pH above approximately pH 5. The existence of the pH dependent charge portion of the cation exchange capacity of soils, widely accepted for many years, is attributable in part to the characteristic functional groups on organic compounds. The inorganic contribution to pH dependent charge of soils and clays, which has received increasing emphasis in recent years, still is rather incompletely characterized.

In the present paper it is shown that some untreated acid soils have buffer ranges corresponding to exchangeable aluminum and a pH dependent charge buffer range without H resin treatment. Also, it is shown that soils immediately after treatment with H resin not only have exchangeable aluminum but also exhibit a large pH dependent charge buffer range, frequently differentiable into a third range attributable to hydroxy aluminum.

REVIEW OF LITERATURE

Truog (1916) classified soil acidity into active and latent forms, of which the latter was far larger. The fact that differences in the strengths of clay acids and humic acids exist in soils was recognized by Hissink (1924) who interpreted exchangeable bases on the surface of soil particles according to the double layer theory. Bradfield (1927), using potentiometric and conductometric titrations on electrodialized soils, indicated that two distinct reactions occur when acid soils are treated with bases: (1) the replaceable hydrogen is neutralized; (2) colloidal material disintegrates into simpler silicates and aluminates as the solution becomes more alkaline. Inflection points in these titrations were obtained at pH 7.0 and 8.5 using $Ba(OH)_2$ and NaOH titrants, respectively. The variance in inflection points was explained by the stronger hydrolysis of the Na clay system.

The instability of H clay and its conversion to Al clay with time has been well confirmed (Paver and Marshall, 1934; Slabaugh, 1952; Harward and Coleman, 1954; Low, 1955; Aldrich and Buchanan, 1958; Schwertmann, 1961). The cation exchange capacity of clays was shown to be reduced by the precipitation of $Al(OH)_3$ in the clay micelles (Paver and Marshall, 1934; Shen and Rich, 1962). In other work Rich (1960) reduced the cation exchange capacity of vermiculite (2–0.2μ) from 134 to 1 meq per 100 g with an 8-day treatment of a hydroxy Al solution. The ammonium fixation was also reduced greatly by a small amount of interlayer aluminum. Cation exchange capacity of soils studies by Dion (1944) increased after the removal of iron by a tartrate treatment.

Iron released from the lattice during acid weathering becomes hydrolyzed even more strongly than aluminum, thereby exposing exchange sites for the adsorption of ions as magnesium which are also released during acid weathering (Barshad, 1960). Page and Whittig (1961) titrated H-montmorillonite suspensions containing added increments of $Fe(NO_3)_3$ and showed the similar titration curves of sorbed iron and hydronium.

Various ideas have been advanced to explain the shape of titration curves of acid soils. Schofield (1939) showed that the sign and charge carried by a clay depends upon the pH environment. The variable negative charge or acid group was attributed to the dissociation of H from a Si–OH bond whereas a positive charge results upon Al–OH formation from Al=O. Allophanic type soil clays develop much buffering in the pH range of 6.0–7.5 (Fieldes and Schofield, 1960). This effect was attributed to tetrahedral aluminum since the octahedral aluminum in crystalline minerals does not exhibit a buffer capacity. Micaceous clay minerals containing up to 1/3 aluminum substitution for silica do not have a large variable charge, indicating that the active tetrahedral aluminum sites must involve a broken edge reaction. Practical results agreed with theory in showing that the broken bonds from tetrahedral aluminum sites had special affinities for anions containing oxygen.

The neutralization curves of acid soils and clays have also been investigated from the viewpoint of interlayer surfaces and edges. Garrels and Christ (1956) carefully looked at the beidellite titration curve prepared by Marshall and Bergman (1942) and calculated two equilibrium constants for the neutralization of clay acids, attributed to the interlayer surfaces and edge charges. A free energy calculation indicated that H was bonded to the edges more strongly than the center surface sites whereas K has no preference. Pommer and Carroll (1960) discontinuously titrated H-montmorillonite with NaOH and also concluded that the equivalents of base utilized before the first equivalence point correspond to a reaction with the interlayer surfaces, while that beyond the first inflection corresponded on an edge reaction. Jonas (1963) reached the opposite assignment of the edge and interlayer surface reactions in the neutralizations of H resin treated montmorillonite, based on two size fractions.

The presence of interlayer aluminum was suggested by Brown (1953) when he observed lattice spacings from diffractograms of vermiculite-like material which were dissimilar from the common clay minerals. The same phenomena was observed by Rich and Obenshain (1955). Upon investigation they concluded that non-exchangeable aluminum existed in the interlayer position, thus restricting collapse of the clay mineral upon K saturation.

Aluminum ions occur in many forms (in combination with $(-OH_2)_6$; $OH(-OH_2)_5$; and various polymeric ions); therefore, the specific type of "aluminum ions" will be indicated in the present discussion as far as the species is known. The mechanism of liberation of monomeric trivalent aluminum ions or alumino-hexahydronium, $Al(OH_2)_6{}^{3+}$, ions from layer silicate edges through proton binding to silica and the resulting interlayer polymerization of the release monomeric Al ions was described by Jackson (1960, 1963a). The aluminum polymers formed (by steric pinching and hydronium release on hydrolysis and polymerization of monomeric trivalent aluminum ions) enlarge during the process of pedochemical weathering with the formation of the intergradient vermiculite-chlorite structure (Dixon and Jackson, 1962).

Soil acidity and its neutralization has been organized into 5 groups by Jackson (1963a) according to the strength of the proton retaining sites: Range I, exchangeable H or $OH_3{}^+$; Range II, exchangeable Al^{3+}; Range III, positive hydroxy aluminum polymers (containing $Al-OH_2$ terminal groups); Range IV, residual weaker $Al-OH_2$ groups in hydroxy alumina; Range V, aluminosilicate dissolution reactions. The third buffer titration range was shown by Schwertmann and Jackson (1963) to develop spontaneously during aging of an H–Al montmorillonite system. Treatment with H resin restored the original titration curve of the H–Al montmorillonite, showing that aging did not alter the layer lattices by creating more crystal edges. Further work by Schwertmann and Jackson (1964) on vermiculite and soils indicated numerous occurrences in soils of a pH dependent charge between pH 5.5 and 7.6, and showed that pure hydroxy aluminum (partially neutralized $AlCl_3$) solution exhibited the same buffer range when similarly titrated. Titration Range III in an acid vermiculite increased with ageing and could be partially restored only with H resin treatment. The X-ray diffractogram of both the acid aged vermiculite and hydroxy aluminum treated vermiculite showed reduced collapsibility upon K saturation and heat treatment, thus indicating the presence of polymers in an interlayer position. Titration Range III (between pH 5.5 and 7.6) was attributed to the neutralization of protons released from $Al{-}OH_2$ groups. The reaction for titration Range II, monomeric trivalent aluminum (Jackson, 1960).

$$Al(-OH_2)_6{}^{3+} + NaOH \rightarrow Al(-OH_2)_5(OH)^{2\cdot 5+} + H_2O,$$

is the same as for titration Range III (Schwertmann and Jackson, 1963, 1964),

$$\begin{gathered} Al_x(OH)_{2\cdot 5x}(OH_2)_n{}^{0\cdot 5x+}Cl_{0\cdot 5x} + 0.5X\ NaOH \rightarrow \\ Al_x(OH)_{3x}(OH_2)_{n-0\cdot 5x} + 0.5X\ NaCl + 0.5X\ H_2O, \end{gathered}$$

except that the $Al{-}OH_2$ groups of Range III are in polymeric terminal positions. The pH dependent charge in natural soils without H resin treatment was attributed to the occurrence of hydroxy aluminum polymers in soil clays, formed under natural weather conditions, and equivalent to ageing H resin treated layer silicates.

It is important to note that the addition of a neutral salt such as KCl or KNO_3 is required to obtain well defined inflections in titration curves (Harward and Coleman, 1954; Bernstein, 1959; Schwertmann and Jackson, 1963, 1964). The presence of a neutral salt reduces the Donnan effect by displacing the titratable cations from the colloid surfaces.

The pH dependent charge is very important in determining the lime requirement of Wisconsin soils (Keeney and Corey, 1963). To correctly evaluate the lime necessary to raise the pH of the soil in the field, one must use a laboratory procedure which is sensitive to the pH dependent charge in the soil. The S–M–P buffer (Shoemaker, McLean, and Pratt, 1961) method for rapid lime requirement determination of soils, for example, reflects the nature of pH dependent charge and measures the lime requirement of soils, including both the monomeric trivalent aluminum ions and pH dependent charge portion of the acid exchange complex of soils.

EXPERIMENTAL PROCEDURE

One gram samples of untreated soils, H resin treated soils or H resin treated bentonite were titrated with 0.0283 N NaOH in the presence of 25 ml of 1 N KCl by a Metrohm Potentiograph Model E336 (titration speed =0.0283 meq/min). The H resin treated soil samples were prepared for titration by equilibration with 2.5 ml of H saturated Amberlite IR–120 resin (washed free from chlorides) for 3 hr. A silk screen was used to remove the resin from the soil suspension before the titration with NaOH. For comparison, montmorillonite (Upton, Wyoming bentonite) was saturated with OH_3^+ by a 10-min H resin treatment. A high speed magnetic stirrer was utilized during the NaOH titration, thereby holding constant any suspension effect which was present. The added KCl electrolyte, which had a concentration of approximately 0.5 N at the end of the titration, served to reduce the junction potential at the salt bridge.

The effect of iron and aluminum ions on the pH dependent charge was determined by adding various increments of $FeCl_3$ and (or) $AlCl_3$ solution (as indicated with the results) to 0.1 g of H resin treated montmorillonite (treated with 2.5 ml H resin for 30 min) and titrating with NaOH as previously indicated.

The ordinary pH values of the untreated soils were also determined (a) in a thin paste of soil in distilled water (Jackson, 1958) and (b) in a 0.5 N KCl suspension of soil with a soil–water ratio of 1 : 50. The pH measurements were determined with a glass electrode in conjunction with a Metrohm Potentiograph, Model E 336. These determinations were in addition to the values obtained from the titration curves.

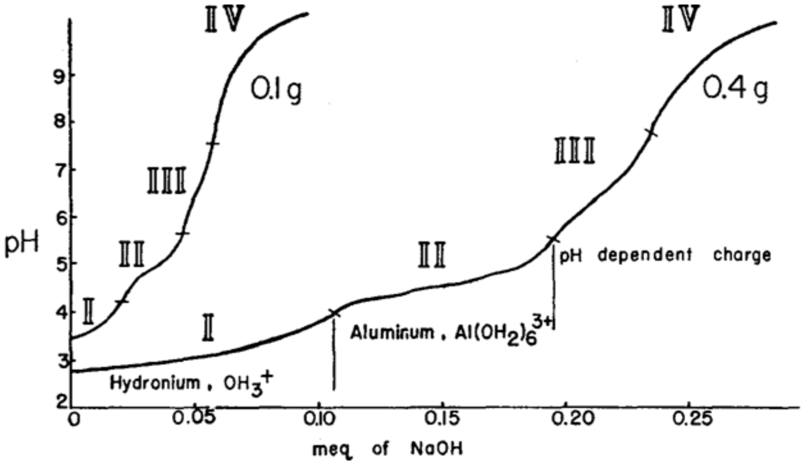


FIGURE 1.—NaOH titration of H resin treated montmorillonite (Wyoming bentonite) in 0.5 N KCl.

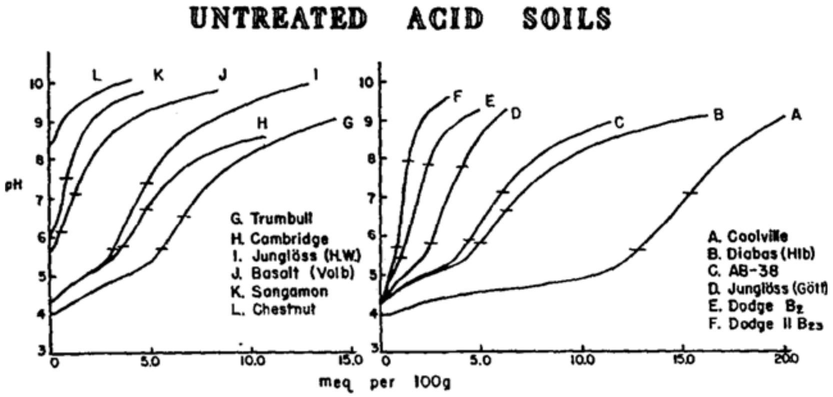


Figure 2.—NaOH titration curves of untreated soils of varying acidity: A (very acid) to L (slightly calcareous), all in 0.5 n KCl. Junglöss and diabas are German terms for young loess and diabase derived soils.

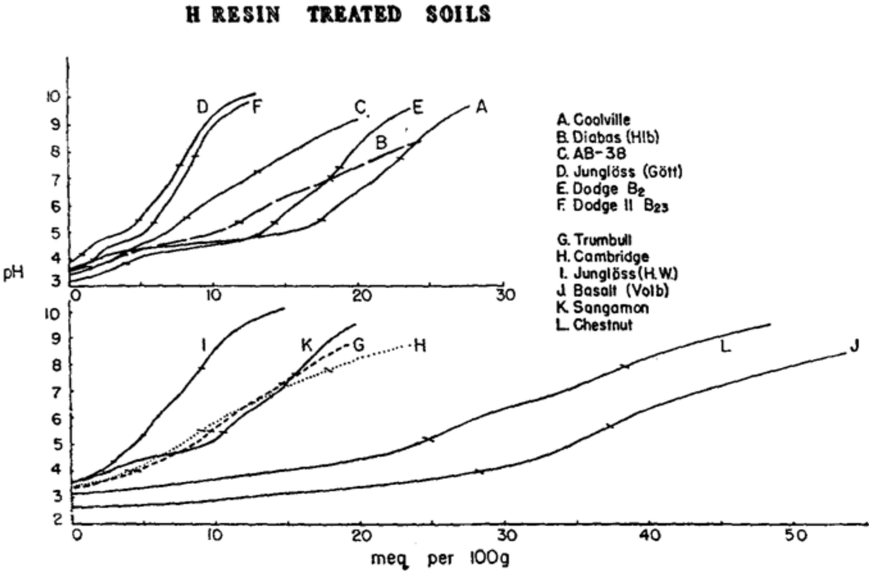


Figure 3.—NaOH titration curves of H resin treated soils in 0.5 n KCl, showing varying buffer curve shapes.

The organic carbon content of the soils was determined by a dry combustion method (Steyermark, 1951) using the Sargent microcombustion apparatus.

RESULTS

Titration of H *and* Al *montmorillonite.*—The neutralization curves of H resin treated montmorillonite from bentonite are shown in Fig. 1. The 0.4 g sample has an initial pH of 2.7 while the 0.1 g sample has an initial pH of 3.5. The result with a 0.1 g sample of montmorillonite is included for comparison to the curve position of soils with lower exchange capacity in Figs. 2 and 3.

Of the four ranges of buffer capacity (I, II, III, IV in Fig. 1; Jackson, 1963a) Ranges I and II correspond to hydronium or "hydrogen" and spontaneously generated aluminum, respectively (Slabaugh, 1952; Harward and Coleman, 1954; Low, 1955; Chernov, 1959). Range III or "third range", which is more extensively developed on ageing of the acid bentonite sample (Jackson, 1960; Schwertmann and Jackson, 1963), corresponds to neutralization of excess protons of $Al{-}OH_2$ groups of hydroxy Al edges, and is part of the pH dependent charge range. The hydroxy Al edges correspond to the "broken edges" existing in a gibbsitic type lattice or the edges of chlorite or other layer silicate edges, all of which are (+) below their isoelectric pH (Jackson, 1963a) and act as proton donors through the reaction

$$XAl{-}OH_2^{0\cdot5+} \longrightarrow XAl{-}OH^{0\cdot5-} + H^+$$

as the pH is raised. X represents the remainder of the layer.

The Range IV pH dependent charge, above pH 7.6 (Fig. 1), which is smaller for this freshly prepared acid montmorillonite than for aged acid montmorillonite (Schwertmann and Jackson, 1963) and for many H resin treated soils (Fig. 3), corresponds to further neutralization of protons released from $Al{-}OH_2$ groups at edges and possibly includes layer silicate edges, since both Al and Si pass into solution in NaOH solution of this alkalinity. Range IV grades rather continuously into Range V (Jackson, 1963a) buffering by extensive dissolution of clay by aluminate and soluble silicate (Bradfield, 1927) formation.

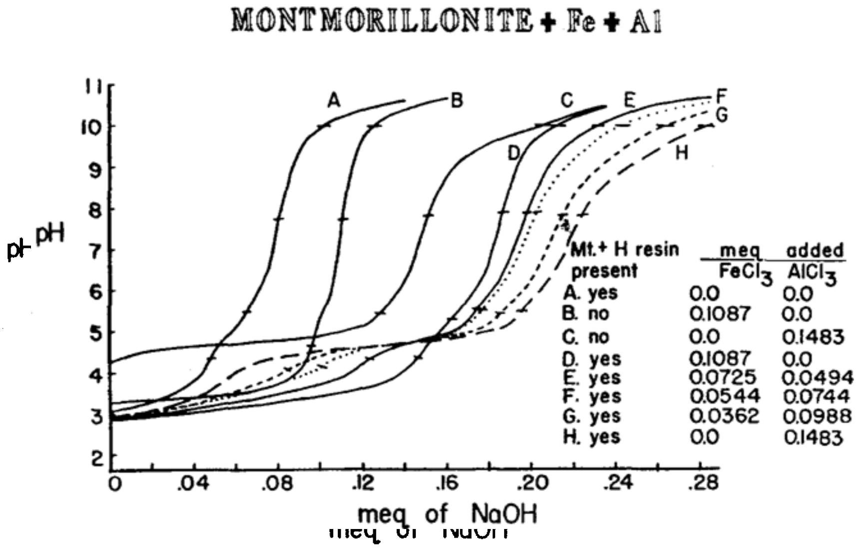
Titration of untreated soils.—The NaOH titration curves of several acid soils reveal a pH dependent charge buffer range in addition to exchangeable hydrogen and aluminum (Fig. 2). The third buffer range (Schwertmann and Jackson, 1963) is sufficiently developed to have discrete inflection points in some soils (A and I, Fig. 2) while with most of the soils, the entire pH dependent charge buffer range is continuous. The magnitude of the inorganic pH dependent charge as well as the discreteness of the third buffer range appears to be closely related to the presence of exchangeable aluminum. Thus the Coolville soil has the most sharply defined third buffer zone as well as the greatest quantity of exchangeable aluminum.

Titration of H *resin treated soils.*—The third buffer range becomes well defined in all soils with the exception of the basalt-derived soil after a

3-hr H resin treatment (J, Fig. 3). Following the H resin treatment, all soils decrease in pH, reflecting the exchange of OH_3^+ from the resin for exchangeable cations (predominantly Ca^{++} and Mg^{++}) on the soil colloid. Monomeric trivalent aluminum immediately appears in the system, replacing OH_3^+ and other ions on the exchange complex (Fig. 1). The release of Al^{3+} by OH_3^+ is shown by the large increase in titratable aluminum (Harward and Coleman, 1954; Low, 1955; Schwertmann and Jackson, 1963, 1964) identifiable by comparison to Fig. 1. The source of this titratable aluminum could be from either acid soluble hydroxy aluminum compounds or deterioration of the mineral lattice itself (Jackson, 1960, 1963a). The discreteness of the third buffer range increases as the exchangeable Al^{3+} (Range II) increases (Fig. 3 compared to Fig. 2).

The fact that the third buffer range develops spontaneously in acid clays with many weeks of time (Schwertmann and Jackson, 1963, 1964) whereas the third buffer range is present immediately after a H resin treatment of soils indicates that third range buffering is already present in soils as a result of weathering in nature. The presence of interlayer hydroxy aluminum is indicated in most of these soils by their X-ray diffractograms. For example, the diffractogram of the Chestnut soil is given by Jackson (1963b).

Titration of H *resin treated montmorillonite* + $FeCl_3$ *and* (*or*) $AlCl_3$.—The pH dependent charge of an H resin treated montmorillonite increases with



Mt.+ H resin present	meq added FeCl$_3$	AlCl$_3$
A. yes	0.0	0.0
B. no	0.1087	0.0
C. no	0.0	0.1483
D. yes	0.1087	0.0
E. yes	0.0725	0.0494
F. yes	0.0544	0.0744
G. yes	0.0362	0.0988
H. yes	0.0	0.1483

FIGURE 4.—NaOH titration curves of H resin treated montmorillonite (Wyoming bentonite), $FeCl_3$, $AlCl_3$ and combinations of a constant amount of the montmorillonite with the stated amounts of $FeCl_3$ and (or) $AlCl_3$, all in 0.5 N KCl.

the addition of an $AlCl_3$ solution (Fig. 4, curve E compared to A). The addition of $FeCl_3$ does not increase the pH dependent charge over the H resin treated check montmorillonite (Fig. 4, curve D compared to A). Similar titration curve slope relationships were obtained with the pure (no montmorillonite added) $AlCl_3$ and $FeCl_3$ (Fig. 4, curve B compared to C).

As the titer of aluminum added to the acidified montmorillonite increases, the pH dependent charge increases (curves E, F, G, and H, Fig. 4) achieving a maximum in the system to which pure $AlCl_3$ was added (curve H).

The presence of OH_3^+ cannot be differentiated from that of Fe^{3+} by titration in a mixed ionic system (Fig. 4, curves A, D, and E). The inflection point for these two ionic species occurs at approximately pH 4 whereas the monomeric trivalent aluminum may be identified in similar systems by the virtue of its titration range of pH 4 to pH 5.6.

Buffer range magnitudes in the soils.—The buffer ranges from the untreated and H resin treated soils are given in Table 1. The endpoints of the different buffer zones in the inorganic fraction were selected according to inflection points except for those soils in which the organic pH dependent charge overshadowed that of the inorganic component. In these soils, arbitrary pH cutoff values of 4.0, 5.6, and 7.6 were utilized to indicate the individual ranges (Schwertmann and Jackson, 1963).

No Range I (OH_3^+, Fe^{3+}) appears in the soils titrated prior to H resin treatment; however, following the H resin treatment, almost all soils decreased in pH indicating the presence of OH_3^+ and Fe^{3+} on the exchange sites. With the H resin treatment, the quantity of the monomeric trivalent aluminum ions increased as expected. The slight decrease in monomeric aluminum in the Junglöss (Hild. Wld.) is accounted for by a slightly higher inflection pH obtained at the $Al^{3+}-OH_3^+$ boundary. Buffer Range III is a rather constant value in the untreated soils although its boundary sharpness varies from indistinct to definite inflections (Fig. 2). In the H resin soil system, Range III magnitudes increase in all soils.

DISCUSSION

The neutralization curves were carried out rapidly and were continuously recorded, thus detecting inflection points not always noted in earlier work. Discontinuous potentiometric and conductometric titration curves (based on equilibrium points reported by literature cited in the review section above) usually have not differentiated between Ranges II, III, and IV, probably for one or two reasons: (1) an insufficient number of points on the neutralization curve have been obtained and thus a detailed plot of the curve has not been possible, or (2) with a series of equilibrium points, the weakly acidic groups are actually not sufficiently different in strength to give observable inflections. Rapid titration, as used in the present

TABLE 1.—BUFFER RANGES OF SOILS, UNTREATED AND AFTER H RESIN TREATMENT

Soil	Locality	Untreated				H resin treated			
		Initial pH	Buffer range I meq/100 g	Buffer range II meq/100 g	Buffer range III meq/100 g	Initial pH	Buffer range I meq/100 g	Buffer range II meq/100 g	Buffer range III meq/100 g
A. Coolville	Ohio	4.00	—	12.7	2.6	3.68	2.0	15.3	5.6
B. Diabas (Hlb)	Germany	4.40	—	4.8	1.3	3.60	3.1	8.7	6.3
C. AB-38	Ohio	4.40	—	4.2	1.8	3.48	3.8	4.2	4.9
D. Junglöss (Göttingen)	Germany	4.40	—	2.4	1.6	3.96	—	4.8	2.9
E. Dodge B_2	Wisconsin	4.40	—	1.0	1.4	3.24	4.0	10.2	4.7
F. Dodge IIB_{23}	Wisconsin	4.48	—	0.9	0.6	3.56	1.7	4.2	2.8
G. Trumbull	Ohio	4.04	—	5.5	1.3	3.40	4.5	5.2	5.0
H. Cambridge	Ohio	4.40	—	3.7	1.1	3.44	3.8	5.2	8.8
I. Junglöss (Hild. Wld.)	Germany	4.44	—	3.1	1.7	3.64	2.9	2.1	4.1
J. Basalt (Vol b)	Germany	5.64	—	0.5	0.7	2.64	27.9	8.9	9.7
K. Sangamon	Illinois	6.20	—	—	0.9	3.64	2.3	8.1	5.0
L. Chestnut	Turkey	8.44	—	—	—	3.10	—	26.0	13.3

study, differentiates between proton sources by their rate of release, analogous to differential thermal analysis (DTA) which dynamically records a series of different $OH^- + H^+ \longrightarrow H_2O$ rates dependent on different bonding of OH groups.

The titration curves of the various soils indicate a considerable range of magnitude in the pH dependent cation exchange charge (Table 1). The untreated soils showing the largest pH dependent charge above 7.6 contained a higher percentage of organic matter (Trumbull, Cambridge, and Diabas, Table 2). Pratt (1961), assuming that clay and organic matter acted as separate components, calculated that organic carbon contributed 24 times more than clay per unit weight to the pH dependent charge. The presence of the pH dependent charge from the organic fraction would conceal the upper inflection of the third buffer range in the soils of the present study. This can be seen by comparing (Fig. 2) the Coolville soil (low in organic matter content, Table 2) and the Trumbull soil (higher organic matter content). The initial pH in 0.5 N KCl (Table 2) of these two untreated soils is very similar but yet only the Coolville exhibits discrete third buffer range. While the quantity of monomeric trivalent aluminum most likely does influence the amount of pH dependent charge, the presence of this form of aluminum is not a requirement for a discrete third range to appear. Junglöss (Hild. Wld., soil I) which has neither as acid a pH nor as much titratable aluminum as the Coolville soil exhibits

TABLE 2.—THE pH AND ORGANIC MATTER CONTENTS OF THE SOILS

Soil	pH		Organic matter (per cent)
	In H_2O (thin paste)	In 0.5 N KCl 1 to 50*	
A. Coolville	4.45	4.00	0.52
B. Diabas (Hlb)	5.10	4.40	2.11
C. AB-38	4.40	4.40	2.41
D. Junglöss (Göttingen)	4.62	4.40	0.51
E. Dodge B_2	5.02	4.40	0.40
F. Dodge IIB_{23}	4.98	4.48	0.09
G. Trumbull	3.98	4.04	5.79
H. Cambridge	4.30	4.40	5.74
I. Junglöss (Hild. Wld.)	4.10	4.44	0.13
J. Basalt (Vol b)	6.30	5.64	0.10
K. Sangamon	6.70	6.20	0.53
L. Chestnut	7.65	8.44	1.82

* Soil to solution ratio; this high dilution may account for the higher pH in KCl than water for a few soils. For most soils the acidic cations replaced in the KCl more than offset the greater dilution.

a discrete third buffer range. The Junglöss (Hild, Wld.) soil is, however, very low in organic matter content.

In summary, a discrete third range is likely to appear in untreated soils provided (a) the initial pH in KCl is below pH 4.5 with the presence of monomeric trivalent Al and (b) the organic matter content is low.

An entirely different shape of titration curve results from treatment of the soils with H resin. Most soils, with the notable exception of the Basalt soil, show well defined buffer ranges and an increase in pH dependent charge as a result of the treatment. The increase in pH dependent charge may occur as a result of the unblocking of reactive sites by the H resin treatment. This treatment could activate an iron–aluminum complex and expose fresh reactive surfaces which would require neutralization to raise the pH of the soil. The iron and aluminum titer should increase through such activation. An increase in monomeric trivalent aluminum was observed (Fig. 3 compared to Fig. 2), but any iron increase could only be implied because of the similar titration ranges of OH_3^+ and Fe^{3+}.

A comparison of the Dodge soil with the Sangamon and Coolville soils illustrates the importance of acid ageing during soil development. The Dodge soil from southern Wisconsin, developed from till overlaid by loessial material, contains much octahedral iron in the layer silicate clays. In the Tama soil, another southwestern Wisconsin loessial soil, the formula for the fine clay was calculated as $(Si_{7\cdot65}Al_{0\cdot35})$ $(Al_{2\cdot43}$ $Fe_{1\cdot14}$ $Mg_{0\cdot38})$ (Glenn *et al.*, 1960), similar to that of Miami soil (Sawhney and Jackson, 1958). The weathering of this clay was shown to be evident but not extensive. The iron associated with the clay is thus still high and serves as a buffer against development of extreme acidity (Range I, Jackson, 1963a). Furthermore, the iron released appears from the results with the Dodge IIB_{23} horizon to serve in a pH dependent charge blocking mechanism.

The above two iron relationships in acid weathering have an important bearing on lime requirement of soils. When there is sufficient octahedral iron remaining in a clay system, the acid weathering process appears to reduce the pH dependent charge, but upon activation by naturally acid weathering conditions (simulated here by H resin treatments), the pH dependent sites are activated and contribute to an increased lime requirement. The Coolville soil, with its low pH and large amount of monomeric trivalent aluminum is in such a strongly acid weathered condition, with correspondingly large lime requirement. It also has a large pH dependent charge, which has been triggered by the weathering of the iron components. The H resin treatment does not improve the already good third buffer range inflections since the soil is naturally in an activated state with regard to hydroxy aluminum in the interlayer space.

The beautifully discrete ranges in Sangamon soil (a bright red Sangamon age Paleosol) after the H resin treatment suggests the presence in this soil of a highly aluminous surface for titration. The Sangamon soil had perhaps undergone a very acid weathering regime prior to its burial by the calcareous loessial material which raised its pH to 6.2 (Table 1). During this acid weathering, the clay minerals appear (from the diffractogram) to have degraded, with the release of iron and aluminum thereby forming pH dependent charge sites. Calcium bicarbonate leached from the overlaid loessial deposits has neutralized the ancient acid soil and decreased the pH dependent charge. However, an H resin treatment of the Sangamon soil readily activates a discrete third buffer range.

Similarly, the Dodge IIB_{23} (soil F, Fig. 2) has a very low pH dependent charge in the original titration and, besides developing a discrete Al^{3+} titration range after H resin treatment, shows an increase in pH dependent charge range of exchange capacity. Although the Dodge soils have a very low buffer capacity (Fig. 2), there is a normal drop of pH when the measurements by the thin paste and KCl methods are compared (Table 2). The pH determined by the 0.5 N KCl method would be expected to be lower in all soils had the soil : water dilution been less.

The interpretation of experimental results involving an H resin treatment must be carefully considered as to the several reactions brought about by the H resin. In addition to the simple OH_3^+ saturation of the clay complex, one must realize that there is an increase in monomeric trivalent aluminum and in the pH dependent charge reflected in the titration curve. Therefore, the components in the H resin treated system may be chemically different from those of the natural soil.

SUMMARY AND CONCLUSIONS

1. Four distinct buffer ranges are discernible in the titration curve of an H resin treated montmorillonite (highly aluminum octahedral layer, Wyoming bentonite source) that had been attributed to hydronium, monomeric trivalent aluminum, polymeric hydroxy aluminum, and other pH dependent charges.
2. The presence of added ferric iron and the absence of titratable aluminum slightly decreases the pH dependent charge in H resin treated montmorillonite. As the ratio of aluminum added to iron increases, the magnitude of the pH dependent charge increases until the maximum is obtained with aluminum saturation. No endpoint differentiation is observed between the hydronium and the soluble ferric iron during the titration of the acid montmorillonite containing added $FeCl_3$.
3. Acid soils show varying amounts of pH dependent charge, which is most extensive when significant amounts of monomeric trivalent aluminum are present. The pH dependent charge is least developed in acid soils (pH 4.5 in 0.5 N KCl) having no monomeric trivalent aluminum and having brown iron oxide cementation (and fragic soil structure).
4. Treatment of soils with H resin develops a pH dependent charge to

a marked degree in both acid and neutral soils, the discrete buffer zones being visible in most of them. The organic sources of pH dependent charge appear to alter the titration curves sufficiently to conceal discrete inorganic buffer zones of the neutralization curves in some soils. The pH dependent charge developed is related to the exchangeable monomeric trivalent aluminum, but the quantity of pH dependent charge does not remain constant per unit quantity of monomeric aluminum.

5. The intensity of the acid weathering process of soils plays an important role in the development of pH dependent charge and the determination of lime requirement of acid soils. More NaOH titration (and thus more liming) is required to neutralize a soil if its exchange sites have been unblocked and aluminum activated by highly acid weathering.

ACKNOWLEDGMENTS

This contribution from the Department of Soil Science was supported in part by grants from the National Science Foundation and through the Research Committee of the University of Wisconsin Graduate School from Wisconsin Alumni Research Foundation.

REFERENCES

Aldrich, D. G., and Buchanan, J. R. (1958) Anomalies in techniques for preparing H-bentonites: *Soil Sci. Soc. Amer. Proc.*, v.22, pp.281–285.

Barshad, I. (1960) Significance of the presence of exchangeable magnesium ions in acidified clays: *Science*, v.131, pp.988–990.

Bernstein, F. (1959) Distribution of water and electrolyte between homoionic clays and saturating NaCl solutions: In *Clays and Clay Minerals, 8th Conf.*, Pergamon Press, London, pp.122–149.

Bradfield, R. (1927) The saturation capacity of colloidal clay soils: *1st Congr. Intern. Soc. Soil Sci.*, v.4, pp.858–868.

Brown, G. (1953) The dioctahedral analogue of vermiculite: *Clay Min. Bull.*, v.2, pp.64–69.

Chernov, V. A. (1959) Genesis of exchangeable aluminum in soils: *Sov. Soil Sci.*, v.10, pp.1150–1156.

Dion, H. G. (1944) Iron oxide removal from clays and its influence on base exchange properties and X-ray diffraction patterns of the clays: *Soil Sci.*, v.58, pp.411–424.

Dixon, J. B., and Jackson, M. L. (1962) Properties of intergradient chlorite-expansible layer silicates of soils: *Soil Sci. Soc. Amer. Proc.*, v.26, pp.358–362.

Fieldes, M., and Schofield, R. K. (1960) Mechanisms of ion adsorption by inorganic soil colloids: *New Zealand J. of Sci.*, v.3, pp.563–579.

Garrels, R. M., and Christ, C. L. (1956) Application of cation exchange reactions to the beidellite of the Putnam silt loam soils: *Amer. J. Sci.*, v.254, pp.372–379.

Glenn, R. C., Jackson, M. L., Hole, F. D., and Lee, G. B. (1960) Chemical weathering of layer silicate clays in loess-derived Tama silt loam of southwestern Wisconsin: In *Clays and Clay Minerals, 8th Conf.*, Pergamon Press, London, pp.63–83.

Harward, M. E., and Coleman, N. T. (1954) Some properties of H- and Al-clays and exchange resins: *Soil Sci.*, v.78, pp.181–188.

Hissink, D. J. (1924) Base exchange in soils: *Trans. Faraday Soc.*, v.20, pp.551–566.

Jackson, M. L. (1958) *Soil Chemical Analysis*: Prentice-Hall, Englewood Cliffs, N. J., pp.45–46.

Jackson, M. L. (1960) Structural role of hydronium in layer silicates during soil genesis: *Trans. Intern. Congr. Soil Sci.*, 7th Congr., Madison, v.2, pp.445–455.

Jackson, M. L. (1963a) Aluminum bonding in soils: A unifying principle in soil science: *Soil Sci. Soc. Amer. Proc.*, v.27, pp.1–10.

Jackson, M. L. (1963b) Interlaying of expansible layer silicates in soils by chemical weathering: *Clays and Clay Minerals, 11th Conf.*, Pergamon Press, London, pp.29–46.

Jonas, E. C. (1963) Ion exchange at edge and interlayer in montmorillonite differing in size: *Science*, v.140, pp.75–76.

Keeney, D. R., and Corey, R. B. (1963) Factors affecting the lime requirements of Wisconsin soils: *Soil Sci. Soc. Amer. Proc.*, v.27, pp.277–280.

Low, P. F. (1955) The role of aluminum in the titration of bentonite: *Soil Sci. Soc. Amer. Proc.*, v.19, pp.135–139.

Marshall, C. E., and Bergman, W. E. (1942) The electro-chemical properties of mineral membranes. II. Measurement of potassium-ion activities in colloidal clays: *Jour. Phys. Chemistry*, v.46, pp.52–61.

Page, A. L., and Whittig, L. D. (1961) Iron adsorption by montmorillonite systems: I. Preliminary studies, II. Determination of adsorbed iron: *Soil Sci. Soc. Amer. Proc.*, v.25, pp.278–286.

Paver, H., and Marshall, C. E. (1934) The role of aluminum in the reactions of the clays: *Jour. Soc. Chem. Ind.*, v.53, pp.750–760.

Pommer, A. M., and Carroll, D. (1960) Interpretation of potentiometric titration of H-montmorillonite: *Nature*, v.185, pp.595–596.

Pratt, P. F. (1961) Effects of pH on the cation-exchange capacity of surface soils: *Soil Sci. Soc. Amer. Proc.*, v.25, pp.96–98.

Rich, C. I. (1960) Aluminum in interlayers of vermiculite: *Soil Sci. Soc. Amer. Proc.*, v.24, pp.26–32.

Rich, C. I., and Obenshain, S. S. (1955) Chemical and clay mineral properties of a red–yellow podzolic soil derived from muscovite schist: *Soil Sci. Soc. Amer. Proc.*, v.19, pp.334–339.

Sawhney, B. L., and Jackson, M. L. (1958) Soil montmorillonite formulas: *Soil Sci. Soc. Amer. Proc.*, v.22, pp.115–118.

Schofield, R. K. (1939) The electrical charges on clay particles: *Soils and Fertilizers*, v.2, pp.1–5.

Schwertmann, U. (1961) Uber das lösliche und austauschbare aluminium im Boden und seine Wirkung auf die Pflanze: *Landw. Forsch.*, v.14, pp.53–59.

Schwertmann, U., and Jackson, M. L. (1963) Hydrogen–aluminum clays: A third buffer range appearing in potentiometric titration: *Science*, v.139, pp.1052–1054.

Schwertmann, U., and Jackson, M. L. (1964) Influence of hydroxy aluminum ions on' pH titration curves of hydronium–aluminum clays: *Soil Sci. Soc. Amer. Proc.*, v.28, pp. 179–183 (in press).

Shen, M. J., and Rich, C. I. (1962) Aluminum fixation in montmorillonite: *Soil Sci. Soc. Amer. Proc.*, v.26, pp.33–36.

Shoemaker, H. E., McLean, E. O., and Pratt, P. F. (1961) Buffer methods for determining lime requirement of soils with appreciable amounts of extractable aluminum: *Soil Sci. Soc. Amer. Proc.*, v.25, pp.274–277.

Slabaugh, W. H. (1952) The heat of neutralization of hydrogen-bentonite: *J. Amer. Chem. Soc.*, v.74, pp.4462–4464.

Steyermark, A. (1951) *Quantitative Organic Microanalysis*: The Blakeston Company, New York, pp.82–121.

Truog, E. (1916) A new apparatus for the determination of soil carbonates and new methods for the determination of soil acidity: *Jour. Ind. Eng. Chem.*, v.8, pp.341–345.