

## pH DEPENDENT ION EXCHANGE PROPERTIES OF SOILS AND CLAYS FROM MAZAMA PUMICE\*

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**Abstract**—Cation exchange capacity (CEC) measurements were made for whole pumice soil samples by several methods, including standard procedures involving cation saturation, excess salt removal, and cation displacement steps, and a  $^{45}\text{Ca}^{2+}$  radioisotope dilution procedure. Results indicated that the vesicular pores of the pumice soil material affected attainment of ion diffusion equilibria, and, hence, introduced a large source of error in the measurements. On this basis, the validity of ion exchange values obtained for these soils was concluded to be subject to considerable doubt. More important, however, the solute and/or solution exclusion or retention exhibited by pumice particles during the course of CEC procedures was thought to be highly significant with respect to the probable influence exerted on physical, chemical, and biological properties of the soils in the field situation.

Interpretation of pH dependent cation and anion exchange capacity measurements of the  $<2\mu$  clay fraction of the pumice soils was confounded by the occurrence of hydroxy interlayered 2:1 phyllosilicate materials in admixture with the amorphous components. Since the interlayered materials contributed an indeterminate proportion of the total pH dependent charge of the mixture, it was further concluded that the measurement of this property was of little direct value in assessing the relative amounts of amorphous and crystalline components in the clay fractions of the soils investigated. However, the values obtained revealed fundamental aspects of ion exchange behavior which are important to understanding the complex systems involved.

### INTRODUCTION

ION EXCHANGE properties of soil clay systems are a function of permanent and pH dependent surface charge. Permanent charge is negative and due to isomorphous cation substitution in the lattice structure of phyllosilicate clay minerals. The sign and magnitude of pH dependent charge, on the other hand, is contingent upon the reaction of the soil and has been attributed directly or indirectly to the presence of amorphous colloids, such as allophanic aluminosilicates and hydrous iron and aluminum oxides (Birrell, 1958; Wada and Ataka, 1958; Fieldes and Schofield, 1960; Iimura, 1961), and to the occurrence of exposed edges and bonds of phyllosilicate minerals (Hendricks, 1945; Kelly, 1948; Schofield, 1949; Fieldes and Schofield, 1960). Recent investigations have shown that expression of the permanent negative charge of 2:1 expanding lattice silicates also can become pH dependent when certain hydroxy polymers, espe-

cially of aluminum, occupy interlayer positions (Rich 1960; Barnhisel and Rich, 1963; Frink and Peech, 1963; Clark, 1964; Coleman *et al.*, 1964; de Villiers and Jackson 1967a, 1967b).

In soils which contain predominantly amorphous materials in the clay-size fraction, the nature and magnitude of electric charge carried by the micelles is almost entirely a function of pH. This is the case for many soils of New Zealand and Japan wherein volcanic ash and/or pumice parent materials weather to kaolinitic minerals via allophane (Fieldes, 1962), with infrequent occurrence of expanding layer phyllosilicates. The amorphous components may exhibit pH dependent cation exchange capacities in excess of 100 me/100 g (Aomine and Jackson, 1959). Occurrence of rather large pH dependent anion exchange capacities has also been attributed to the presence of amorphous clays in soils derived from volcanic materials since crystalline clay components usually exhibit little of this tendency. Consequently, investigators have been able to utilize the property of pH dependent ion exchange capacities in evaluating the importance of amorphous versus crystalline clay minerals in those soils.

The soils of the present investigation are forming in a deposit of pumiceous lapilli and ash result-

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ing from eruption of Mt. Mazama (site of present Crater Lake, Oregon) approximately 6600 yr ago (Allison, 1966). The samples were taken across a climatic transect of the deposit (Chichester *et al.*, 1969). Results of differential dissolution analysis had shown that amorphous components predominated in the  $< 2\mu$  size fraction of these soils (Chichester *et al.*, 1969). In light of these findings and the data reported from New Zealand and Japan, the decision was made to determine pH dependent ion exchange properties of soils on Mazama pumice and to assess the utility of those properties in evaluating the relative significance of amorphous and crystalline clay components.

Ion exchange studies were initially conducted on whole soil samples. These were later abandoned due to effects of the internal porosity of pumice particles on attainment of exchange equilibrium. Certain of these preliminary data will be discussed in conjunction with the present study in that it reflects a rather unique aspect of the ion exchange behavior of the soils under investigation.

#### CATION EXCHANGE CAPACITIES OF WHOLE-SOIL SAMPLES

##### *Experimental procedures*

*Materials.* Soils were sampled by horizon from four sites along a weathering transect established on the Mazama pumice fall in central Oregon. Three of the soils were Entisols developing in a pumice mantle of 135 cm or greater in depth under *Pinus ponderosa*/*Purshia tridentata*, *Pinus ponderosa*/*Ceanothus velutinus*, and *Abies concolor*/*Ceanothus velutinus* vegetation, respectively. The fourth soil, located at the wettest end of the transect, was an unclassified, shallow (43 cm) podsolized soil forming under the influence of *Tsuga mertensiana*/*Rhododendron albiflorum* vegetation type. Detailed site descriptions, soil sampling methods, and methods of sample preparation have been described previously (Chichester *et al.*, 1969).

*Ion exchange methods.* Cation exchange capacity (CEC) measurements of the air-dry whole-soil samples were made at pH 7. The  $\text{NH}_4\text{OAc-EtOH-HCl}$  method employed by the Oregon State University Soil Testing Laboratory (Alban and Kellogg, 1959) plus several modifications were used. Modifications included: substitution of  $\text{Ca}(\text{OAc})_2$  as the index ion solution, substitution of  $\text{NaOAc}$  as the displacement solution, and variations in the number and duration of saturation and/or exchange washes. Isotopic exchange was also measured by the  $^{45}\text{Ca}^{2+}$  method of Blume and Smith (1954). Modifications were included to increase both the time of contact of the sample with the  $^{45}\text{Ca}^{2+}$  saturating solution and the length of the isotopic equilibration period.

##### *Results and discussion*

Considerable abrasion of gravel size pumice occurred when the soil samples were mechanically shaken with the saturating solution during the CEC procedure (Alban and Kellogg, 1959). Modification of the procedure to eliminate extensive shaking (and hence reduce abrasion) showed that abrasion had had the effect of reducing apparent CEC values by approximately 15 per cent. This is opposite to the normal relationship of particle size. To further test the effect of particle size on measured CEC one-half of a sample of  $> 2$  mm pumice gravels was crushed to pass a 2 mm screen and the CEC determined with  $\text{NH}_4\text{OAc}$  on both crushed and uncrushed portions. The crushed material had a measured CEC equal to only 56 per cent of the uncrushed control. It was believed that the effect of grinding is to reduce salt trapping in the pores of pumice particles. Attention was therefore focused on testing the hypothesis that particle porosity affected CEC measurement in these soils by physically restricting the attainment of ion diffusion equilibria during CEC procedures.

The apparent CEC increased with time of sample-solution contact (period of index ion diffusion) during saturation of the exchange complex (Table 1). Comparison of the data for the  $< 2$  mm with that for the  $> 2$  mm particle size material shows the relatively greater effect of internal porosity in the larger particles. Borchardt *et al.*, (1968) have since shown by mercury intrusion that as the pumice particle size decreases, the relative contribution of particle-to-particle pores increases and the contribution of vesicular pores decreases. There was a much greater percent increase in apparent CEC with time of sample-solution contact for the particles of lesser diameter (Table 1). This probably reflects a greater accessibility of the porespace in the smaller particles, relative to that in the larger ones, with respect to ion diffusion.

Further investigation showed that it was as difficult to remove the index ions from the pumice pores as it had been to introduce them. Pumice soil samples which had been in contact with  $\text{NH}_4\text{OAc}$  solution for several hours were washed with ethanol or ethanol followed by distilled water to remove excess salts. The amount of  $\text{NH}_4^+$  ion subsequently displaced by 0.1N HCl was inversely related to the number of washes the sample had received (Table 2). While similar behavior can be observed with non-pumiceous soils, it is apparent that much more extensive washing is necessary to remove excess salts in pumice samples. Other pumice soil samples were "saturated" by equilibration overnight with  $\text{Ca}(\text{OAc})_2$  solution. After 4 16-hr extractions with  $\text{NaOAc}$  displacing solution, the fifth extraction still contained from 3 to 8 me of  $\text{Ca}^{2+}$ /

Table 1. Ammonium displacement from Mazama pumice soil material as a function of time of sample contact with cation solution (NH<sub>4</sub>OAc)

Soil sample	NH <sub>4</sub> <sup>+</sup> displaced by 0.1 N HCl (me/100 g)*				
	0.50 hr	4.75 hr	21.50 hr	42.00 hr	160.00 hr
Antelope unit:					
Cl horizon, ≤ 2 mm particle size	5.00	n.d.	n.d.	n.d.	15.80
Cl horizon, > 2 mm particle size	24.12	26.35	33.19	39.29	44.85

\*Following indicated period of contact with cation solution plus five washes with 95% EtOH to remove "excess" salts.

Table 2. Cation retention by Mazama pumice soils as measured by the quantity of cation removed in the last of several successive wash treatments

Soil sample	Index cation (as acetate)	Wash treatments		Index cation in final wash (me/100 g)
		Preliminary	Final	
Antelope unit:				
Cl horizon		5, 5-min, 95% EtOH		22.36
Cl	NH <sub>4</sub> <sup>+</sup>	13, 5-min, 95% EtOH	1, 30-min,	7.50
Cl		13, 5-min, 95% EtOH plus 5, 5-min, H <sub>2</sub> O	HCl, 0.1 N	4.07
Al horizon				5.60
AC	Ca <sup>2+</sup>	4, 16-hr, NaOAc, 1N	1, 16-hr	2.70
Cl			NaOAc, 1 N	4.00
C2				5.40
Walker rim:				
Al horizon				4.80
AC	Ca <sup>2+</sup>	4, 16-hr, NaOAc, 1 N	1, 16-hr,	2.10
Cl			NaOAc, 1 N	6.80
C2				7.50

100 g (Table 2). This is again evidence of a very slow rate of ion movement from the pumice vesicles.

Because of the difficulties in attaining index cation equilibration with the pumice soil samples and in washing the samples free of excess salt solution, a radioisotope equilibration method (Blume and Smith, 1954) was attempted. The method provides a means for determining ion exchange in the presence of neutral salts and thereby circumvents the necessity of washing the sample free of these salts following saturation of the exchange complex. Once exchange equilibrium is reached, the CEC of the sample is calculated on the basis of isotope dilution ratios. The samples were equilibrated with <sup>40</sup>Ca(OAc)<sub>2</sub> for 24 hr in an evacuated desiccator. They were then tagged with <sup>45</sup>CaCl<sub>2</sub> and aliquots were counted each day. The rates of exchange were very slow and isotope equilibrium was not attained even after 9 days (Table 3). This again

indicates the slowness of diffusion through the vesicular pores of pumice.

For the preceding data, non-equilibrium between vesicles of the pumice matrix and the external solution probably existed regardless of the method used. The process of ion equilibration must occur each time the ionic environment is altered during the CEC procedure, i.e., during initial index ion saturation, removal of excess index ion solution, and index ion displacement. The length of time required to achieve ion equilibrium, as well as the uncertainty of when the equilibrium is obtained, raise a question on the validity of the CEC measurement for these porous systems. On the other hand, the importance of these data should be stressed in that they indicate the tremendous influence of the internal porosity of the pumice particles on the retention of dissolved salts—an influence which most certainly can be extrapolated to the field

Table 3. Isotopic exchange in  $^{40}\text{Ca}^{2+}$  saturated Mazama pumice soil material as a function of time

Soil sample	$^{40}\text{Ca}^{2+}$ activity in supernatant $^{40}\text{Ca}(\text{OAc})_2$ solution (c.p.m./ $\mu\text{l}$ )*				
	1 day	3 days	5 days	7 days	9 days
Antelope unit:					
C1a horizon	5.5	5.0	4.9	4.6	4.5
C1b	5.6	5.2	4.8	4.8	4.5
C2a horizon	6.0	5.7	5.3	n.d.	5.3
C2b	6.3	6.0	n.d.	5.8	5.6
Reference solution	2.8	n.d.	2.8	2.8	2.7

\*Counts taken at indicated times elapsed since tagging of sample suspension. Values corrected for background radiation.

situation and behavior with respect to the natural soil solution.

#### pH DEPENDENT ION EXCHANGE CAPACITIES OF SOIL CLAY SAMPLES

##### Experimental procedures

**Materials.** The  $< 2\mu$  fraction was separated from each horizon of the pumice soils described earlier. About two-thirds of the total quantity of clay obtained from each sample was treated for removal of amorphous hydrous oxides of iron, aluminum, and silicon by differential dissolution (Chichester *et al.*, 1969). Ion exchange determinations were made on both the untreated and treated portions of the clays, i.e., with and without the amorphous component.

**Methods.** The pH dependent exchange capacities were measured essentially according to the procedure of Schofield (1949) and of Wada and Ataka (1958) (Fig. 1). Clay samples were washed with 30 ml volumes of 0.1 N NaCl solution adjusted to the desired saturation pH by the addition of either HCl or NaOH. When, after a minimum of five washes, the measured pH of the supernatant NaCl solution was found to remain equal to the adjusted pH, two further washes at that pH were given. No significant change in the pH of supernatant solutions from these two washes was taken to indicate attainment of equilibrium. Excess NaCl was determined gravimetrically (Fig. 1) to avoid possible hydrolytic loss of exchangeable ions during removal of salt by washing.

The total sodium plus chloride was displaced from the clay sample in three washes of 25 ml of 0.1 N  $\text{Ca}(\text{NO}_3)_2$  each (Fig. 1). The washes were combined for analyses. Sodium analysis was performed on a Beckman model DU flame emission spectrophotometer. Chloride was determined

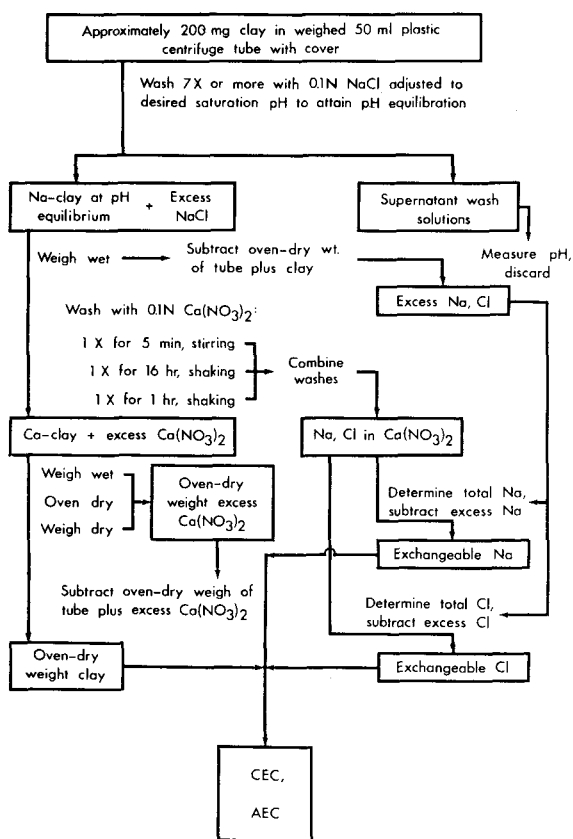


Fig. 1. Flow sheet for the determination of pH dependent ion exchange capacity.

volumetrically by mercurimetric titration (Clarke, 1950; Goldman, 1959).

The clay samples were not oven dried prior to measurement of exchange capacities in order to avoid irreversible dehydration of amorphous com-

ponents and possible effect on exchange properties. Oven-dry sample weights were calculated by subtracting the gravimetrically determined  $\text{Ca}(\text{NO}_3)_2$  and the tube tare from the oven-dry weight of the tube plus Ca clay plus excess  $\text{Ca}(\text{NO}_3)_2$ . The cation and anion exchange capacities were calculated from the results of total sodium and chloride analyses corrected for excess salt (Fig. 1). The values obtained were plotted as a function of equilibrium pH.

### RESULTS AND DISCUSSION

The pH dependent exchange capacities of samples from the Antelope Unit (AU) site at the drier end of the weathering transect are typical of the soils investigated (Figs. 2-5). For purposes of comparison, a summary of ion exchange data for the Antelope Unit, Royce Mountain, and Salt Creek sites is presented in Table 4. Similar data were not obtained for the Walker Rim profile owing to an insufficient amount of clay-size material from that soil. The values shown in the table represent the pH ranges over which the maximum change in CEC or AEC occurred. This was not equivalent in most cases to the entire range of pH over which the experiment was conducted.

*Cation exchange capacity.* In general the plots of CEC vs. pH assumed skewed S-shaped patterns, with the sharpest increase in CEC evident in the pH range from 5.00 to 7.00 (Figs. 2-5). The differences among samples appeared to be mainly in the magnitude of change in exchange capacity with pH. Variability between samples was much greater among those from which amorphous mater-

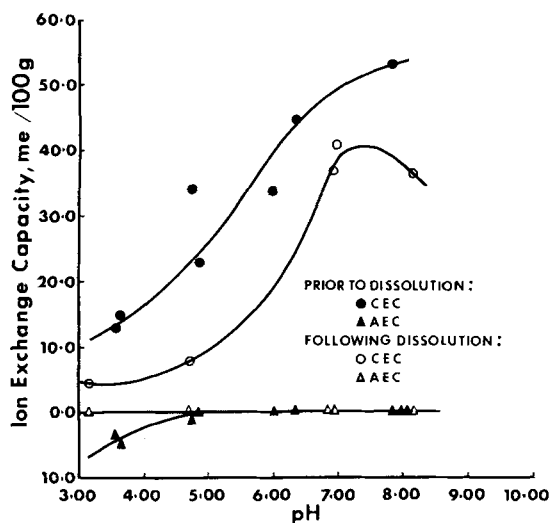


Fig. 2. Ion exchange capacity of the Antelope Unit A1 horizon clay sample as a function of pH.

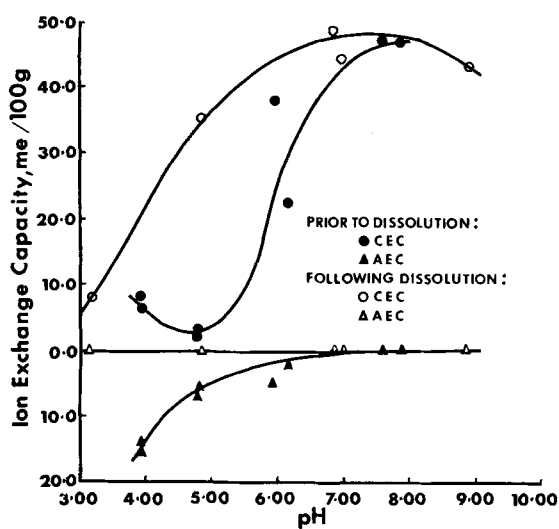


Fig. 3. Ion exchange capacity of the Antelope Unit AC horizon clay sample as a function of pH.

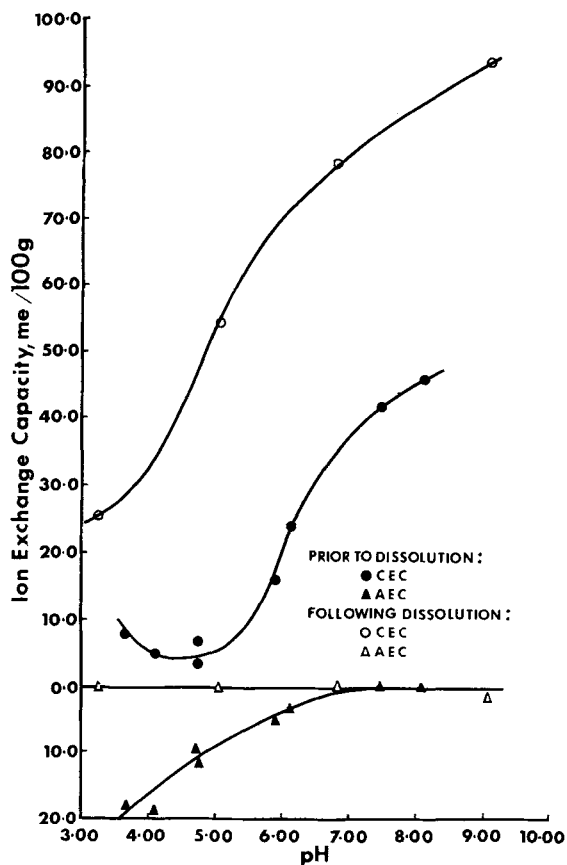


Fig. 4. Ion exchange capacity of the Antelope Unit C1 horizon clay sample as a function of pH.

Table 4. pH dependent change in ion exchange capacity of Mazama pumice soil clay samples

Soil sample	Amorphous component present			Amorphous component removed		
	Cation exchange capacity (CEC) pH range	Anion exchange capacity (AEC) pH range	Corresponding range of CEC (me/100 g)*	Cation exchange capacity (CEC) pH range	Anion exchange capacity (AEC) pH range	Corresponding range of CEC (me/100 g)†
Antelope unit:						
A1 horizon	3.6-8.0	3.6-4.8	12.4-53.8	3.2-6.9	3.2-6.9	3.8-39.9
AC	4.8-7.6	3.9-7.6	2.2-47.4	3.2-6.8	3.2-6.8	8.0-48.6
Cl	4.7-8.1	4.1-7.4	3.6-45.6	3.2-9.1	3.2-9.1	25.5-92.8
C2	3.6-8.0	3.6-6.2	9.2-54.6	3.2-6.8	3.2-6.8	15.4-49.1
Royce mountain:						
A1 horizon	4.6-8.4	3.6-4.0	5.8-53.9	3.5-7.0	3.5-7.0	13.6-48.5
AC	5.4-8.1	3.6-6.5	2.1-35.5	4.7-6.8	4.7-6.8	16.7-46.8
Cl	4.6-7.8	3.8-7.8	5.1-41.5	4.6-6.5	4.6-6.5	18.6-63.8
C2	5.5-7.8	4.0-7.6	3.5-48.2	3.6-6.8	3.6-6.8	25.6-48.1
Salt creek:						
B3 horizon	3.5-7.6	3.5-6.4	8.8-46.6	3.1-8.4	3.1-8.4	19.7-50.8
C	3.5-7.3	3.5-9.0	5.0-23.0	3.1-6.6	3.1-6.6	21.8-56.0

\*Original material.

†Residue after removal of amorphous material.

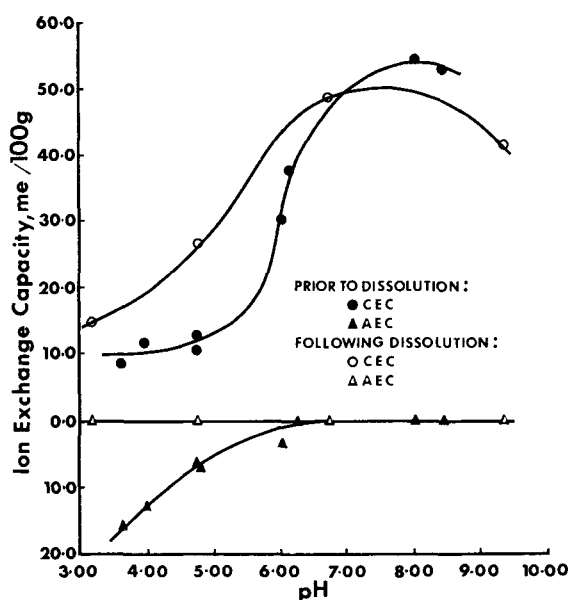


Fig. 5. Ion exchange capacity of the Antelope Unit C2 horizon clay sample as a function of pH.

ials had been removed. The magnitude of CEC values at any given pH was increased by removal of the non-crystalline clay material (Figs. 3-5). This is believed to be due to the concentration of 2:1 phyllosilicates of relatively high permanent negative charge in the samples during the differential dissolution treatment. The AU-Al sample (Fig. 2) is an exception in that all CEC values were lower following treatment. The reason for this behavior is not apparent from the clay mineralogy data (Chichester *et al.*, 1969). The change in CEC with pH for most samples after dissolution treatment was about the same magnitude or less than that exhibited by the same samples prior to treatment. The AU-CI horizon sample (Fig. 4) is an exception in that it showed a relatively large pH dependent CEC following differential dissolution.

Fieldes and Schofield (1960) have suggested that pH dependent CEC in amorphous clays is due largely to the tetrahedral aluminum sites of allophanic silicon-aluminum co-precipitates. These sites would be effective in that portion of the curve above pH 4.5 (Milliken, Mills, and Oblad, 1950; Plank, 1953). At the upper end of the pH range, the dissociation of aluminosilicic acid groups might be an additional source of negative charge (Plank, 1953; Iimura, 1961). The degree to which these mechanisms may explain pH dependent cation exchange in Mazama pumice soil clays is difficult to assess. Previous findings (Chichester *et al.*, 1969) indicated that the amorphous clay component of

these soils is most likely a mixture of varying proportions of hydrous oxides of silicon, aluminum, and iron, as well as silicon-aluminum co-precipitates. However, since the hydrous oxides mentioned either do not function as cation exchangers, or do so only at pH's above that of the largest observed CEC changes, it is reasonable to assume that tetrahedrally coordinated aluminum of the co-precipitates is the primary site of cation exchange reactions in the amorphous clay materials under investigation.

Subsequent to initiation of the ion exchange studies, a complex suite of 2:1 phyllosilicates was identified in the  $< 2\mu$  residue following dissolution of amorphous material (Chichester *et al.*, 1969). The suite included beidellite, montmorillonite, vermiculite, a micaceous component, chloritic intergrades, and chlorite. The presence of these components seriously affect the use of pH dependent charge to assess the nature of the amorphous materials. The complicating factor is the variation in exchange capacity of chloritic intergrades with change in pH of the system. At pH values around 5.0, non-exchangeable polymers of aluminum (and/or iron) exist in the interlayer positions effectively blocking the sites due to permanent charge (Coleman *et al.*, 1964). Certain samples exhibited an increase in CEC once pH values were lower than 4.0 or 4.5. This was probably due to the conversion of some of the polymerized interlayer ions to exchangeable form, e.g.,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  and/or  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ , in the presence of hydrogen ions (Clark, 1964; Coleman *et al.*, 1964). As the pH of the index ion saturation solution is increased during the determination of ion exchange capacities, the interlayer hydroxy polymers are thought to be gradually displaced (Rich, 1960; Clark, 1964) or deprotonated in place (Jackson, 1960; de Villiers and Jackson, 1965, 1967a, 1967b). This would expose an increasing number of permanent charge exchange sites and result in the pH dependent increase in CEC which was exhibited by the samples. The amount of increase would be a function of the ease with which the hydroxy interlayer was displaced and of the charge density of the phyllosilicate matrix. Above pH 7.0, the data show a leveling off or decrease in cation adsorption for most samples. This behavior might be due to the precipitation of polymers of hydroxy aluminum (and/or iron) external to the lattice edge (Hsu and Bates, 1964). Such a precipitate could conceivably block the accessibility of some of the permanent charge exchange sites, although not actually occupying these sites.

Other sources of pH-dependent CEC in the samples following differential dissolution might include coatings of particles of amorphous material

not effectively removed, and the various groups which arise in the phyllosilicate minerals at lattice edges (Fieldes and Schofield, 1960).

*Anion exchange capacity.* The values of anion retention exhibited by each of the samples containing the amorphous clay component decrease with an increase in pH (Figs. 2–5). The magnitude of change in anion exchange capacity (AEC) with pH varied considerably among samples, as did the range in pH over which the change occurred. The surface horizon sample of each profile, for example, AU–Al (Fig. 2), exhibited the lowest value for AEC and also attained a zero value at lower pH than other horizon samples. The subsurface horizon samples showed larger AEC values at low pH, and the range of pH over which anion exchange occurred widened to beyond 6.00, and even 7.00 in certain cases (Figs. 3–5). None of the samples treated for differential dissolution exhibited measurable anion retention at the pH values investigated. de Villiers and Jackson (1967b) have reported slight Cl-retention by partially chloritized vermiculite, especially between pH 4 and 5. The phenomenon was attributed to ligand exchange at –Al–OH–Al–bridge sites of polymeric units rather than to electrostatic exchange.

The pH dependent anion adsorption by samples prior to removal of amorphous material was largely attributed to the presence of hydroxy compounds of aluminum and/or iron. The monomeric or polymeric forms of these compounds possess a positive charge which is inversely related to pH. This was reflected in the increase in AEC with decrease in pH for all samples in the range from 9.0 to 3.5. The differences in magnitude of AEC values among samples appeared to be a function of the quantity of aluminum plus iron extracted from each by means of the dissolution treatments (Chichester *et al.*, 1969).

A second probable mechanism for anion adsorption in these samples would be the transformation of tetrahedral aluminum sites of silicon–aluminum co-precipitates to octahedral sites as the pH is decreased. This would contribute to an increase in anion adsorption and a decrease in cation adsorption simultaneously.

#### SUMMARY AND CONCLUSIONS

Rates of exchange between the porous matrix of pumice particles and the bulk solution are extremely slow. Consequently exchange capacity measurements by conventional methods on soil samples which contain pumice should be regarded with suspicion. The values obtained are highly variable and strongly dependent upon the interaction of pumice structure and methodology. The data reflect salt trapping in the pores more than

electrostatic ion exchange capacity. A valid measure of ion exchange properties can be had only by the use of procedural modifications which allow the attainment of ion equilibrium at each step.

The ion exchange studies with the soil samples have indicated the effect which the vesicular pores of pumice material exert on solute and solution movement. The significance of this relationship with respect to physical, chemical, and biological properties of these soils certainly bears further elucidation.

Soil clays from Mazama pumice which were treated for dissolution of amorphous material expressed a pH dependent negative charge equal to or greater than that measured for samples prior to such treatment. The behavior was attributed to the pH dependent mobilization of hydroxy interlayer material in chloritic intergrade minerals present in the samples. The extent to which amorphous clays relative to these mobile interlayer hydroxy Al and/or Fe polymers of associated 2:1 phyllosilicate minerals are to be implicated in exhibited pH dependent anion exchange behavior is also difficult to determine. These factors confounded the interpretation of the data and did not permit evaluation of the nature of the amorphous materials. The relative contribution of crystalline and amorphous phases to the pH dependent charge was not discernable.

The pH dependent cation and anion exchange capacities are significant characteristics of clays from soils on Mazama pumice. These properties are to be attributed to the total system—both crystalline and amorphous.

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**Résumé** – Des mesures de la capacité d'échange des cations (CEC) ont été effectuées sur des échantillons de ponce tirés du sol par plusieurs méthodes, y compris les méthodes standards concernant la saturation des cations, la suppression de l'excédent de sel et les phases de déplacement des cations et un procédé de dilution radioisotope  $^{45}\text{Ca}^{2+}$ . Les résultats ont indiqué que les pores vésiculaires de la ponce affectaient la réalisation de l'équilibre de diffusion ionique et, de ce fait, introduisaient une grande source d'erreur dans les mesures. Sur cette base, on a conclu que la validité des valeurs d'échange des ions obtenues pour ces sols faisait l'objet d'un doute considérable. Toutefois, ce qui est plus important, on a été conduit à penser que le soluté et/ou l'exclusion ou la rétention de solution que montraient des particules de ponce au cours des procédés CEC était très important par rapport à l'influence probable exercée sur les propriétés physiques, chimiques et biologiques des sols dans des conditions réelles d'essai.

**Kurzreferat** – Es wurden Messungen der Kapazität des Kationenaustausches für vollständige Bimssteinbödenproben durchgeführt unter Verwendung verschiedener Methode einschliesslich der Standard-verfahren mit Kationensättigung, Entfernung des Salzüberschusses, und Kationen-verdrängungsstufen, sowie einer  $^{45}\text{Ca}^{2+}$  Radioisotop-Verdünnungsmethode. Die Resultate deuten darauf hin, dass die blasigen Poren des Bimssteinmaterials die Einstellung von Ionendiffusionsgleichgewichten beeinflussen und auf diese Weise eine beträchtliche Fehlerquelle in den Messungen darstellten. Im Hinblick darauf wurde die Gültigkeit der Ionenaustauschwerte, die für diese Böden erhalten worden waren, in Zweifel gezogen. Darüber hinaus erschien es jedoch, dass die durch die Bimssteinteilchen während der oben erwähnten Verfahren ausgeübte Ausschliessung oder Zurückhaltung des gelösten Stoffes und/oder der Lösung äusserst belangvoll in Bezug auf die wahrscheinliche, auf die physikalischen, chemischen und biologischen Eigenschaften der Böden ausgeübte Wirkung im Felde sei.

Eine Auswertung der pH-abhängigen Messungen der Kation- und Anionenaustauschkapazität der  $<2\mu$  Tonfraktion der Bimssteinböden, scheiterte am Auftreten von Hydroxy-zwischengeschichteten 2:1 Phyllosilikatmaterialien in Mischung mit den amorphen Bestandteilen. Da die zwischengeschichteten Materiale einen unbestimmten Beitrag an die gesamte pH-abhängige Ladung der Mischung leisteten, wurde ferner gefolgert, dass die Messung dieser Eigenschaften wenig unmittelbaren Wert für die Beurteilung der relativen Mengen von amorphen und kristallinen Bestandteilen der Tonfraktionen der untersuchten Böden hatte. Immerhin offenbarten die erhaltenen Werte grundlegende Aspekte im Ionenaustauschverhalten, die für ein Verständnis der betreffenden, komplexen Systeme von Wichtigkeit sind.

**Резюме**—Для образцов пемзовых почв проведено измерение катионно-обменной емкости с использованием нескольких методов, включая стандартные методики: насыщение катионами, удаление избытка соли, изучение ступеней катионного смещения и радио изотопное разбавление  $^{45}\text{Ca}^{2+}$ . Полученные результаты показали, что ячеистые поры в материале пемзовых почв влияют на достижение равновесия ионной диффузии и вследствие этого являются источником существенных ошибок в измерениях. По этой причине подвергается значительным сомнениям достоверность значений ионнообменной емкости, полученных для этих почв. Более важным, однако, является то, что особенности исключения и удержания растворителя и растворимого вещества, проявляемые частицами в процессе определения ионнообменной емкости, являются весьма существенными с точки зрения их возможного влияния на физические, химические и биологические свойства почв в природных условиях.

Интерпретация измерений зависящей от pH катионной и анионной обменной емкости глинистых фракций < 2 пемзовых почв была затруднена наличием гидроксидно-смешаннослойного 2:1 филлосиликатного материала, находящегося в смеси с аморфным компонентом. Так как на смешаннослойный материал приходится не поддающаяся оценке часть общего заряда смеси, зависящего от pH, был сделан вывод о том, что измерение этого свойства имеет лишь небольшое значение для оценки относительного количества аморфного и кристаллического компонента в глинистых фракциях исследованных почв. Тем не менее полученные значения выявляют фундаментальные аспекты ионнообменной способности, которые являются весьма важными для понимания рассмотренных сложных систем.