LIMING OF HIGHLY WEATHERED SOILS OF THE HUMID TROPICS

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BIOGRAPHICAL SKETCH

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I. INTRODUCTION

Many soils found in the humid tropics are acid, highly leached, and highly weathered and thus differ greatly from the soils of the temperate regions. Also, they may possess different electrochemical properties (62). A great majority of these highly-weathered soils are oxisols (56) containing kaolinite, gibbsite, and sesquioxides as the major components of the clay fraction. Such soils have relatively low cation exchange capacity (CEC) and an appreciable content of exchangeable aluminum (41).

Aluminum ions have been recognized to play a significant role in the acidity of these soils (5, 7, 22). Presumably Al^{3+} and H^+ counter the negative charge on the surfaces of the clay minerals and iron and aluminum oxides arising mainly from the unsatisfied valencies on crystal edges resulting from termination of an ionic lattice or from dissociation of H^+ on hydroxyl groups. The total acidity (Al^{3+} + H^+) is normally determined by extraction with an unbuffered salt solution (27, 58). However, in highly weathered soils which exhibit a constant surface potential, the charge is determined by the potential determining ions, H^+ and OH^-. In such soils, the concentration of the unbuffered salt, like KCl, likely has a significant influence on the amount of aluminum extracted by the salt solution.

Highly-weathered soils are known to contain appreciable amounts of crystalline iron and aluminum oxides and hydroxides, kaolinite and halloysite. Consequently, they have a large hydroxyl surface from exposed octahedral AlOH and FeOH groups on the planar surfaces and crystal

edges. The charge of these materials is known to be largely pH-dependent (11, 57, 59). Coleman, Weed, and McCracken (8) regarded the sum of the cations Ca^{++}, Mg^{++}, and Al^{3+} displaced from acid soils by 1N KCl as a measure of the permanent charge CEC. They assigned the pH-dependent charge to ionization of weakly acidic functional groups in clay minerals, iron and aluminum hydrous oxides, and soil organic matter. De Villiers and Jackson (12, 13) attributed the variation in CEC to deprotonation of hydroxy-alumina interlayers of pedogenic aluminous chlorite. They found a great deal of aluminous, pedogenic chlorite in moderately and highly-weathered soils. They concluded that this presence of pedogenic chlorite is a common property of soil clays exhibiting pH-dependent acidity.

Lime is usually added to acid soils in amounts equivalent to the total titratable acidity or what is commonly called the exchange acidity as determined by the $BaCl_2$-triethanolamine method (38). It is generally agreed that accurate measurement of the maximum amount of acidity that can be neutralized by an excess of $CaCO_3$ is very difficult. Also there is no general agreement on the method for determining the lime requirement of highly-weathered soils. Some investigators (23, 44) suggested that the lime requirement of soils of the humid tropics should be estimated by multiplying the amount of exchangeable aluminum, as determined by 1N KCl, by an empirical factor of 1.5 or 2. Surprisingly enough, some soils of the humid tropics are known to have only a very small amount of salt extractable aluminum even at low pH values. Hence, lime requirement for these soils, as estimated by this method, would be extremely minimal. Moreover, applications of such minimal amounts of lime would have very insignificant effect in increasing the effective CEC of these

soils with very low inherent capacity to retain cations such as K^+ and NH_4^+ applied as fertilizer salts.

Lime requirement is often defined as the amount of $CaCO_3$ that must be applied to a soil to obtain a maximum yield of some specific crop. Accordingly, it would be necessary to determine a lime requirement for every specific crop. This was not the purpose of this investigation. Rather it was concerned with the chemical aspects of liming, the reactions of acid soils with $CaCO_3$, and evaluation of several common laboratory methods for determining the lime requirement of soils. The three objectives of this investigation were:

a) to study the nature of acidity of soils from the humid tropics or more specifically the significance of exchangeable aluminum as extracted by neutral salt solutions.

b) to evaluate the criteria of lime requirement by comparing the results of two commonly used laboratory methods for determining the lime requirement with the maximum amount of $CaCO_3$ that can react with these soils when they have reached equilibrium with an excess of $CaCO_3$ at the partial pressure of CO_2 of the air, and

c) to study the fate of Ca^{++} applied as $CaCO_3$ to acid tropical soils with especial reference to losses of Ca^{++} by leaching and "fixation" into nonexchangeable form.

II. SOILS USED AND SOME CHEMICAL CHARACTERISTICS

Eleven samples of the surface and subsoil from highly-weathered soils of the humid tropics were used in the present study. One surface soil sample from New York was also included for comparison.

Soil samples were selected from several different locations known to represent extensive areas of the humid tropics. They were collected in Brazil and Colombia in South America, and in Puerto Rico in the Caribbean.

1. Location and Classification of Soils

Soils from Brazil were collected from two different locations. The first location was from the State of Sao Paulo and the second location was from the Campo Cerrado region, Central Plateau of Brazil. Samples from Sao Paulo were used by Van Raij (61) in his study of the distribution of electric charges as a function of pH and salt concentration. Soil names used in this thesis were adapted from the Soil Taxonomy of the United States (56).

Acrohumox. This is an oxisol sampled in Campinas, State of Sao Paulo, Brazil and its description can be found elesewhere (49). It was classified as Humic Red Yellow Latosol by Brazilian pedologists. For purposes of future reference, the surface soil was assigned No. 1 and the subsoil was assigned No. 2.

Acrorthox. This oxisol was collected in Ribeirao Preto, State of Sao Paulo, Brazil. It was classified as Latosol Roxo by Brazilian pedologists. The surface and the subsoil from this location were numbered 3 and 4, respectively.

Typic Haplustox. This soil was sampled in Carimagua pit, in the Llanos Orientales of Colombia, South America. The results of some chemical and mineralogical studies of this oxisol were reported by Weaver (64). Only the surface soil, No. 5, was used in this study.

Tropeptic Haplorthox. This soil sample was collected from Barranquitas, Puerto Rico, at the Cornell experimental site. This oxisol is known as Catalina series. It is of clayey texture, oxidic, and isohyperthermic. It was formerly classified as Reddish Brown Laterite. Only the subsoil, No. 6, was used in this investigation.

Aquic Tropohumult. This is an ultisol sampled in Corozal, Puerto Rico, at the Cornell experimental site. This soil is known as Carreras series. It is clayey, kaolinitic, isohyperthermic and was formerly called Humatas (F.H. Beinroth, University of Puerto Rico, Agr. Exper. St., Rio Piedras, P.R.; personal communication, 1972). Only the subsoil, No. 7, was used in the present study. It was formerly classified as Reddish Brown Laterite.

Typic Haplustox. This is an oxisol collected from the "Estacao experimental de Brazilia" of the Ministry of Agriculture. It was classified as "Red Yellow Latosol vermelho escuro distrofico textura argilosa, fase cerradao" by Brazilian pedologists. Both the surface soil, No. 8, and the subsoil, No. 9, were used in the present study.

Typic Haplustox. This is very similar to the soil described above. It was classified as Dark Red Latosol. The surface soil, No. 10, and subsoil, No. 11, were collected from this location.

Typic Fragiochrept. This is a typical soil of humid temperate regions and was collected from the Mount Pleasant experimental farm at

Cornell University. It is an inceptisol known as Mardin series. Its texture was silt loam and only the surface sample, No. 12, which represented the plowed layer was collected.

All soils were air-dried and passed through a 2-mm sieve.

2. Some Chemical Characteristics of the Soils

Some chemical properties of the soils studied are summarized in Table 1. The data for Acrorthox were adapted from Van Raij's Thesis (61).

The organic matter content was determined by the Walkley-Black chromic acid titration method (19).

Soil pH measurements were made both in H_2O and in 0.01M $CaCl_2$ according to the method described by Peech (39). The glass electrode was immersed in the sediment and the calomel electrode was immersed in the clear supernatant solution to avoid errors due to the liquid junction potential in the suspension. The pH determinations were made using 10g of soil and 20 ml of distilled water. After making the pH measurements in water, 1 ml of 0.21M $CaCl_2$ was added to the soil suspension and the suspension was again stirred with a glass stirring rod. The pH was then measured as previously described and reported as "pH in 0.01M $CaCl_2$".

The exchangeable calcium and magnesium were determined by extraction with 1N KCl. A 7.5-g sample of soil was mixed with 30 ml of extracting solution in a 50-ml polycarbonate centrifuge tube. The contents were mixed for 5 minutes with a motor stirrer fitted with a glass rod and Tygon policeman. After mixing, the soil suspensions were centrifuged for 20 minutes at 18,000 rpm in a Sorvall superspeed refrigerated centrifuge maintained at 25°C. The samples were extracted successively 9 times with 1N KCl and the clear supernatant solutions were collected in a 250-ml volumetric flasks.

TABLE 1. Some Chemical Characteristics of the Soils Studied

Soil No.	Soil Name*	Depth	Organic Matter	pH in H_2O	pH in 0.01M $CaCl_2$	Exchangeable Ca^{++}	Exchangeable Mg^{++}
		cm	%			meq/100g	meq/100g
1	Acrohumox-A_p (Brazil)	0-20	2.93	5.01	4.30	1.93	0.40
2	Acrohumox-B_2 (Brazil)	200-230	0.57	4.95	4.25	0.03	0.08
3	Acrorthox-A_p (Brazil)	0-20	4.32	5.30	4.80	1.76	0.67
4	Acrorthox-B_2 (Brazil)	100-200	1.14	5.90	5.70	0.33	0.12
5	Haplustox-A_p (Colombia)	0-15	3.41	4.15	3.95	0.07	0.06
6	Haplortox-B_1 (Puerto Rico)	61-91	1.09	5.00	4.25	0.50	0.52
7	Tropohumult-B_1 (Puerto Rico)	61-91	0.59	4.61	4.00	1.60	0.20
8	Haplustox-A_p (Brazil)	0-15	3.40	4.75	4.20	0.05	0.07
9	Haplustox-B_1 (Brazil)	45-60	1.50	5.25	4.55	0.03	0.04
10	Haplustox-A_p (Brazil)	0-15	3.52	4.35	4.00	0.04	0.05
11	Haplustox-B_1 (Brazil)	45-60	1.74	4.85	4.05	0.03	0.03
12	Fragiochrept-A_p (New York)	0-15	3.23	4.40	4.00	0.99	0.21

* Soil description and series name for each soil are given in the text by country of origin as known today.

The concentrations of calcium and magnesium were determined, after diluting an appropriate aliquot, using a Perkin Elmer 290B atomic absorption spectrophotometer. The results are summarized in Table 1.

Most of the soils studied have not been under intensive cultivation in recent years. All soils were fairly acid. The difference between the pH observed in H_2O and in 0.01M $CaCl_2$ is not a good indication of the net charge due to low concentration of the salt. However, Van Raij (61) found that Acrorthox-B_2, Soil No. 4, showed a higher pH in 1N KCl than in H_2O. This is an indication of a net positive charge. The zero point of charge (ZPC) was found to be 3.84 for Acrorthox-A_p, Soil No. 3, and 6.16 for Acrorthox-B_2, Soil No. 4. Haplorthox-B_1, Soil No.6, and Tropohumult-B_1, Soil No. 7, are known to have a very low ZPC (65).

The amounts of exchangeable calcium and magnesium found in most of the soils were very low. No attempt was made to determine the amount of exchangeable potassium which is known to be extremely low.

Mineralogical studies (63, 64, 65) show that in addition to the presence of hematite, goethite, gibbsite, and kaolinite in the clay size fraction, there was an appreciable proportion of aluminous chlorite in most of the soils used in this study.

III. SIGNIFICANCE OF SALT-EXTRACTABLE ALUMINUM

1. Introduction

In acid soils, exchangeable aluminum is generally recognized as the predominant cation. The determination of exchangeable aluminum is based on the assumption that aluminum ions are counter ions balancing excess negative charge on the surface of the solid phase. Consequently, aluminum ions can be displaced by exchange with another cation. For this purpose 1N KCl, 1N NaCl and 1N $CaCl_2$ solutions are commonly used.

In general, it has been found that the amount of aluminum displaced by 1N salt solution is highly correlated with the pH of the soil. At pH values below 5.5, the degree of saturation of the soil with Al^{3+} is high and decreases sharply as the pH increases above this value. At high pH values, the aluminum ion is known to hydrolyze rapidly and is precipitated as $Al(OH)_3$. The methods in current use for determining exchangeable aluminum by extraction with a concentrated salt solution are not satisfactory. It has been shown that the aluminum extracted by a salt solution represents both exchangeable as well as nonexchangeable aluminum (14, 45, 50). The problem becomes more complicated when dealing with soils with significant amounts of hydrous oxides of iron and aluminum. Using the potentiometric titration technique, Little (29) found that soils rich in sesquioxides consistently gave smaller values for exchangeable aluminum than those obtained by neutral salt extraction.

It is evident that the measurement of exchangeable aluminum by extraction with a salt solution in tropical soils is subject to some ambiguity.

2. Examination of Methods for Determining Exchangeable Aluminum

A new method for the determination of exchangeable aluminum in acid soils was proposed by Skeen and Sumner (54, 55). Critical examination of this method for the determination of exchangeable aluminum in soils is warranted in view of the increasing use of this method (21, 53). The method is described in detail and the inherent sources of error are also discussed. This method is based on the assumption that the exchangeable aluminum in soils can be effectively displaced only by a long series of successive extractions with a neutral salt extracting solution acidified to the original pH of the soil. It should be obvious that leaching of a soil with a salt solution is equivalent to an infinite number of extractions. In the successive extraction procedure, the period of contact and the ratio of soil to solution are kept constant and it is tacitly assumed that a constant amount of nonexchangeable aluminum is extracted during each extraction.

The linear portion of the characteristic curve obtained by plotting cumulative amounts of extracted aluminum as a function of the number of extractions, shown in Fig. 1, is believed to represent a constant amount of nonexchangeable aluminum extracted upon successive extractions. Extrapolation of this linear portion of the curve to zero number of extractions should give the exchangeable aluminum content of the soil.

It should be obvious that the amount of nonexchangeable Al^{3+} extracted, for example by dissolution of $Al(OH)_3$, should be considerably lower during the first three or four extractions because of the common ion effect resulting from exchange of the adsorbed Al^{3+} by the added salt solution on the solubility of $Al(OH)_3$. The effect of this would be to yield too low a value for exchangeable Al^{3+} obtained by extrapolation,

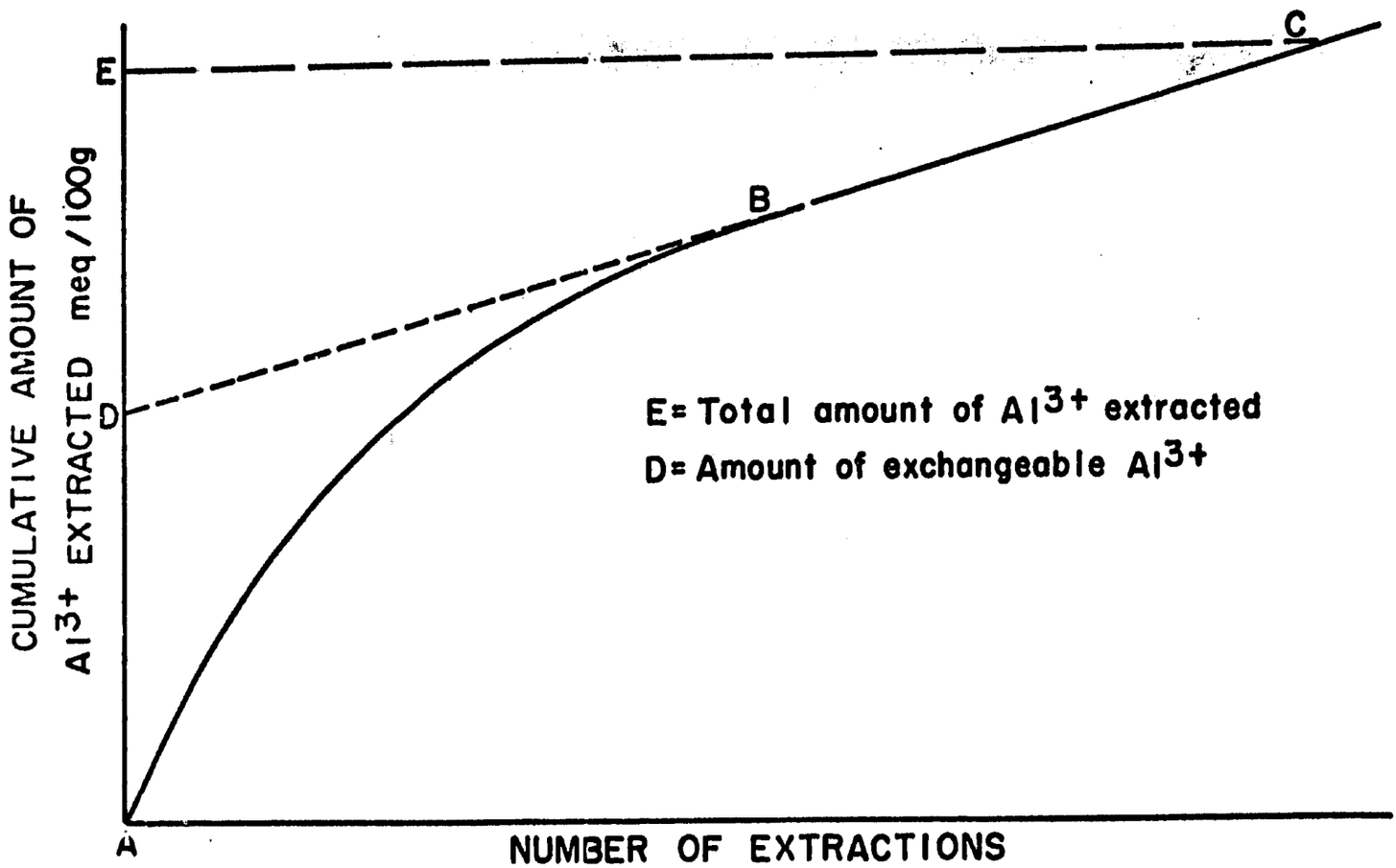

FIG. 1. Characteristic curve of cumulative amount of aluminum extracted from acid soils upon successive extraction with 1N KCl

especially so if the slope of the linear portion of the curve (cumulative amount of Al^{3+} extracted vs number of extractions) is steep.

A family of curves representing the extraction of aluminum with 1N NH_4Cl at varying pH values from an acid soil (pH 3.7 in 0.01M $CaCl_2$) obtained by Sivasubramaniam and Talibudeen (53) is reproduced in Fig. 2. The slope of the curve varies with the pH of the extracting solution. Extrapolation of each curve gives a different value for "exchangeable aluminum" indicating the uncertainty of the point of intercept. The authors claim that extrapolation of curves representing cumulative amounts of Al^{3+} extracted with 1N HN_4Cl at pH 4.1 and 4.5 yield the same amount of exchangeable Al^{3+}, indicating that extraction of an acid soil at or near the soil pH gives a reliable measurement of the amount of exchangeable Al^{3+}. It is difficult to see why the amount of exchangeable aluminum extrapolated at pH 4.5 should differ so markedly from that extrapolated at pH 4.6.

3. Theoretical Considerations Underlying the Adsorption of Aluminum Ions by Tropical Soils

Highly-weathered soils develop positive charges by absorption of hydrogen ions at low pH values and develop negative charges by dissociation of surface hydroxyl groups at high pH values (62).

Ionic exchange is an important property of soils. Cations are held electrostatically by the negative charge of the colloids. The cation exchange capacity can be approximated by the net negative charge. Consequently, the higher the negative charge, the higher will be the effective cation exchange capacity. In tropical soils in which a substantial amount of positive charge may be present, anions such as nitrate and

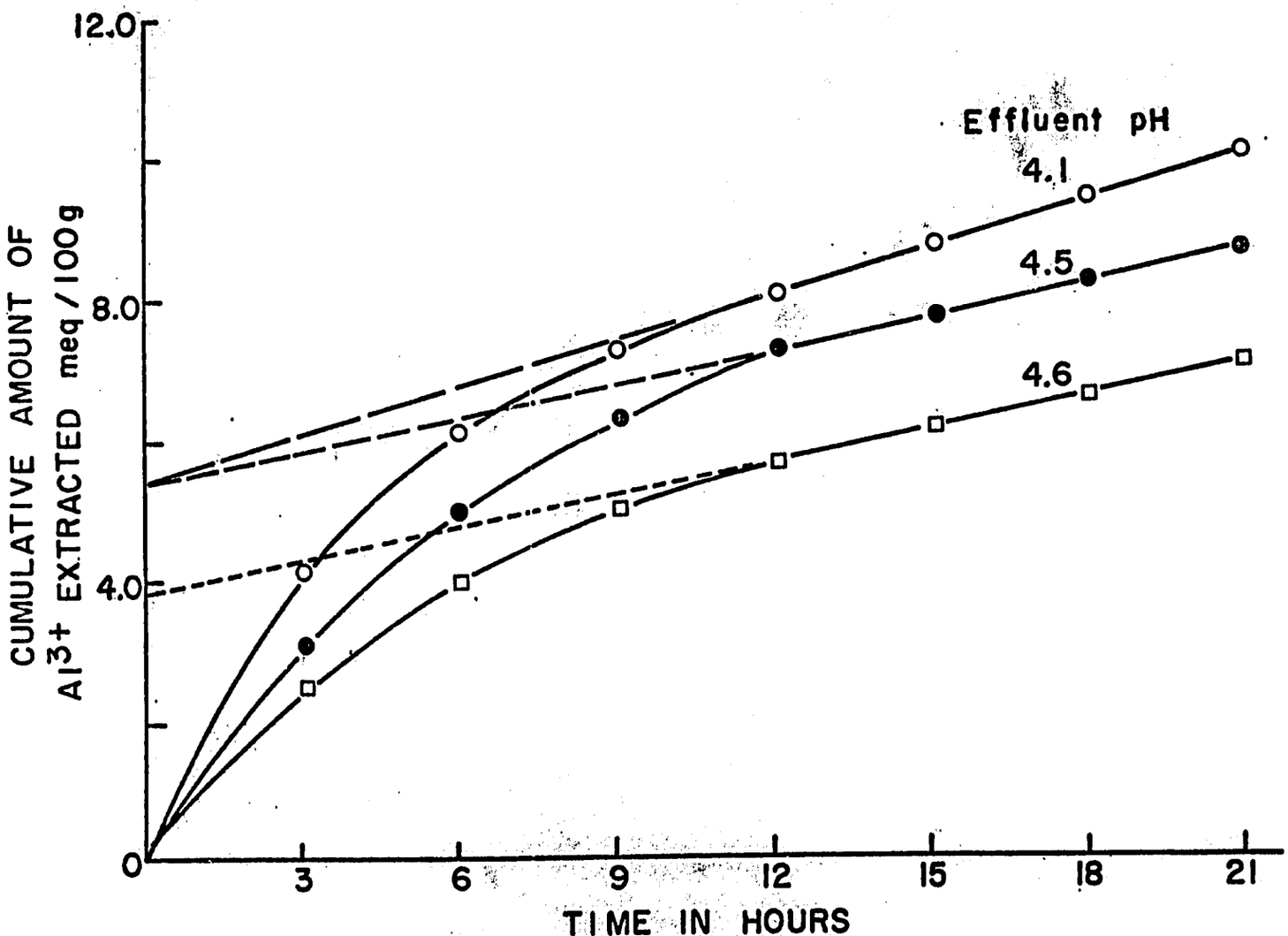

FIG. 2. Extraction of Al^{3+} with N NH_4Cl from an acid soil at varying pH values (After Sivasubramaniam and Talibudeen 1972)

sulfate are also absorbed (16, 33, 52).

Among the cations held by the negative charge, Al^{3+} is known to be the most abundant exchangeable cation in acid soils. In highly-weathered soils with high zero point of charge (ZPC), it is evident that at low soil pH, the net charge is positive and Al^{3+} should be repelled by the surface positive charge. In the case of a mosaic surface, on which both negative and positive charges are present, a relatively low amount of exchangeable aluminum would be expected to counter the negative charge. On the other hand, if only positive charges are present, there should be no adsorbed aluminum ions and the concentration of Al^{3+} found in the extract should be independent of the concentration of the salt solution used in determining the amount of exchangeable aluminum. Accordingly two experiments, described below, were undertaken to test this hypothesis.

4. Experimental Part

A. Effect of salt concentration on the amount of exchangeable aluminum extracted

Three soils were selected for this experiment. They were Haplorthox-B_1, Soil No. 6, (Catalina), Tropohumult-B_1, Soil No. 7, (Carreras), and Fragiochrept-A_p, Soil No. 12, (Mardin).

A 5-g sample of soil was mixed for 5 minutes with 50 ml of 1N KCl in a 90-ml glass centrifuge tube, using a motor stirrer, and centrifuged for 15 minutes at 2100 rpm in an International centrifuge, Model K. The clear supernatant solution was decanted and saved for the determination of pH, total acidity by titration (67), and aluminum by the aluminon method (18). This extraction procedure was repeated successively 20 times, except for the Catalina soil which was extracted only 12 times. A correction was applied for the occluded salt solution after each

extraction in bringing the total volume of the extracting solution to 50 ml.

The same extraction procedure was repeated with the same soils using 0.1N KCl extracting solution. The results are summarized in Tables 2 and 3 and the cumulative amounts of aluminum removed upon successive extractions by the two concentrations of KCl have been plotted in Fig. 3, 4, and 5.

B. Effect of net surface charge on the amount of aluminum extracted by salt solutions

Two Brazilian soils (Acrorthox-A_p, Soil No. 3 and Acrorthox-B_2, Soil No. 4) whose zero point of charge was known, one Puerto Rican soil (Tropohumult-B_1, Soil No. 7), and a soil from New York State (Fragiochrept-A_p, Soil No. 12) were used for this experiment.

The positive charge of tropical soils can be increased by decreasing the soil pH. This can be easily done by adding acid, and if the zero point of charge is known, the net charge of the soil can be predicted.

To a 10-g sample of each soil in a 50-ml beaker, 20 ml of 1N KCl was added. A known amount of standard HCl was added to the soil suspension in each beaker to bring the pH to 3.0 and 3.5 for the soil from New York as well as for the soil from Puerto Rico, and to 3.0, 3.5, 4.0, and 4.5 for the soils from Brazil. An untreated sample was carried along for control. The suspensions were placed in a humidified chamber for one week and the pH values were adjusted further by adding standard HCl. The soil suspensions were then transferred to 90-ml glass centrifuge tubes using additional 1N KCl to effect the transfer. The volume was adjusted to 50 ml, and after stirring the suspensions were allowed to stand overnight. The soil suspensions were then centrifuged for 15 minutes at

TABLE 2. Successive extraction of aluminum with 1N KCl from two tropical soils and a New York soil

Extraction Number	Soil No. 6 Haplorthox-B_1			Soil No. 7 Tropohumult-B_1			Soil No. 12 Fragiochrept-A_p		
	pH	Total acidity*	Al^{3+}	pH	Total acidity*	Al^{3+}	pH	Total acidity*	Al^{3+}
		—meq/100g—			—meq/100g—			—meq/100g—	
1	4.31	3.08	2.91	4.05	11.48	9.91	3.68	3.16	2.07
2	4.40	0.68	0.66	4.28	1.36	0.87	3.85	0.96	0.65
3	4.45	0.38	0.34	4.40	0.48	0.37	3.95	0.48	0.30
4	4.49	0.20	0.21	4.48	0.28	0.26	4.05	0.32	0.22
5	4.52	ND†	0.15	4.51	0.16	0.12	4.10	ND†	0.17
6	4.58	—	0.11	4.55	0.12	0.10	4.12	—	0.16
7	4.61	—	0.09	4.60	ND†	0.08	4.19	—	0.14
8	4.52	—	0.07	4.65	—	0.06	4.25	—	0.10
9	4.62	—	0.06	4.68	—	0.05	4.30	—	0.08
10	4.65	—	0.05	4.71	—	0.04	4.35	—	0.07
11	4.59	—	0.04	4.75	—	0.03	4.42	—	0.06
12	4.68	—	0.04	4.92	—	0.02	4.65	—	0.05
13	ND†	—	ND†	4.70	—	0.04	4.35	—	0.10
14	—	—	—	4.72	—	0.03	4.45	—	0.07
15	—	—	—	4.78	—	0.02	4.50	—	0.05
16	—	—	—	4.85	—	0.02	4.58	—	0.05
17	—	—	—	4.86	—	0.02	4.60	—	0.04
18	—	—	—	4.90	—	0.01	4.63	—	0.04
19	—	—	—	4.90	—	0.01	4.64	—	0.04
20	—	—	—	4.95	—	0.02	4.72	—	0.03

* Total acidity represents the sum of $Al^{3+} + H^+$

† Not determined

TABLE 3. Successive extraction of aluminum with 0.1N KCl from two tropical soils and a New York soil

Extraction Number	Soil No. 6 Haplorthox-B_1			Soil No. 7 Tropohumult-B_1			Soil No. 12 Fragiochrept-A_p		
	pH	Total Acidity*	Al^{3+}	pH	Total Acidity*	Al^{3+}	pH	Total Acidity*	Al^{3+}
		—meq/100g—			—meq/100g—			—meq/100g—	
1	4.20	2.28	2.19	4.00	6.48	5.67	3.85	1.88	1.13
2	4.35	0.88	0.78	4.11	2.36	1.73	3.98	0.68	0.55
3	4.45	0.38	0.36	4.22	1.28	1.13	4.05	0.36	0.28
4	4.49	0.20	0.22	4.30	0.68	0.69	4.12	0.28	0.18
5	4.50	ND†	0.16	4.38	0.40	0.38	4.20	ND†	0.14
6	4.55	—	0.12	4.40	0.36	0.29	4.25	—	0.13
7	4.57	—	0.09	4.45	ND†	0.20	4.31	—	0.11
8	4.61	—	0.07	4.55	—	0.14	4.39	—	0.08
9	4.55	—	0.06	4.58	—	0.11	4.45	—	0.06
10	4.58	—	0.05	4.65	—	0.09	4.50	—	0.06
11	4.60	—	0.05	4.67	—	0.07	4.55	—	0.05
12	4.66	—	0.04	4.85	—	0.06	4.75	—	0.04
13	ND†	—	ND†	4.65	—	0.07	4.49	—	0.07
14	—	—	—	4.70	—	0.06	4.55	—	0.05
15	—	—	—	4.72	—	0.05	4.62	—	0.04
16	—	—	—	4.80	—	0.04	4.68	—	0.04
17	—	—	—	4.82	—	0.03	4.70	—	0.03
18	—	—	—	4.85	—	0.03	4.71	—	0.03
19	—	—	—	4.85	—	0.02	4.73	—	0.03
20	—	—	—	4.91	—	0.02	4.80	—	0.03

* Total acidity represents the sum of $Al^{3+} + H^+$

† Not determined

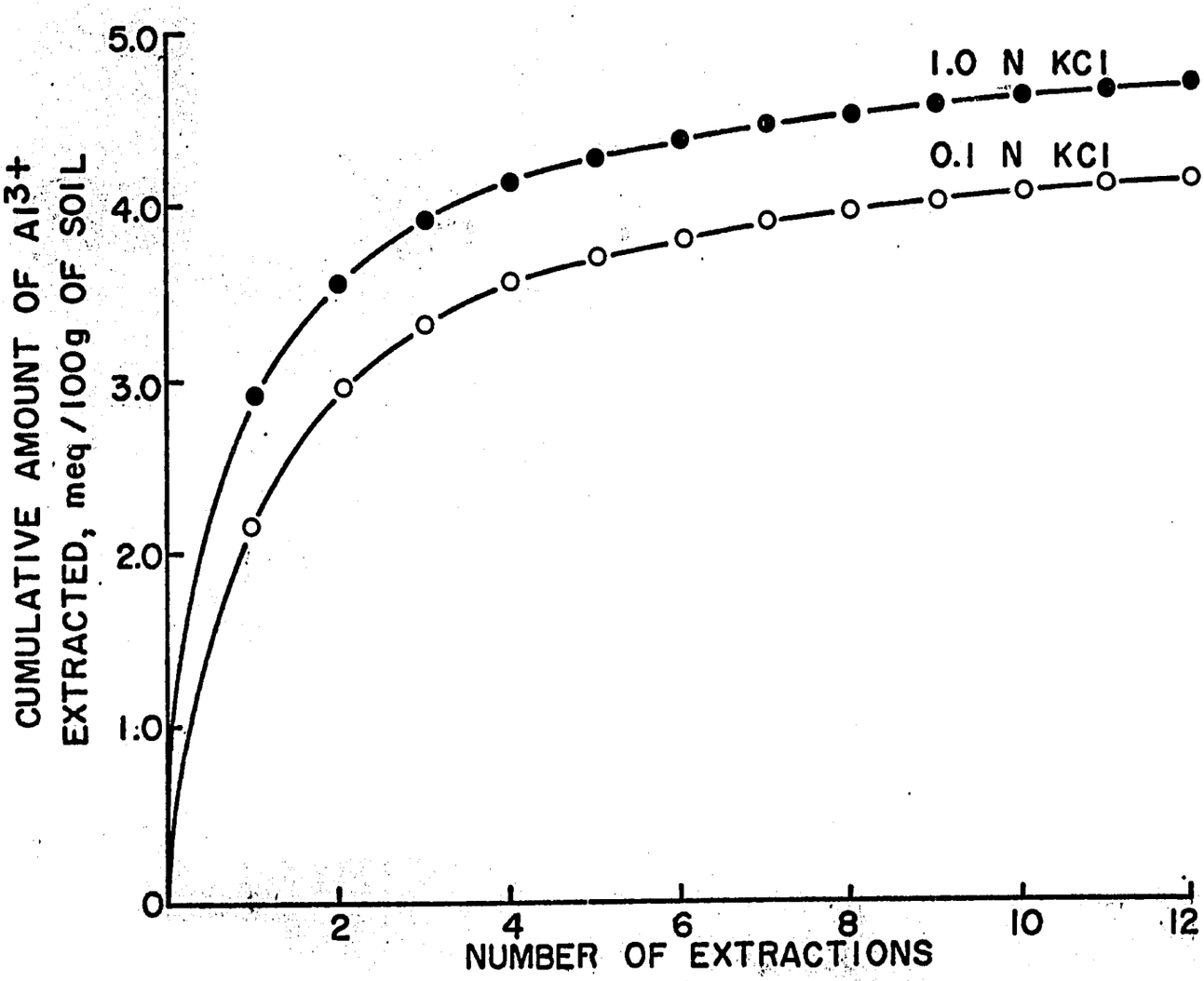

FIG. 3. Cumulative amounts of Al^{3+} extracted by 0.1N and 1.0N KCl from Haplorthox-B_1 (Soil No. 6)

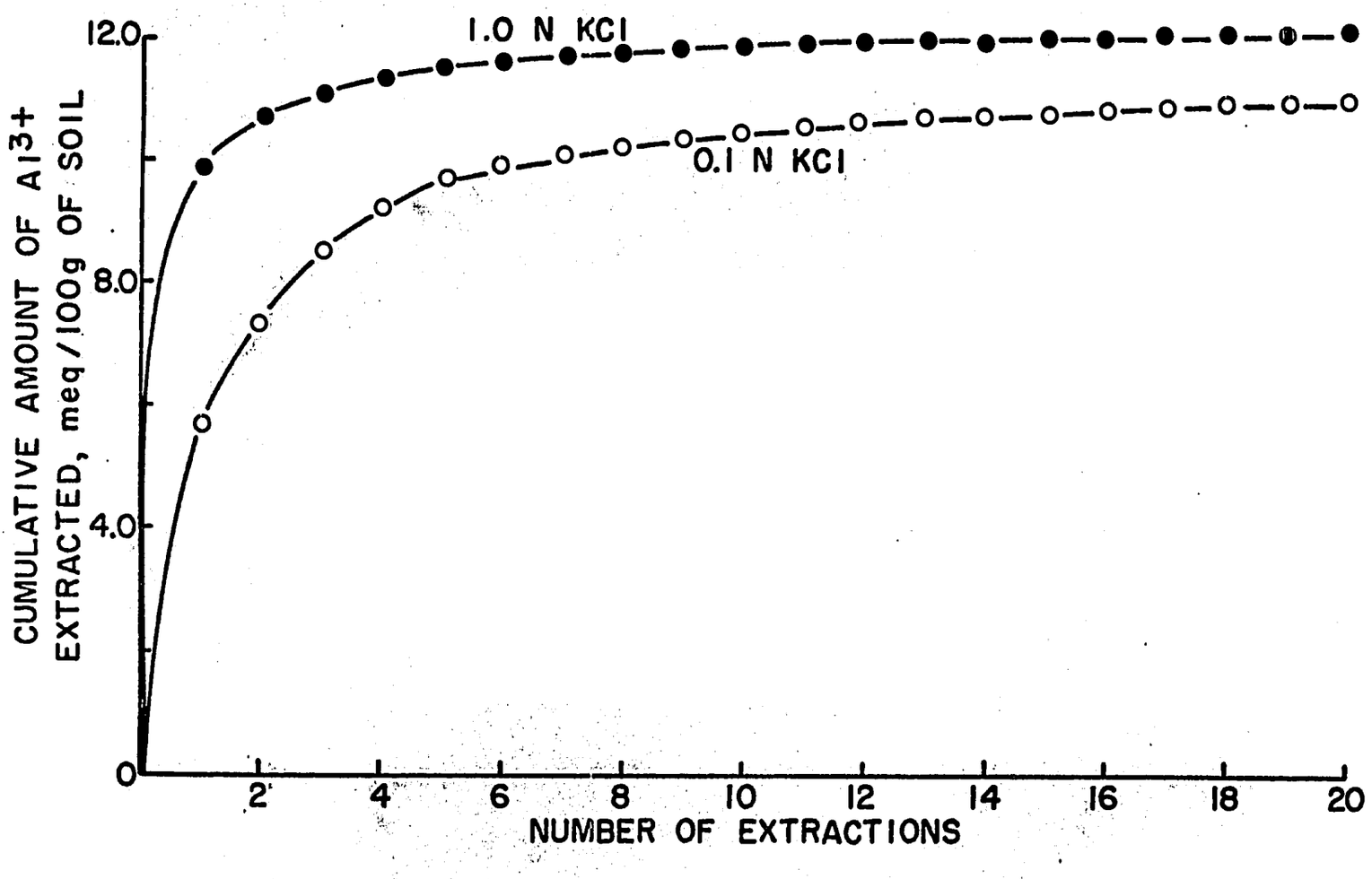

FIG. 4. Cumulative amounts of Al^{3+} extracted by 0.1N and 1.0N KCl from Tropohumult-B_1 (Soil No. 7)

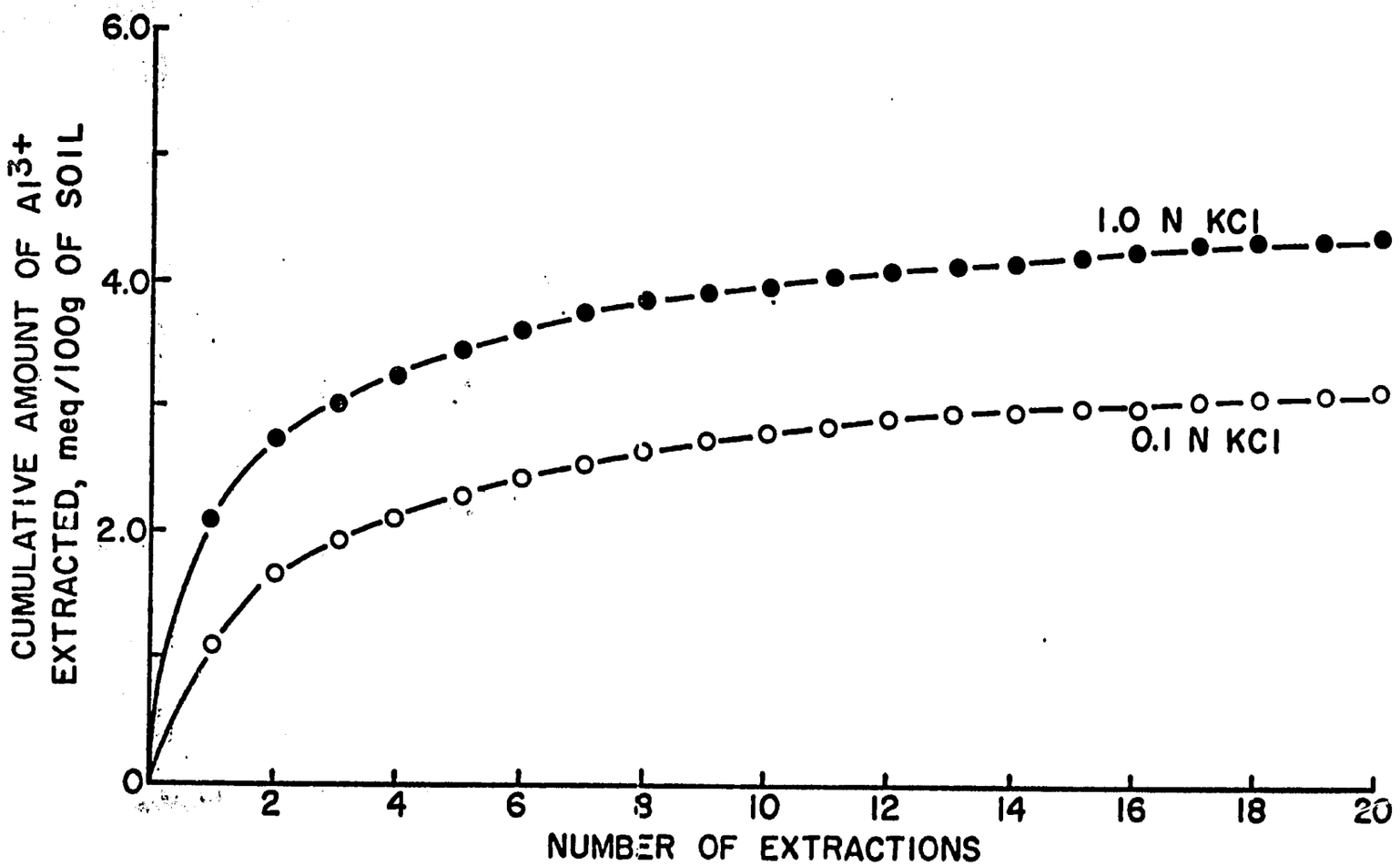

FIG. 5. Cumulative amounts of Al^{3+} extracted by 0.1N and 1.0N KCl from Fragiochrept-A_p (Soil No. 12)

2100 rpm in an International centrifuge, Model K, and the supernatant solution was decanted. The pH values of the extracts were measured by the glass electrode. The total acidity was determined by titration (67) and the aluminum concentration was determined colorimetrically by the aluminon method (18). The same extraction procedure and determinations were made using 0.1N KCl and 0.01M $CaCl_2$ as the extracting solution. The results are summarized in Tables 4, 5, and 6.

C. Results and discussion

Upon successive extraction of aluminum by two concentrations of KCl, the pH of the supernatant solution was found to increase gradually (Tables 2 and 3) while the amount of aluminum extracted decreased sharply. It is interesting to note, however, that the pH did not increase above the critical point at which aluminum could be precipitated. With both concentrations of KCl, 50% or more of the total aluminum was extracted in the first extraction. The amount of aluminum extracted by 1N KCl was always greater than the amount extracted by 0.1N KCl. It is obvious that the cumulative amount of aluminum obtained upon exhaustive successive extractions is dependent on the concentration of KCl.

The inefficiency of the 0.1N KCl solution to exchange aluminum ions cannot be explained by the mass action effect. If it were the case, the exchangeable aluminum extracted by 1N KCl would have been greater than that extracted by 0.1N KCl only in the first few extracts, but the amount of aluminum extracted by 0.1N KCl would have continued to increase until the total amount of aluminum extracted by KCl at both concentrations was the same as illustrated in Fig. 6.

These soils are dominated by sesquioxides which are known to exhibit

TABLE 4. The final pH values and the amounts of Al^{3+} extracted by the three salt solutions

Soil No.	Soil Name*	Final pH after extraction			Al^{3+} extracted in		
		1NKCl	0.1NKCl	0.01M$CaCl_2$	1NKCl	0.1NKCl	0.01M$CaCl_2$
					meq/100g		
3	Acrorthox-A_p	3.40	3.40	3.55	7.20	4.23	4.14
		3.81	3.75	3.76	3.01	1.72	0.54
		4.22	4.26	4.19	0.50	0.28	0.19
		4.62	4.70	4.61	0.10	0.03	0.02
		4.88†	5.28†	5.05†	0.03	0.00	0.01
4	Acrorthox-B_2	3.70	3.55	3.55	7.68	5.41	3.89
		3.91	3.81	3.85	3.99	2.87	1.53
		4.25	4.20	4.15	0.67	0.49	0.32
		4.68	4.60	4.55	0.07	0.04	0.03
		6.01†	5.90†	5.80†	0.00	0.00	0.00
7	Tropohumult-B_1	3.30	3.28	3.31	15.03	10.30	4.51
		3.71	3.65	3.68	12.74	7.99	2.79
		3.98†	3.90†	3.95†	10.18	6.14	1.39
12	Fragiochrept-A_p	3.40	3.35	3.39	7.47	5.35	3.40
		3.73	3.72	3.80	5.05	3.21	1.37
		3.91†	3.95†	4.29†	3.91	2.13	0.37

* For soil description see Section II of the text

† From unadjusted soil pH

TABLE 5. The amount of Al^{3+} extracted and the recovery of the total acidity at different pH values upon extraction with 1N KCl

Soil No.	Soil Name*	Extract pH	Amt of HCl added	Al^{3+} Extracted	Total acidity†	Recovery of added acid‡	H^+ adsorbed
			meq/100g				
3	Acrorthox-A_p	3.40	11.47	7.20	9.40	9.23	+2.24
		3.81	6.43	3.01	3.94	3.77	+2.66
		4.22	3.16	0.50	1.20	1.03	+2.13
		4.62	0.82	0.10	0.24	0.07	+0.75
		4.88§	0.00	0.03	0.17	—	—
4	Acrorthox-B_2	3.70	12.87	7.68	9.43	9.36	+3.51
		3.91	8.54	3.99	5.14	5.07	+3.47
		4.25	4.45	0.67	1.27	1.20	+3.25
		4.68	2.69	0.07	0.24	0.17	+2.52
		6.01§	0.00	0.00	0.07	—	—
7	Tropohumult-B_1	3.30	5.38	15.03	17.28	6.65	-1.27
		3.71	2.57	12.74	14.06	3.43	-0.86
		3.98§	0.00	0.18	10.63	—	—
12	Fragiochrept-A_p	3.40	4.68	7.47	10.01	5.21	-0.53
		3.73	1.40	5.05	6.51	1.71	-0.31
		3.91§	0.00	3.91	4.80	—	—

* For soil description see Section II of the text

† Total acidity represents Al^{3+} + H^+

‡ Recovery of the added acid as H^+ and Al^{3+}

§ Unadjusted soil pH

TABLE 6. The amount of Al^{3+} extracted and the recovery of the total acidity at different pH values upon extraction with 0.1N KCl

Soil No.	Soil Name*	Extract pH	Amt of HCl added	Al^{3+} Extracted	Total acidity†	Recovery of added acid‡	H^+ adsorbed
			meq/100g				
3	Acrorthox-A_p	3.40	9.48	4.23	5.55	5.45	+4.03
		3.75	5.85	1.72	2.30	2.20	+3.65
		4.26	3.28	0.28	0.58	0.48	+2.80
		4.70	1.52	0.03	0.20	0.10	+1.42
		5.28§	0.00	0.00	0.10	—	—
4	Acrorthox-B_2	3.55	10.18	5.41	6.92	6.85	+3.33
		3.81	6.43	2.87	3.60	3.53	+2.90
		4.20	3.39	0.49	0.92	0.85	+2.54
		4.60	2.11	0.01	0.17	0.10	+2.01
		5.90§	0.00	0.00	0.07	—	—
7	Tropohumult-B_1	3.28	5.50	10.30	11.90	5.21	+0.29
		3.65	2.57	7.99	7.27	0.58	+1.99
		3.90§	0.00	6.14	6.69	—	—
12	Fragiochrept-A_p	3.35	4.91	5.35	7.37	4.63	+0.28
		3.72	1.52	3.21	4.18	1.44	+0.08
		3.95§	0.00	2.13	2.74	—	—

* For soil description see Section II of the text

† Total acidity represents Al^{3+} + H^+

‡ Recovery of the added acid as H^+ and Al^{3+}

§ Unadjusted soil pH

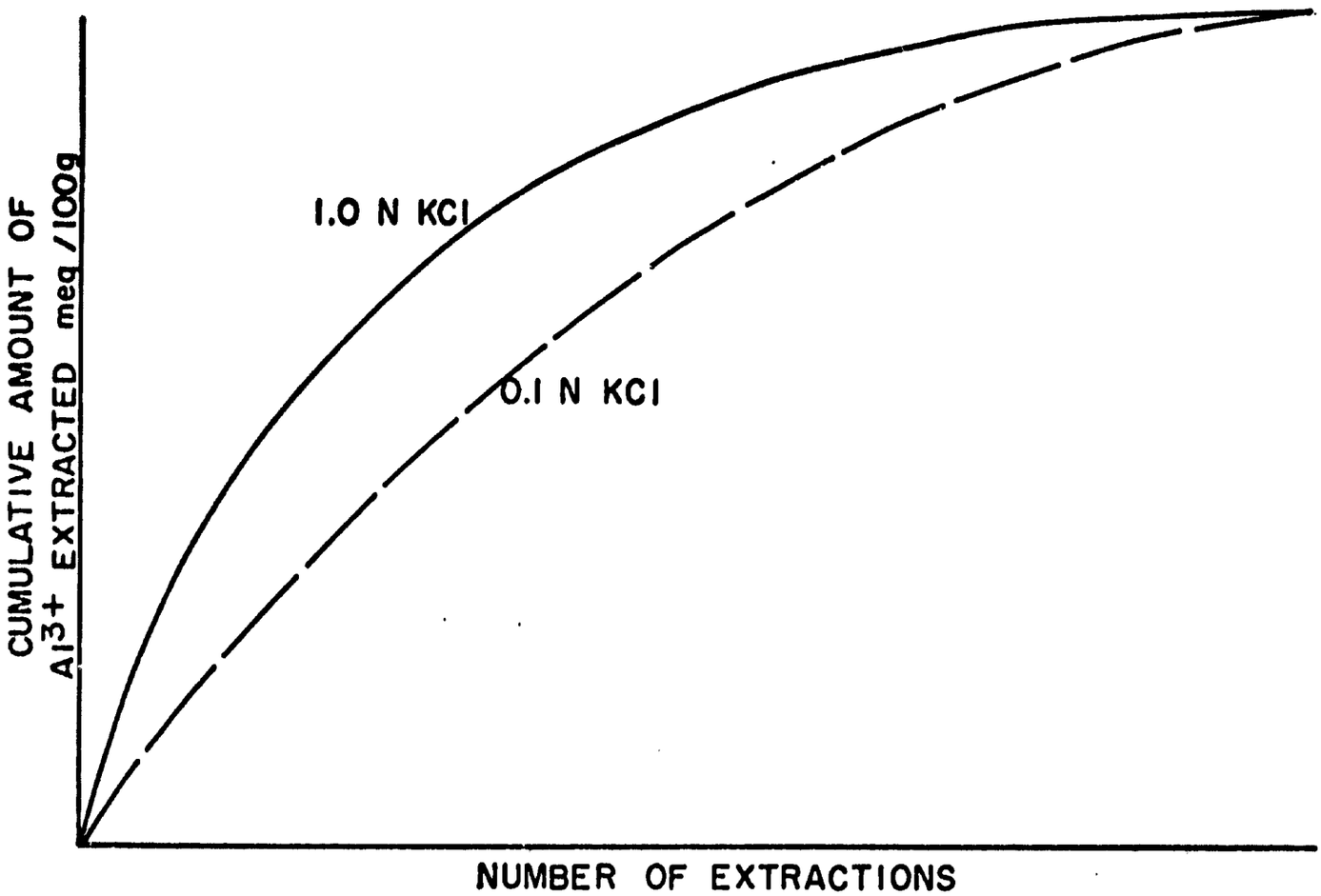

FIG. 6. Idealized curves showing the cumulative amounts of exchangeable Al^{3+} extracted by 0.1N and 1.0N KCl

a constant surface potential. This salt effect on the amount of aluminum extracted can be explained by the following stepwise reactions:

$$\underline{R}OH^{*} + KCl \rightarrow \underline{R}O^{-}...K^{+} + HCl \qquad (111\text{-}1)$$

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O \qquad (111\text{-}2)$$

On the negative side of the ZPC, the effect of the addition of salt should be to increase the surface negative charge of the hydrous oxides of iron and aluminum by dissociation of the -OH groups. The hydrogen ions released should, in turn, dissolve the aluminum hydroxide, present in the soils, to produce equivalent amounts of Al^{3+}. Thus, the greater the concentration of salt in such a system, the greater should be the amount of hydrogen ions released by dissociation of the surface hydroxyl groups and the greater should be the amount of "exchangeable" aluminum extracted from the soil.

Surprisingly enough, the results obtained for Mardin silt loam from New York were similar to those obtained for the highly-weathered soils of the humid tropics. But this soil is known to contain a large amount of pH-dependent charge (2) even though the clay fraction has been found to consist of aluminous chlorite, illite, and other 2:1 clay minerals having a permanent charge. Presumably the surfaces of these 2:1 clay minerals are coated with hydrous iron and aluminum oxides which essentially determine the colloid chemical properties. These 2:1 type clay minerals coated with hydrous iron and aluminum oxides may thus be regarded as resembling colloids with a constant surface potential rather than a constant surface charge. Therefore, the difference between the amounts of aluminum

---

* The underlined atom indicates group belonging to solid phase.

extracted by the two salt concentrations in Mardin silt loam could be well explained by the same mechanism suggested for the tropical soils.

The surface net negative charge can be increased upon addition of salt only if the pH of the soil lies on the negative side of the zero point of charge. On the other hand, the net negative charge can be decreased and may be actually reversed upon decreasing the soil pH. Acidification of the soil, for example by addition of HCl, should effect the adsorption of hydrogen ions as follows:

$$\underline{R}OH + HCl \rightarrow \underline{R}OH_2^+ \ldots Cl \qquad (111\text{-}3)$$

The excess of the added acid should react with $Al(OH)_3$ bringing Al^{3+} into solution

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O \qquad (111\text{-}4)$$

However, both of these two reactions seem to be competitive and the second seems to take precedence. Acrorthox-A_p, Soil No. 3, and Acrorthox-B_2, Soil No. 4, are known to have a net positive charge at pH lower than 3.8 and 6.2 respectively. The zero point of charge of the other soils is not known, but it is known to be very low especially for the Fragiochrept-A_p, Soil No. 12, which has a significant amount of permanent negative charge.

As can be seen from the results presented in Table 4, the amount of aluminum extracted by 1N and 0.1N KCl solutions was largely dependent on the pH of the soil. The lower the pH value of the soil, the higher was the amount of aluminum extracted. Moreover, a significant difference was found between the amounts of aluminum extracted by the three salt solutions at the same pH even when the pH of the soil was on the positive side of the zero point of charge, under which condition Al^{3+} should not have been adsorbed by the soil. Indeed, it was found that the higher the

concentration of the salt solution, the greater was the amount of aluminum extracted. The 0.01M $CaCl_2$ extracting solution was the least effective.

The existence of some negative charges even when the net surface charge is positive cannot be precluded. Some idea as to the relative significance of the two reactions (111-3 and 111-4) may be gained from the data presented in Tables 5 and 6. A considerable amount of the added acid was adsorbed in increasing the positive charge especially in Acrorthox-A_p, Soil No. 3, and Acrorthox-B_2, Soil No. 4. As may be expected, the lower the pH, the greater was the amount of H^+ adsorbed and the greater was the amount of positive charge developed.

Based on these findings, it is evident that extraction of soils, containing large amounts of hydrous iron and aluminum oxides, by 1N KCl in determining the amount of exchangeable aluminum is quite meaningless inasmuch as the amount of Al^{3+} extracted depends on the salt concentration. It should be obvious that any definition of exchangeable aluminum extractable by neutral salt solutions can be defended only on operational basis. The amount of aluminum extracted by 0.01M $CaCl_2$ solution represents perhaps a more realistic measure of the exchangeable aluminum content of the soil under field conditions.

IV. COMPARISON OF SOIL ACIDITY AS DETERMINED BY 1N KCl AND $BaCl_2$-TEA METHODS WITH THE MAXIMUM AMOUNT OF $CaCO_3$ FOUND TO REACT WITH THE SOILS.

1. Introduction

Soil pH as measured in water or in a salt solution has been most commonly used as a measure of soil acidity. In highly leached soils of the humid tropics, the exchange acidity constitutes a major proportion of the cation exchange capacity. Moreover, in many instances, these soils containing substantial amounts of iron and aluminum oxides have a net positive charge at low pH values.

Calcium carbonate is generally added to acid soils to neutralize soil acidity. In general, liming recommendations are based on raising soil pH to some specific value. However, soil pH value alone is not a good basis for liming recommendations because of the variation of the exchange capacity of soils. Many methods have been proposed for measuring the lime requirement of soils. Usually some highly buffered salt solution at pH 7 or pH 8 is employed.

In tropical soils, the pH-dependent acidity is an important component of the soil acidity. These soils are known to contain pedogenic aluminous chlorite (12, 63, 64) which has a great capacity to react with lime.

Since in acid soils, the aluminum ion is the most abundant cation and largely responsible for soil acidity, many investigators (6, 17, 23, 44) have suggested that lime should be added to acid soils in amounts equivalent to neutralize the exchangeable aluminum. They proposed that lime recommendations be based on the exchangeable aluminum content of the

soil as determined by extraction with 1N KCl.

A comparison has been made in the present study of the maximum amount of $CaCO_3$ found to react with the soil with the exchangeable Al^{3+} extracted by 1N KCl and the exchange acidity as determined by the $BaCl_2$-triethanolamine method.

2. Experimental procedure

A. Determination of exchange acidity by $BaCl_2$-TEA method

Exchange acidity was determined by $BaCl_2$-triethanolamine method (38). A 10-g portion of soil was mixed with 100 ml of 0.5N $BaCl_2$-triethanolamine extracting solution adjusted to pH 8.0. The mixture was allowed to stand overnight and filtered through Whatman No. 32 filter paper. A volume of 250 ml of leachate was collected. The exchange acidity was determined by titrating with standard HCl using a mixed indicator of bromocresol green and methyl red. The results are given in Table 7-column 3.

B. Determination of exchangeable aluminum by 1N KCl

The exchangeable aluminum extractable by 1N KCl was determined by Yuan's procedure (67). A 10-g sample of soil was mixed with 50 ml of 1N KCl in a 125-ml Erlenmeyer flask and allowed to stand for a period of one hour with intermittent shaking. The mixture was filtered through a Büchner funnel fitted with No. 32 Whatman filter paper. Additional KCl solution was leached through the soil in small portions at a time until 225 ml of the extract had been collected. The extract was transferred to a 250-ml volumetric flask and made up to volume with 1N KCl. Two 100-ml aliquots were transferred into 500-ml Erlenmeyer flasks, boiled for a few minutes to expel CO_2, and then cooled to room temperature. The first aliquot was titrated with standard NaOH to the phenolphtalein end point for total titrable acidity ($H^+ + Al^{3+}$). To the second 100-ml aliquot of

TABLE 7. Comparison of the maximum amount of $CaCO_3$ found to react with acid soils with the exchange acidity and the amount of exchangeable aluminum.

Soil No.	Soil Name*	Exchange acidity by $BaCl_2$-TEA	1N KCl extractable Al^{3+}	Amount of $CaCO_3$ reacted with soil
		meq/100g		
1	Acrohumox-A_p	9.90	0.90	7.79
2	Acrohumox-B_2	6.70	0.30	4.63
5	Haplustox-A_p	18.70	3.90	15.40
6	Haplorthox-B_1	16.70	4.12	15.53
7	Tropohumult-B_1	20.60	11.03	18.62
8	Haplustox-A_p	13.10	0.75	8.24
9	Haplustox-B_1	8.70	0.15	4.95
10	Haplustox-A_p	15.80	2.25	9.82
11	Haplustox-B_1	12.10	1.86	8.60
12	Fragiochrept-A_p	16.40	3.38	14.86

* For soil description see Section II of the text

the extract, 10 ml of 4% NaF solution was added and the mixture was again titrated to the phenolphtalein end point. This second titration gives only the amount of exchangeable H^+. The results are given in Table 7.

C. Determination of maximum amount of $CaCO_3$ that can react with the soils

The maximum amount of $CaCO_3$ that can react with the soils was determined as follows: a known excess amount of $CaCO_3$ was mixed with 20 g of soil in a 50-ml beaker. After moistening with 20 ml of H_2O, the soils were allowed to equilibrate with $CaCO_3$ at the partial pressure of CO_2 existing in the atmosphere and at a temperature of 25°C for 10 weeks with alternate wetting and drying and occasional mixing. At the end of the reaction period, the soil pH was measured in H_2O and in 0.01M $CaCl_2$. The specific conductance was also measured in 1:2 soil-water extracts. The concentration of calcium in the 1:2 soil-water extract was calculated using the following relationship

$$c = \frac{K}{\Lambda} \times 1000 \qquad \text{(IV-1)}$$

where c is the concentration of salt expressed in equivalent per liter, K is the electrical conductivity in mho per cm, and Λ is the equivalent conductance at concentration c. The salt present was assumed to be $CaCl_2$. The activity of Ca^{++} was calculated from the total concentration of Ca^{++} present using the Guntelberg approximation of the Debye-Hückel equation to estimate the activity coefficient,

$$-\log \gamma_i = \frac{AZ_i^2\sqrt{\mu}}{1+\sqrt{\mu}} \qquad \text{(IV-2)}$$

where γ_i is the activity coefficient of the ion with valency Z_i and μ is the the ionic strength of the solution and is given by

$$\mu = \frac{1}{2} \Sigma C_i Z_i^2 \qquad \text{(IV-3)}$$

in which C_i is the molar concentration of ions. A in equation (IV-2) is a constant and has the value of 0.508 at 25°C.

The activity of Ca^{++} is given by

$$a_{Ca^{++}} = \left[Ca^{++}\right] \gamma_{Ca^{++}} \qquad \text{(IV-4)}$$

where $a_{Ca^{++}}$ is the activity and $\left[Ca^{++}\right]$ is the molar concentration. The value of pH $-\frac{1}{2}$pCa for a soil solution in equilibrium with a soil containing an excess of $CaCO_3$ is uniquely fixed by the partial pressure of CO_2 in the soil air and at the partial pressure of CO_2 of the atmosphere is equal to 6.60 (39). Thus it should be possible to calculate the pH of a soil in equilibrium with $CaCO_3$ if the activity of Ca^{++} in solution is known.

After equilibration of the soils with $CaCO_3$ for 10 weeks, the amount of residual $CaCO_3$ was determined by the Schollenberger method (1). The amount of $CaCO_3$ that had reacted with the soil was found by subtracting the amount of residual carbonate found from the amount originally added to the soil. The results are presented in Tables 7 and 8.

3. Discussion

After equilibration of the soils with an excess of $CaCO_3$, the pH values of all soils as measured in 0.01M $CaCl_2$ were in general much lower than those predicted (Table 9). The obvious explanation is that the soils had not reached equilibrium with the partial pressure of CO_2 of the air. The somewhat lower observed pH values of the soils would indicate that the partial pressure of CO_2 of the soil air was higher than that of the atmosphere due to microbiological activity. The degree of Ca^{++} saturation,

TABLE 8. Amount of $CaCO_3$ applied and the amount found to react with the acid soils

Soil No.	Soil Name*	Amount of $CaCO_3$ applied to soil	not reacted with soil	reacted with soil
		meq/100g		
1	Acrohumox-A_p	10.60	2.81	7.79
2	Acrohumox-B_2	10.60	5.97	4.63
5	Haplustox-A_p	21.20	5.80	15.40
6	Haplorthox-B_1	31.80	16.27	15.53
7	Tropohumult-B_1	37.10	18.48	18.62
8	Haplustox-A_p	10.60	2.36	8.24
9	Haplustox-B_1	10.60	5.65	4.95
10	Haplustox-A_p	10.60	0.78	9.82
11	Haplustox-B_1	10.60	2.00	8.60
12	Fragiochrept-A_p	31.80	16.94	14.86

* For soil description see Section II of the text

TABLE 9. The pH values and other pertinent data for the soils equilibrated for 10 weeks with an excess of $CaCO_3$

Soil No.	Soil Name	pH in H_2O	pH in 0.01M $CaCl_2$	EC*	Total† Ca^{++}	$a_{Ca^{++}}$‡	Calculated pH in 0.01M $CaCl_2$
				mmhos/cm	mMoles	$x10^3$	
1	Acrohumox-A_p	7.40	7.10	0.23	10.9	5.4	7.73
2	Acrohumox-B_2	7.55	7.30	0.37	11.5	5.6	7.72
5	Haplustox-A_p	7.60	7.20	0.19	10.7	5.3	7.74
6	Haplorthox-B_1	7.60	7.40	0.90	13.6	6.3	7.70
7	Tropohumult-B_1	7.60	7.40	0.80	13.2	6.1	7.70
8	Haplustox-A_p	7.50	6.90	0.19	10.7	5.3	7.74
9	Haplustox-B_1	7.80	7.20	0.14	10.6	5.3	7.74
10	Haplustox-A_p	7.20	6.60	0.16	10.6	5.3	7.74
11	Haplustox-B_1	7.60	7.05	0.14	10.5	5.3	7.74
12	Fragiochrept-A_p	7.70	7.20	0.37	11.5	5.6	7.72

*EC = Electrical conductivity of 1:2 soil-water extracts

†Total Ca^{++} in 1:2 soil - 0.01M $CaCl_2$ extract

‡$a_{Ca^{++}}$ = activity of Calcium in 1:2 soil -0.01M $CaCl_2$ extract

however, should not have been affected very much by the slightly lower observed pH values.

The amounts of $CaCO_3$ found to react with the soils after incubation for 10 weeks with an excess of precipitated $CaCO_3$ were much higher than the acidity (Al^{3+} + H^+) extracted by 1N KCl but were found to be in better agreement with the exchange acidity as determined by the $BaCl_2$-triethanolamine method, especially for soils Nos. 5, 6, 7 and 12 which were known to contain Al-chlorite (2, 63, 64). Thus the KCl-extractable acidity greatly underestimated whereas the exchange acidity by the $BaCl_2$-triethanolamine method overestimated the lime requirement of most of the soils examined in this study.

The $BaCl_2$-triethanolamine method, however, should provide a satisfactory bench mark for the full lime requirement of these soils. The actual amount of $CaCO_3$ to be applied will vary depending upon the plant to be grown and the type of soil. Also it should be obvious that the effective cation exchange capacity of tropical soils can be markedly increased by liming as can be seen from the data given in Table 8. However, many investigators (3, 25, 35, 44) have reported that liming of tropical soils to high pH values results in adverse effects, contrary to the results obtained on soils of the temperate regions. There are many theories advanced in attempt to explain the over-liming injury (24, 36, 42, 47). Some investigators have suggested that liming causes a deterioration of the structure of the soils of the humid tropics by reducing the aggregation of clays. Others have maintained that liming of tropical soils decreases the availability of some nutritive elements. The real cause of this adverse effect remains to be demonstrated.

V. FATE OF CALCIUM APPLIED AS $CaCO_3$ TO ACID TROPICAL SOILS

1. Introduction

In many soils of the temperate regions, it is known that Ca^{++} is held very strongly by the permanent negative charges of the mineral colloids. Very little of the Ca^{++} applied as $CaCO_3$ moves to lower depths in the profile. In highly-weathered soils where the negative charge is mainly pH dependent, it has been reported that Ca^{++} and other cations are not held as strongly as in their counterpart soils of the temperate regions (25, 32, 46, 66). Also, appreciable losses of Ca^{++} by leaching have been reported in soils of the humid tropics (31).

Other investigators (34, 43, 60) have presented some evidence that Ca^{++} can be "fixed" into nonexchangeable form by the highly-weathered soils. Accordingly, an attempt has been made in the present study to determine the fate of Ca^{++} applied as $CaCO_3$ to soils of the humid tropics. This has involved measurement of the loss of Ca^{++} by leaching and the extent of fixation of Ca^{++} into nonexchangeable form.

2. Preparation of Ca^{++}-saturated soils.

A 60-g sample of soil was mixed with amounts of $CaCO_3$ equivalent to the maximum amount of $CaCO_3$ that had been found to react with the moist soils upon incubation for 10 weeks. The $CaCO_3$-treated soils were moistened and allowed to react for the same period of time with alternate wetting and drying. At the end of the reaction period, the pH values were measured in H_2O and in 0.01M $CaCl_2$ and are shown in Table 10.

Ca^{++}-saturated soils were also prepared by bubbling CO_2 into the $CaCO_3$-treated soil suspension so as to transform all the $CaCO_3$ into

TABLE 10. Comparison of pH values of Ca^{++}-saturated soils as prepared by two methods

Soil No.	Soil Name*	Amount of $CaCO_3$ applied	Ca^{++}-saturated soils as prepared by Incubation: pH in H_2O	Incubation: pH in .01M $CaCl_2$	Bubbling CO_2: pH in H_2O	Bubbling CO_2: pH in .01M $CaCl_2$
		—meq/100g—				
1	Acrohumox-A_p	7.79	7.10	6.60	7.09	6.80
2	Acrohumox-B_2	4.63	7.30	6.95	7.40	6.95
5	Haplustox-A_p	15.40	7.55	7.00	7.29	6.85
6	Haplorthox-B_1	15.53	7.31	7.20	7.50	7.05
7	Tropohumult-B_1	18.62	7.05	6.91	7.25	6.95
8	Haplustox-A_p	8.24	7.16	6.61	7.16	6.50
9	Haplustox-B_1	4.95	ND†	ND†	7.58	6.81
10	Haplustox-A_p	9.82	6.86	6.40	6.89	6.38
11	Haplustox-B_1	8.60	7.60	6.90	7.20	6.78
12	Fragiochrept-A_p	14.86	ND†	ND†	7.20	6.80

* For soil description see Section II of the text

† Not determined

$Ca(HCO_3)_2$. This is essentially the method described by Patel and Truog (37). The soil suspensions were then allowed to stand overnight and evaporated to dryness on a steam hot plate. After evaporation, the soils were again moistened and allowed to air-dry. The pH values were measured in H_2O and in 0.01M $CaCl_2$ and the results are given in Table 10.

As shown in Table 10, a good agreement was found between the pH values of soils prepared by both methods. Shaw (51) also found a good agreement between the results obtained by the steam evaporation method and those obtained by the Bradfield-Allison residual carbonate method (4).

3. Study of loss of adsorbed calcium by leaching

a. Introduction

In the humid tropics, the annual precipitation is very high and losses of adsorbed metal ions, "exchangeable bases", may be expected to be greater than those encountered in the soils of the humid temperate regions. It is conceivable that a rapid loss of these cations would constitute a major problem in the management of these highly-weathered soils. A study was made to acertain the loss of adsorbed Ca^{++} from the fully Ca^{++}-saturated soils upon successive extraction of the soils with water.

b. Experimental procedure

Prepared fully Ca^{++}- saturated soils were submitted to a series of successive extractions with water to simulate the losses by leaching under field conditions.

A 7.5-g sample of soil was mixed with 30 ml of distilled water in a 50-ml polycarbonate centrifuge tube and centrifuged at 18,000 rpm for 20 minutes in a Sorvall RC2-B refrigerated centrifuge maintained at 25°C. The supernatant solution was decanted, and the extraction procedure was

repeated 8 times. After extraction with water, the soil sediment was saved for the determination of exchangeable Ca^{++}. It is interesting to note here that most of the aqueous extracts developed an increasingly yellowish color upon successive extraction. This color was especially pronounced in extracts of the surface samples. Further reference to this phenomenon will be made in a later section.

The extracts were evaporated to dryness on a steam hot plate after addition of 3 ml of 1:1 HCl. This was followed by the addition of 1 ml of HNO_3 and 5 ml of 30% H_2O_2 and evaporation to dryness again. The residue of salts was taken up with 1N HCl containing 0.5% La^{3+} and the volume was made up to exactly 10 ml. The concentration of Ca^{++} in the extracts was determined by atomic absorption using a Perking Elmer model 290B spectrophotometer.

The cumulative amounts of Ca^{++}, expressed in meq per 100 g of soil, have been plotted in Fig. 7 as a function of the number of extractions. The data used to prepare this figure are given in the first and third columns of Tables 11 through 19.

The cumulative amounts of Ca^{++} removed after 8 successive extractions varied widely with different soils ranging from 0.7 to 4.2 meq of Ca^{++} per 100 g of soil. This variation in the cumulative amounts of Ca^{++} removed was largely due to differences in the amounts of Ca^{++} removed in the first three extractions, after which the rate of removal upon further extraction was essentially the same for all soils with the exception of Catalina from Puerto Rico. Contrary to expectation, the cumulative amounts of Ca^{++} removed from the highly weathered soils of the humid tropics were smaller than that removed from a New York soil, Mardin silt loam.

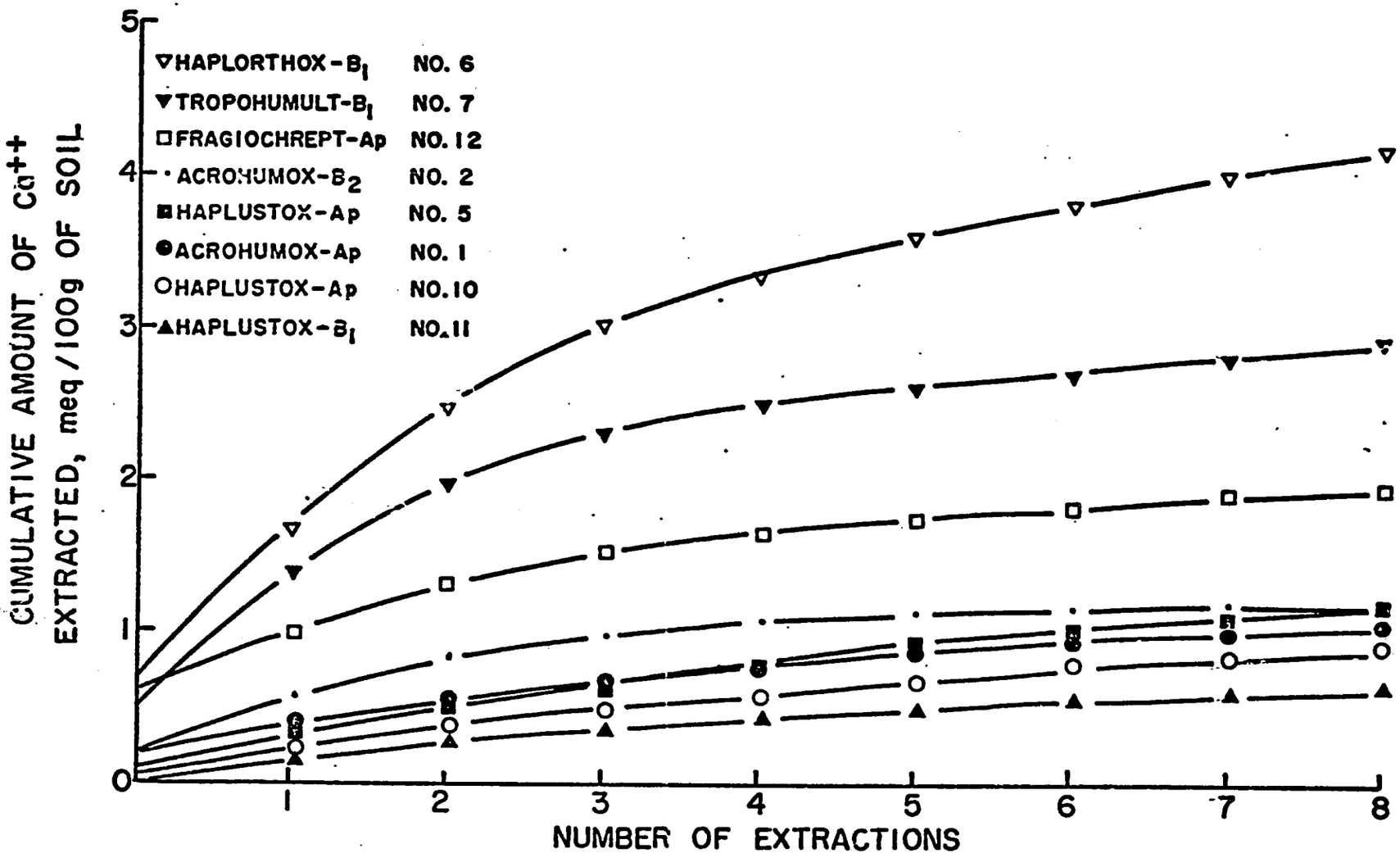

FIG. 7. Loss of adsorbed Ca^{++} upon successive extractions with water

c. Determination of the hydrolysis constant of adsorbed Ca^{++}

Two methods were followed in the determination of the hydrolysis constant of adsorbed Ca^{++}. In the first method, the concentration of Ca^{++} in the aqueous extracts was measured upon successive extraction of the soil with water. In the second method, the concentration of Ca^{++} in the aqueous extract was measured as a function of the volume of dilution.

i. Measurement of the concentration of Ca^{++} in aqueous extracts upon successive extraction

The hydrolysis of adsorbed Ca^{++} can be represented as follows:

$$(RO^-)_2Ca^{++} + 2HOH \rightleftarrows 2ROH + Ca(OH)_2 \qquad \text{(V-1)}$$

Since in highly-weathered soils, the charge is solely determined by potential determining ions and Ca^{++}-soil and $Ca(OH)_2$ are completely dissociated, the net reaction for the hydrolysis of the adsorbed Ca^{++} can be written:

$$RO^- + HOH \rightleftarrows ROH + OH^- \qquad \text{(V-2)}$$

and the equilibrium constant is given by

$$K = \frac{[ROH][OH^-]}{[RO^-]} \qquad \text{(V-3)}$$

in which $[RO^-] = [Ca^{++}] = Ca^{++}$ adsorbed in meq per 100 g of soil

or

$$[Ca^{++}] = \Theta(CEC) \qquad \text{(V-4)}$$

where Θ is the degree of calcium saturation and CEC cation exchange capacity, and

$[ROH] = [H^+] = H^+$ adsorbed in meq per 100 g of soil,

or

$$[H^+] = (1-\theta)CEC \qquad \text{(V-5)}$$

Also, one may substitute $(Ca^{++}) = (OH^-)$ which is the concentration of Ca^{++} in solution, expressed in meq per liter. Hence:

$$K = \frac{(1-\theta)(CEC)(Ca^{++})}{\theta(CEC)} \qquad \text{(V-6)}$$

$$K = \frac{(1-\theta)(Ca^{++})}{\theta} \qquad \text{(V-7)}$$

or

$$(Ca^{++}) \text{ in solution} = K\,\frac{\theta}{1-\theta} \qquad \text{(V-8)}$$

Initially, $\theta = 1$ since $[Ca^{++}] = CEC$

Thus the concentration of Ca^{++} in solution should be proportional to the degree of Ca^{++} saturation of the soil or, more correctly stated, directly proportional to the quotient $\frac{\theta}{1-\theta}$. It should be noted that $\frac{\theta}{1-\theta}$ decreases very rapidly with decreasing degree of Ca^{++} saturation of the soil.

The hydrolysis constant K has been calculated for each of the soils upon progressive extraction with water using equation (V-8) in which Ca^{++} in solution is expressed in meq per liter. The results are given in Tables 11 through 19.

Also in Fig. 8, the concentration of Ca^{++} in the successive extracts has been plotted against the value of $\frac{\theta}{1-\theta}$. The hydrolysis constant is given by the slope of the line. It should be obvious from Fig. 8 that the hydrolysis constant varied widely with different soils. Also in three of the soils, (Nos. 2, 6, and 7) the hydrolysis constant decreased rapidly for the first three extractions after which it remained relatively constant. This may be attributed to the presence of easily hydrolyzable exchange sites. The average hydrolysis constant for each of the soils is

TABLE 11. Concentration of Ca^{++} in successive aqueous extracts of Acrohumox-A_p* (Soil No. 1) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	Θ	$\frac{\Theta}{1-\Theta}$	K
	meq/l	meq/100g				
1	1.06	0.39	9.33	0.96	24.0	0.04
2	0.49	0.18	9.15	0.94	15.9	0.03
3	0.32	0.12	9.03	0.93	13.1	0.02
4	0.19	0.07	8.96	0.92	11.8	0.02
5	0.27	0.10	8.86	0.91	10.3	0.03
6	0.19	0.07	8.79	0.90	9.4	0.02
7	0.19	0.07	8.72	0.90	8.7	0.02
8	0.21	0.08	8.64	0.89	8.0	0.03

* Initial exchangeable Ca^{++} or CEC = 9.72 meq per 100g

TABLE 12. Concentration of Ca^{++} in successive aqueous extracts of Acrohumox-B_2* (Soil No. 2) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	θ	$\frac{\theta}{1-\theta}$	K
	meq/l	meq/100g				
1	1.59	0.59	4.07	0.87	6.87	0.23
2	0.[illegible]6	0.24	3.83	0.82	4.62	0.14
3	0.36	0.13	3.70	0.79	3.85	0.09
4	0.22	0.08	3.62	0.78	3.48	0.06
5	0.16	0.06	3.56	0.76	3.24	0.05
6	0.11	0.04	3.52	0.75	3.08	0.04
7	0.08	0.03	3.49	0.75	2.98	0.03
8	0.08	0.03	3.46	0.74	2.88	0.03

* Initial exchangeable Ca^{++} or CEC = 4.66 meq per 100g

TABLE 13. Concentration of Ca^{++} in successive aqueous extracts of Haplustox-A_p* (Soil No. 5) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	Θ	$\frac{\Theta}{1-\Theta}$	K
	meq/l	meq/100g				
1	0.89	0.33	15.14	0.98	46.6	0.02
2	0.50	0.18	14.96	0.97	29.3	0.02
3	0.42	0.15	14.81	0.96	22.3	0.02
4	0.37	0.13	14.68	0.95	18.6	0.02
5	0.33	0.12	14.56	0.94	15.9	0.02
6	0.28	0.10	14.46	0.93	14.4	0.02
7	0.28	0.10	14.36	0.93	12.9	0.02
8	0.30	0.11	14.25	0.92	11.7	0.03

* Initial exchangeable Ca^{++} or CEC = 15.47 meq per 100g

TABLE 14. Concentration of Ca^{++} in successive aqueous extracts of Haplorthox-B_1* (Soil No. 6) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	θ	$\frac{\theta}{1-\theta}$	K
	meq/l	meq/100g				
1	4.73	1.67	14.36	0.90	8.61	0.55
2	2.30	0.79	13.57	0.85	5.49	0.42
3	1.53	0.54	13.03	0.81	4.35	0.35
4	0.85	0.29	12.74	0.79	3.88	0.22
5	0.82	0.28	12.46	0.77	3.39	0.24
6	0.65	0.22	12.24	0.76	3.24	0.20
7	0.51	0.20	12.04	0.75	3.02	0.17
8	0.37	0.16	11.88	0.74	2.86	0.13

* Initial exchangeable Ca^{++} or CEC = 16.03 meq per 100 g

TABLE 15. Concentration of Ca^{++} in successive aqueous extracts of Tropohumult-B_1* (Soil No. 7) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	Θ	$\frac{\Theta}{1-\Theta}$	K
	meq/l	meq/100g				
1	3.81	1.38	18.84	0.93	13.71	0.28
2	1.72	0.61	18.23	0.90	9.20	0.19
3	0.79	0.28	17.95	0.89	7.93	0.10
4	0.54	0.19	17.76	0.88	7.20	0.08
5	0.37	0.13	17.63	0.87	6.8[illegible]	0.05
6	0.29	0.10	17.53	0.87	6.52	0.04
7	0.26	0.09	17.44	0.86	6.25	0.04
8	0.26	0.09	17.35	0.86	6.04	0.04

* Initial exchangeable Ca^{++} or CEC = 20.22 meq per 100g

TABLE 16. Concentration of Ca^{++} in successive aqueous extracts of Haplustox-A_p* (Soil No. 8) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	θ	$\frac{\theta}{1-\theta}$	K
	meq/l	meq/100g				
1	0.61	0.22	8.07	0.97	36.0	0.02
2	0.33	0.12	7.95	0.96	23.4	0.01
3	0.25	0.09	7.86	0.95	18.2	0.01
4	0.28	0.10	7.76	0.94	14.6	0.02
5	0.28	0.10	7.66	0.92	12.2	0.02
6	0.22	0.08	7.58	0.91	10.6	0.02
7	0.22	0.08	7.50	0.90	9.5	0.02
8	0.25	0.09	7.41	0.89	8.4	0.03

* Initial exchangeable Ca^{++} or CEC = 8.29 meq per 100 g

TABLE 17. Concentration of Ca^{++} in successive aqueous extracts of Haplustox-A_p* (Soil No. 10) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	θ	$\frac{\theta}{1-\theta}$	K
	meq/l	meq/100g				
1	0.67	0.24	9.62	0.98	40.7	0.02
2	0.39	0.14	9.48	0.96	24.6	0.02
3	0.31	0.11	9.37	0.95	19.0	0.02
4	0.28	0.10	9.27	0.94	15.7	0.02
5	0.25	0.09	9.18	0.93	13.5	0.02
6	0.22	0.08	9.10	0.92	12.0	0.02
7	0.22	0.08	9.02	0.92	10.8	0.02
8	0.22	0.08	8.94	0.91	9.8	0.02

* Initial exchangeable Ca^{++} or CEC = 9.86 meq per 100g

TABLE 18. Concentration of Ca^{++} in successive aqueous extracts of Haplustox-B_1* (Soil No. 11) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	θ	$\frac{\theta}{1-\theta}$	K
	meq/l	meq/100g				
1	0.43	0.16	8.47	0.98	51.6	0.01
2	0.27	0.10	8.37	0.97	32.3	0.01
3	0.22	0.08	8.29	0.96	24.6	0.01
4	0.19	0.07	8.22	0.95	19.8	0.01
5	0.19	0.07	8.15	0.94	16.9	0.01
6	0.16	0.06	8.09	0.94	14.9	0.01
7	0.16	0.06	8.03	0.93	13.3	0.01
8	0.16	0.06	7.97	0.92	12.0	0.01

* Initial exchangeable Ca^{++} or CEC = 8.63 meq per 100g

TABLE 19. Concentration of Ca^{++} in successive aqueous extracts of Fragiochrept-A_p* (Soil No. 12) and the calculated hydrolysis constant

Extraction Number	Ca^{++} Extracted		Ca^{++} adsorbed	Θ	$\frac{\Theta}{1-\Theta}$	K
	meq/l	meq/100g				
1	2.76	1.01	14.84	0.94	14.62	0.19
2	0.85	0.30	14.54	0.92	11.10	0.08
3	0.54	0.19	14.35	0.91	9.53	0.06
4	0.34	0.12	14.23	0.90	8.80	0.04
5	0.31	0.11	14.12	0.89	8.17	0.04
6	0.23	0.08	14.04	0.89	7.77	0.03
7	0.20	0.07	13.97	0.88	7.40	0.03
8	0.17	0.06	13.91	0.88	7.20	0.02

* Initial exchangeable Ca^{++} or CEC = 15.85 meq per 100g

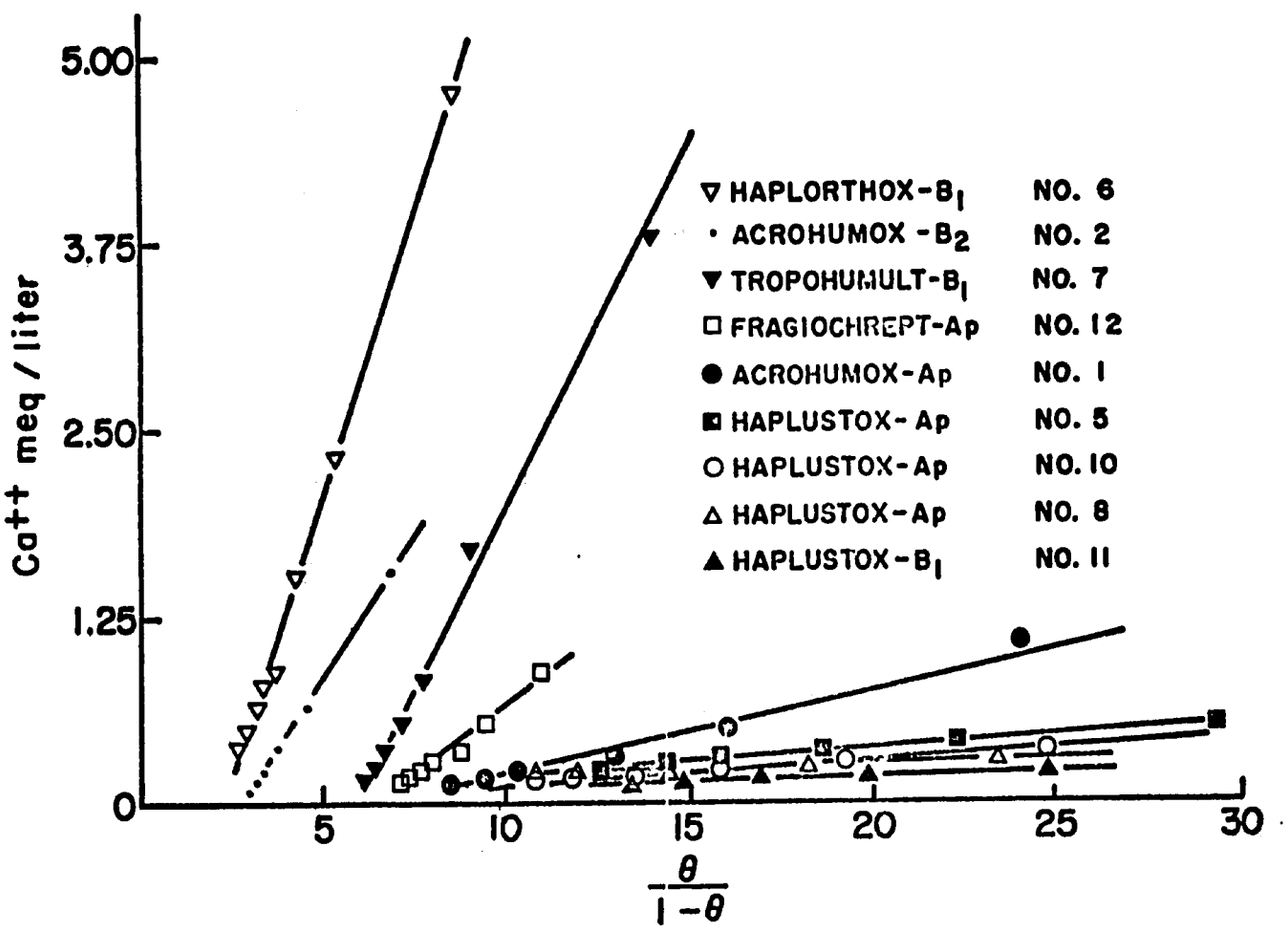

FIG. 8. Concentration of Ca^{++} in successive aqueous extracts of soils as a function of $\frac{\Theta}{1-\Theta}$

shown in Table 20. The hydrolysis constants for the first three extracts have been excluded in calculating the average hydrolysis constant tabulated in Table 20 which corresponds to the slope given by the linear portion of the curves plotted in Fig. 8.

ii. Measurement of the concentration of Ca^{++} in aqueous extracts of soils as a function of the volume of dilution

Drachev (15) and Lisk (28) found that the total quantity of electrolytes extracted by water per unit weight of soil was given by the following equation:

$$x = y\sqrt{v} + b \qquad \text{(V-9)}$$

in which x represents the total amount of soluble electrolytes in meq per 100 g of dry soil, and v is the volume of dilution, or the volume of water per unit weight of soil, and b is the amount of readily soluble salts (chlorides, nitrates) present in the soil. By plotting x versus $\sqrt{v}$, a straight line was obtained with slope equal to y and b as the intercept. In applying this equation to the present study of the hydrolysis of adsorbed Ca^{++}, it was tacitly assumed that Ca^{++}-soil behaves as a salt of a weak acid. The hydrolysis of adsorbed Ca^{++} may be represented as,

$$(RO^-)_2\ Ca^{++} + 2HOH \rightleftarrows 2ROH + Ca(OH)_2 \qquad \text{(V-1)}$$

The net reaction for the hydrolysis can be written,

$$RO^- + HOH \rightleftarrows ROH + OH^- \qquad \text{(V-2)}$$

and

$$K = \frac{[ROH][OH^-]}{[RO^-]}$$

TABLE 20. Comparison of the average hydrolysis constant of adsorbed Ca^{++} obtained for different soils

Soil No.	Soil Name*	K	Soil No.	Soil Name*	K
1	Acrohumox-A_p	.02	8	Haplustox-A_p	.02
2	Acrohumox-B_2	.04	10	Haplustox-A_p	.02
5	Haplustox-A_p	.02	11	Haplustox-B_1	.01
6	Haplorthox-B_1	.19	12	Fragiochrept-A_p	.03
7	Tropohumult-B_1	.05			

* For soil description see Section II of the text

in which $[OH^-]$, $[ROH]$ and $[RO^-]$ are expressed in meq per liter. If the degree of hydrolysis is x and the original concentration of Ca^{++}-soil or adsorbed Ca^{++} is C, also expressed in meq per liter, then

$$[ROH] = x\ C \tag{V-10}$$

$$[OH^-] = x\ C \tag{V-11}$$

$$[RO^-] = (1-x)\ C \tag{V-12}$$

Therefore,

$$K = \frac{C^2x^2}{(1-x)C} = \frac{Cx^2}{(1-x)} \tag{V-13}$$

or

$$\frac{x^2}{1-x} = \frac{K}{C} = Kv \tag{V-14}$$

where $v = \frac{1}{C}$ = volume of dilution expressed in liters per meq of adsorbed Ca^{++}.

Hence,

$$\frac{x}{\sqrt{1-x}} = \sqrt{K}\ \sqrt{v} \tag{V-15}$$

when x is small the quantity $\frac{x}{\sqrt{1-x}} \approx x$ and

$$x = \sqrt{K}\ \sqrt{v} \tag{V-16}$$

Thus, the degree of hydrolysis is directly proportional to the square root of the volume of dilution, and the amount of Ca^{++} per unit weight of soil brought into solution by hydrolysis should follow the equation used by Drachev.

Accordingly Ca^{++}-saturated soils were extracted with water by varying the volume of dilution (ratio of volume of water:weight of soil) from 1 to 64. The extraction of soils and the determination of Ca^{++} in the aqueous extracts were made in exactly the same manner as that described

in the previous experiment in which the concentration of Ca^{++} in the aqueous extracts was determined upon successive extraction of the soil with water. The amounts of Ca^{++} extracted at various dilutions are given in Table 21. The amount of Ca^{++} extracted, expressed in meq per 100 g of soil, is obviously equal to

$$Ca^{++} \text{ extracted (meq/100g)} = x \text{ CEC} \qquad \text{(V-17)}$$

in which x represents the degree of hydrolysis and CEC is the cation exchange capacity in meq per 100 g of soil and is equal to the initial amount of adsorbed Ca^{++} which is the sum of the native Ca^{++} plus the amount of Ca^{++} applied as $CaCO_3$ in preparation of the fully Ca^{++}-saturated soils.

The values of $\frac{x}{\sqrt{1-x}}$, the corresponding values of $\sqrt{v}$, and the hydrolysis constant calculated using equation (V-15) are given in Tables 22 through 24. The volume of dilution has been calculated using the following equation

$$v \text{ in liter/meq} = \frac{\text{volume of water in liter}}{\text{g of soil}} \times \frac{1}{\text{CEC}_{\text{meq/g}}} \qquad \text{(V-18)}$$

In Fig. 9, $\frac{x}{\sqrt{1-x}}$ has been plotted against $\sqrt{v}$. The average value for the hydrolysis constant corresponding to the linear portion of the curves in Fig. 9 was found to be 0.04 for Acrohumox-A_p (Soil No. 1), 0.32 for Haplorthox-B_1 (Soil No. 6), 0.13 for Tropohumult-B_1 (Soil No. 7), 0.02 for Haplustox-A_p (Soil No. 8), and 0.07 for Fragiochrept-A_p (Soil No. 12). These values for the hydrolysis constant are in fair agreement with those obtained upon successive extraction of the soils with water.

It may be concluded from this study of hydrolysis of the adsorbed Ca^{++} that losses of Ca^{++} by leaching from the highly-weathered soils of

TABLE 21. Amounts of calcium extracted from Ca^{++}-saturated soils at various dilutions with water

ratio $\frac{soil}{water}$	Soil No. 1 Acrohumox-A_p	Soil No. 6 Haplorthox-B_1	Soil No. 7 Tropohumult-B_1	Soil No. 8 Haplustox-A_p	Soil No. 12 Fragiochrept-A_p
	meq/100g				
1:1	0.27	0.45	0.59	0.14	0.46
1:2	0.45	1.07	1.07	0.21	ND*
1:4	0.49	1.57	1.39	0.27	1.01
1:8	0.63	1.97	1.79	0.33	1.09
1:16	0.83	2.67	1.92	0.43	1.39
1:32	0.96	3.20	2.53	0.53	1.60
1:64	0.96	4.27	2.66	0.64	1.81

* ND = not determined

TABLE 22. Hydrolysis of adsorbed Ca^{++} from Acrohumox-A_p (Soil No. 1) and Haplorthox-B_1 (Soil No. 6) upon dilution

ratio $\frac{\text{soil}}{\text{water}}$	Soil No. 1 Acrohumox-A_p			Soil No. 6 Haplorthox-B_1		
	$\frac{x}{\sqrt{1-x}}$	$\sqrt{v}$	K	$\frac{x}{\sqrt{1-x}}$	$\sqrt{v}$	K
1:1	0.028	0.101	0.08	0.028	0.079	0.13
1:2	0.047	0.143	0.11	0.069	0.112	0.38
1:4	0.052	0.203	0.06	0.103	0.158	0.43
1:8	0.067	0.287	0.05	0.131	0.223	0.34
1:16	0.089	0.406	0.05	0.182	0.315	0.33
1:32	0.104	0.574	0.03	0.223	0.447	0.25
1:64	0.104	0.811	0.02	0.311	0.632	0.24

TABLE 23. Hydrolysis of adsorbed Ca^{++} from Tropohumult-B_1 (Soil No. 7) and Haplustox-A_p (Soil No. 8) upon dilution

ratio $\frac{\text{soil}}{\text{water}}$	Soil No. 7 Tropohumult-B_1			Soil No. 8 Haplustox-A_p		
	$\frac{x}{\sqrt{1-x}}$	$\sqrt{v}$	K	$\frac{x}{\sqrt{1-x}}$	$\sqrt{v}$	K
1:1	0.030	0.070	0.18	0.017	0.110	0.02
1:2	0.054	0.099	0.28	0.026	0.155	0.03
1:4	0.071	0.141	0.26	0.033	0.220	0.02
1:8	0.093	0.199	0.22	0.041	0.311	0.02
1:16	0.100	0.281	0.13	0.053	0.439	0.02
1:32	0.134	0.398	0.11	0.066	0.621	0.01
1:64	0.141	0.563	0.06	0.080	0.879	0.01

TABLE 24. Hydrolysis of adsorbed Ca^{++} from Fragiochrept-A_p (Soil No. 12) upon dilution

ratio $\frac{\text{soil}}{\text{water}}$	Soil No. 12 Fragiochrept-A_p		
	$\frac{x}{\sqrt{1-x}}$	$\sqrt{v}$	K
1:1	0.029	0.079	0.14
1:2	ND*	ND*	ND*
1:4	0.066	0.159	0.17
1:8	0.071	0.225	0.10
1:16	0.092	0.318	0.08
1:32	0.106	0.449	0.06
1:64	0.121	0.665	0.04

* ND = Not determined

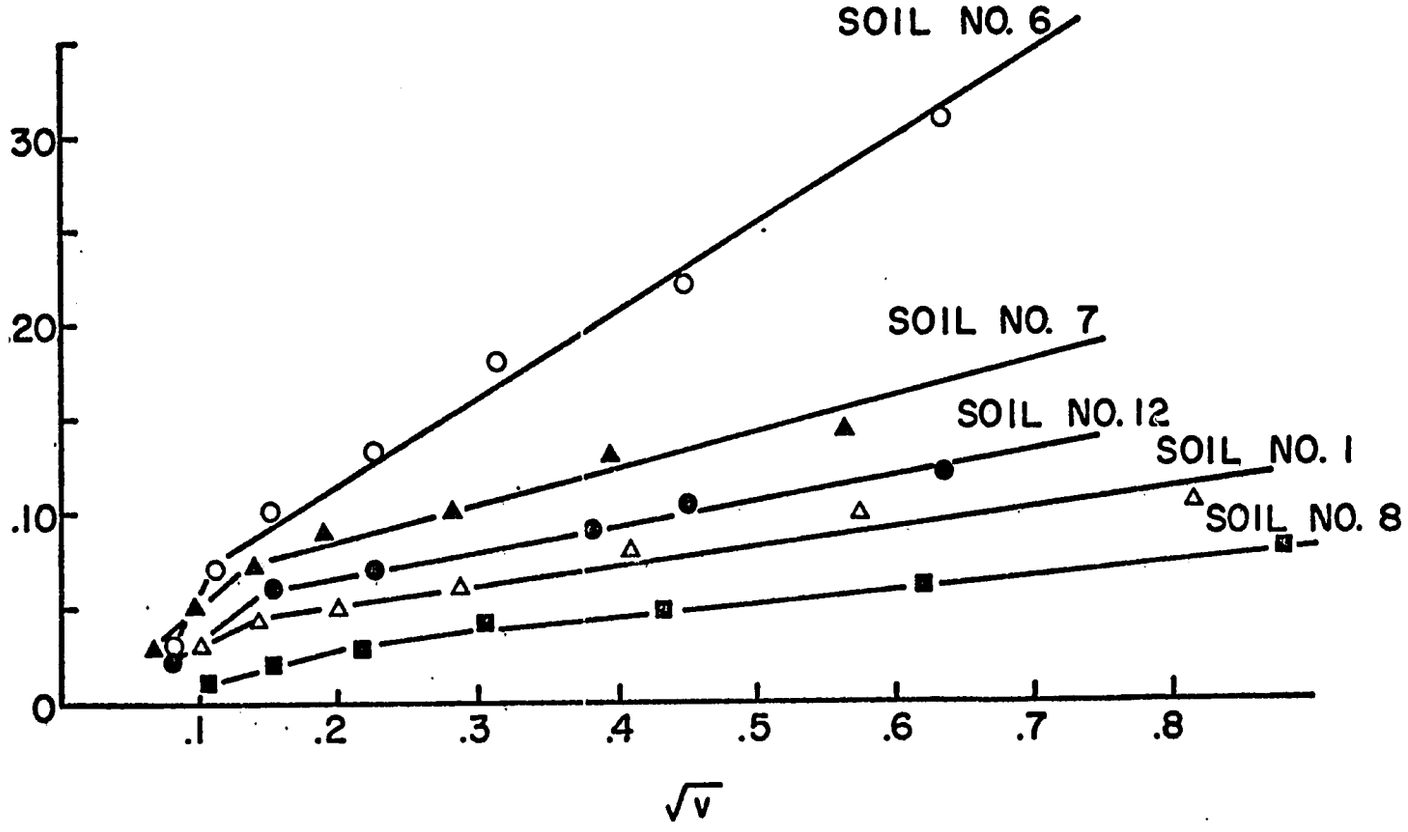

FIG. 9. Hydrolysis of adsorbed Ca^{++} upon dilution

the humid tropics should be no greater than those found for the soils of the temperate regions. Thus the pH-dependent charge of these highly-weathered soils of the tropics is just as effective as the permanent charge of soils of the temperate regions in adsorbing cations and preventing their loss by leaching.

4. Recovery of adsorbed Calcium

Because of recent reports (43, 60) that Ca^{++} may be "fixed" in non-exchangeable forms in highly-weathered soils, an attempt was made in the present study to determine the extent to which the applied Ca^{++} can be recovered by extraction with 1N KCl solution.

a. Analytical procedures

i. Determination of exchangeable Ca^{++} by extraction with 1N KCl

Following 8 successive extractions of the Ca^{++}-saturated soils with water in the study of hydrolysis of the adsorbed Ca^{++} described in the preceding section, the soils were leached with 1N KCl solution using the same method that has been already described for the determination of exchangeable calcium. The concentration of Ca^{++} in the KCl extracts was determined by atomic absorption. The results are presented in Table 25. The total amount of Ca^{++} removed by extraction with water and KCl is considered to be exchangeable. The difference between the total amount of Ca^{++} applied, including the initial exchangeable calcium content of the soil, and the exchangeable calcium extracted with water and 1N KCl is considered as Ca^{++} "fixed" by the soil. Because of the large relative error arising from subtraction of two large quantities to obtain a small one, the Ca^{++} remaining in the soil following extraction with 1N KCl was determined directly by extracting the soil with HCl.

TABLE 25. Removal of adsorbed Ca^{++} upon extractions with water and 1N KCl, and fixation of Ca^{++} by the soils

Soil No.	Soil Name*	Initial Exch. Ca^{++}	Ca^{++} Extracted by			Ca^{++} remaining in soils after extractions		Ca^{++} "fixed"
			H_2O		1N KCl	limed	unlimed	
		meq/100g		%	meq/100g			
1	Acrohumox-A_p	9.72	1.08	11.1	7.50	0.71	0.27	0.44
2	Acrohumox-B_2	4.66	1.20	25.7	3.25	0.06	0.02	0.04
5	Haplustox-A_p	15.47	1.22	7.9	12.33	1.04	0.08	0.96
6	Haplorthox-B_1	16.03	4.15	25.9	10.91	0.46	0.06	0.40
7	Tropohumult-B_1	20.22	2.87	14.2	16.67	0.27	0.02	0.25
8	Haplustox-A_p	8.29	0.88	10.6	6.83	0.42	0.03	0.39
10	Haplustox-A_p	9.86	0.92	9.3	8.54	0.35	0.03	0.32
11	Haplustox-B_1	8.63	0.66	7.6	7.37	0.36	0.02	0.34
12	Fragiochrept-A_p	15.85	1.94	12.2	12.00	1.76	0.66	1.10

* For soil description see Section II of the text

ii. Determination of residual calcium after exhaustive extractions of the soils with water and 1N KCl

Following extraction of the soils with water and 1N KCl, the soils were transferred to a 150-ml beaker and digested with 30 ml of 6N HCl for 2 hours on a steam plate. The soil suspensions were then filtered through No. 32 Whatman paper. A 20-ml aliquot was evaporated until the solution became very viscous and transferred into a 250-ml separatory funnel with Teflon stopcock using enough additional 6N HCl to effect the transfer. The Fe(111) was extracted with diethyl ether (20, 26, 30, 48) in order to avoid its interference in the calcium determination by atomic absorption.

After removal of Fe(111), the extract was transferred to a 150-ml beaker, evaporated to dryness, treated with 1 ml of HNO_3 and 5 ml of 30% H_2O_2, and again evaporated to dryness. This was followed by the addition of 3 ml of 6N HCl and evaporation to dryness. The residue was taken up with 1N HCl containing 0.5% La^{3+}, made up to volume in a 25-ml volumetric flask, and filtered through No. 32 Whatman paper. The Ca^{++} concentration in the final solution was measured by atomic absorption.

In order to correct for the native nonexchangeable calcium present in the soil, the unlimed soils were subjected to the same exhaustive extraction with 1N KCl to remove the exchangeable Ca^{++}, followed by digestion with 30 ml of 6N HCl for 2 hours, and carried through exactly the same procedure described for the limed soils. The difference between the amounts of Ca^{++} extracted by 6N HCl from the limed and the corresponding unlimed soil was considered as "Ca^{++} fixed" by the limed soils. The amounts of "Ca^{++} fixed" reported in Table 25 were obtained in this manner. Also shown in the same table are the total initial exchangeable Ca^{++} and

the amounts of Ca^{++} recovered by extraction with water and 1N KCl.

It will be noted from the results in Table 25 that, with the exception of two soils, Nos. 5 and 12, the amount of Ca^{++} found "fixed" into nonexchangeable form was less than 0.5 meq per 100 g and is hardly significant. Surprisingly enough the New York soil fixed the largest amount of Ca^{++} into nonexchangeable form, probably due to vermiculite which is known to be present in this soil. Thus there is little evidence to indicate that the highly-weathered soils of the humid tropics have the capacity to fix calcium into nonexchangeable form.

VI. MOBILIZATION OF IRON IN SOILS UPON LIMING

In the course of the study of the loss of adsorbed Ca^{++} upon successive extraction of the fully Ca^{++}-saturated soils with water, it was observed that the color of the aqueous extracts became increasingly more yellow upon successive extraction of the soils with water. This increase in the intensity of the yellow color was especially pronounced in about the third extract. Surprisingly enough the extracts of these same soils became virtually colorless when the soils, following extraction with water, were extracted with 1N KCl in order to study the recovery of the adsorbed Ca^{++} in the limed soils in the experiment described in Section V-4.

Moreover, the addition of KCl or HCl to the colored aqueous extracts caused precipitation of some flocculant yellowish material suggesting that the color of the aqueous extracts was due to the presence of some highly dispersed colloid. The yellow color of the aqueous extracts was especially pronounced in the extracts of the limed surface soils, indicating that the color must have been due in part to the presence of organic matter. Accordingly, the following experiment was carried out in order to study the role of organic matter and Ca^{++} in the mobilization of Fe(111) upon successive extraction of the limed and unlimed surface and subsoils with water.

1. Analytical procedures

a. Extraction and determination of pH of the aqueous extracts

A 7.5-g sample of each of the soils was successively extracted with 30 ml of water in a 50-ml polycarbonate centrifuge tube. After addition

of 30 ml of water to the soil, the suspensions were thoroughly stirred with a mechanical stirrer and centrifuged at 18,000 rpm. After decanting the supernatant solution and measuring the pH, the concentration of Fe(111) in the extracts was determined as described below. The results of pH determinations are shown in Table 26.

b. Determination of Fe(111) in the aqueous extracts

The aqueous extracts were evaporated to dryness on a steam hot plate. The residue was treated with 10 ml of aqua regia and again evaporated to dryness. A small amount of 1N HCl was added to dissolve the residue and then the volume was made to 10-ml with dilute HCl. Iron was determined colorimetrically by the αα′-dipyridyl method (9).

In order to determine the effect of liming on the mobilization of Fe(111), the unlimed soils were also subjected to exactly the same procedure described for the limed soils. The results of the determination of Fe(111) are summarized in Tables 27 and 28.

2. Results and discussion

Upon successive extraction of limed soils with water, the pH and the concentration of Fe(111) in the extracts was found to increase. Iron was mobilized markedly in the surface soils after removal of the last traces of soluble salts as shown in Tables 27 and 28. The concentrations of Fe(111) in the extracts of the subsoils were found to be negligibly small, pointing to the important role of organic matter in the mobilization of iron.

To determine whether this mobilization of Fe(111) could be attributed to dispersion of some organo-iron oxide colloid or clay the following experiment was carried out. The free salts were removed from two limed

TABLE 26. pH values of aqueous extracts upon successive extractions of the limed soils with water

Soil No.	Soil Name*	Extractions number							
		1	2	3	4	5	6	7	8
1	Acrohumox-A_p	6.55	7.05	7.00	7.10	7.30	7.10	7.02	7.02
2	Acrohumox-B_2	6.70	6.90	6.80	6.85	7.10	6.90	6.90	6.90
5	Haplustox-A_p	7.00	7.25	7.20	7.25	7.35	7.10	7.10	7.05
6	Haplorthox-B_1	6.80	7.00	7.00	7.00	7.25	7.05	7.00	6.95
7	Tropohumult-B_1	6.75	7.00	7.15	7.25	7.30	7.05	7.15	7.10
8	Haplustox-A_p	6.90	7.05	7.05	7.25	7.28	7.25	7.21	7.15
10	Haplustox-A_p	6.81	7.20	7.25	7.30	7.31	7.20	7.25	7.25
11	Haplustox-B_1	7.00	7.15	7.25	7.25	7.40	7.30	7.35	7.22

* For soil description see Section II of the text

TABLE 27. The concentration of Fe(111) in successive aqueous extracts of unlimed and limed soils (Nos. 1, 2, 5, 6, and 7)

Extractions Number	Soil No. 1 Acrohumox-A_p		Soil No. 2 Acrohumox-B_2	Soil No. 5 Haplustox-A_p		Soil No. 6 Haplorthox-B_1	Soil No. 7 Tropohumult-B_1
	unlimed	limed	limed	unlimed	limed	limed	limed
	ppm Fe(111)						
1	2.9	1.8	0.49	1.66	1.2	5.3	1.2
2	4.5	19.6	0.35	0.44	17.3	7.3	1.2
3	10.1	38.1	0.49	0.42	31.3	2.8	0.5
4	16.9	35.3	0.34	0.56	39.2	2.8	5.6
5	19.3	96.4	0.68	1.25	69.6	1.8	2.8
6	13.3	37.8	1.05	1.36	44.8	5.6	1.8
7	14.1	44.5	0.35	1.48	60.4	14.0	4.5
8	14.1	33.9	1.80	1.60	45.6	7.0	0.7

TABLE 28. The concentration of Fe(111) in successive aqueous extracts of unlimed and limed soils (Nos. 8, 10, 11, and 12)

Extractions Number	Soil No. 8 Haplustox-A_p		Soil No. 10 Haplustox-A_p		Soil No. 11 Haplustox-B_1		Soil No. 12 Fragiochrept-A_p
	unlimed	limed	unlimed	limed	unlimed	limed	limed
	ppm Fe(111)						
1	0.36	2.8	3.02	1.8	0.72	1.0	2.1
2	0.29	8.9	0.56	20.0	0.27	14.0	2.8
3	0.13	53.0	0.70	49.0	0.44	26.0	5.6
4	0.21	65.0	0.84	65.0	0.44	34.0	3.8
5	0.14	135.0	0.74	94.0	0.20	42.0	9.3
6	0.13	89.0	1.11	88.0	0.28	42.0	4.5
7	0.22	119.0	0.74	98.0	0.00	68.0	4.5
8	0.35	80.0	0.82	78.0	0.00	44.0	3.8

surface soils and subsoils by washing the soils 3 times with water in the high speed centrifuge, using 2.5 g of soil and 35 ml of water. Then, the soils were dispersed with 70 ml of water in a 90-ml centrifuge tube. The amount of clay < 2μ in the suspension was determined by the pipet method (10). The results are given in Table 29.

As shown in Table 29, highly-weathered soils can be indeed readily dispersed by liming the acid soils and this could explain the observed deterioration of the structure of tropical soils upon liming (47). But the mobilization of Fe(111) cannot be attributed to dispersion of the clay fraction because it will be noted that the Acrohumox-B_2 (Soil No. 2) which showed the greatest dispersion of the < 2μ clay fraction virtually contained no Fe(111) in the aqueous extracts (cf. Table 27). Indeed very little Fe(111) was found in the aqueous extracts of any of the limed subsoils. It is interesting to note that very little Fe(111) was mobilized by liming the surface soil from New York (Fragiochrept-A_p, Soil No. 12). The concentrations of Fe(111) in the extracts of the unlimed Acrohumox-B_2 (Soil No. 2), Haplorthox-B_1 (Soil No. 6), Tropohumult-B_1 (Soil No. 7), and Fragiochrept-A_p (Soil No. 12) are not reported because they were found to be extremely low.

It may be concluded from the results of Acrohumox-A_p (Soil No. 1) that Fe (111) can be mobilized in the presence of only moderate amounts of adsorbed Ca^{++}. Considerable amounts of Fe(111) were mobilized in the aqueous extracts of this soil which had been limed moderately in the past and which contained only 1.9 meq of Ca^{++} per 100 g. On the other hand, the Ca^{++}-saturated surface soil from New York (Fragiochrept-A_p, Soil No. 12) did not release significant amounts of Fe(111) upon successive extraction with water. This mobilization of Fe(111) in the surface layer

TABLE 29. Dispersion of limed and unlimed soils after washing the soils with water

Soil No.	Soil Name*	Amount of clay < 2μ found in	
		unlimed soil	limed soil
		%	
1	Acrohumox-A_p	11.0	18.8
2	Acrohumox-B_2	1.2	11.0
10	Haplustox-A_p	8.2	14.2
11	Haplustox-B_1	13.1	15.8

* For soil description see Section II of the text

upon liming is obviously a peculiar phenomenon shown only by the highly-weathered soils of the tropics.

Conceivably this release of Fe(111) from the limed surface soils of the humid tropics may be due to desorption of some organo-Fe(111) complex from the surface of iron oxides and/or kaolinite upon liming as a result of the increase of the negative charge on the organo-Fe(111) surface complex. This interesting problem, however, was not pursued any further inasmuch as it had little relevance to the main objective of this investigation. It should be of interest, however, in any study relating to soil genesis and morphology of highly-weathered soils.

VII. SUMMARY

The object of this investigation was to evaluate two commonly used laboratory methods for determining the "lime-requirement" of highly weathered acid soils of the humid tropics and to study the fate of $CaCO_3$ applied to these soils. The standard of comparison for the lime-requirement was the maximum amount of $CaCO_3$ decomposed by the soils upon equilibration of the soils with an excess of $CaCO_3$ and the partial pressure of CO_2 of the air. The two common laboratory methods for determining the lime-requirement of soils examined in the present study were the salt (1N KCl) extractable acidity and the exchange acidity as determined by the $BaCl_2$-triethanolamine (TEA) method. The soil samples used in this study comprised the A_p and B_2 horizons of highly-weathered soils from seven different locations in Brazil, Colombia, and Puerto Rico, known to represent extensive areas of potentially productive agricultural soils.

The cumulative amounts of Al^{3+} removed upon successive extractions of the soils with 1N KCl were found to be greater than those removed by exhaustive successive extractions with 0.1N KCl. This was, in part, attributed to the release of H^+ owing to the increase of the surface negative charge in the presence of the higher electrolyte concentration at pH values above the zero point of charge. The released H^+, upon reaction with $Al(OH)_3$, produced an equivalent amount of salt extractable Al^{3+}. The amount of Al^{3+} removed even upon exhaustive extraction by 1N KCl, however, greatly underestimated the amount of $CaCO_3$ that was found to react with the soils. On the other hand, the exchange acidity as determined by the $BaCl_2$-TEA method agreed closely with the maximum amount of

$CaCO_3$ that was found to react with the soils especially in those that were known to contain aluminous chlorite.

In order to study the loss of the adsorbed Ca^{++} by leaching, the soils were first saturated with Ca^{++} by applying appropriate amounts of $CaCO_3$. The soils were then extracted successively 8 times with water, and the concentration of Ca^{++} in the aqueous extracts was determined by atomic absorption. The cumulative amounts of Ca^{++} removed after 8 successive extractions with water varied widely with different soils primarily due to the differences in the amounts of Ca^{++} removed in the first three extractions, after which the rate of removal was essentially the same for all soils. Contrary to expectation, the cumulative amounts of Ca^{++} removed from the highly-weathered soils of the humid tropics were found to be smaller than that removed from Mardin silt loam, a New York soil, indicating that the pH-dependent charge was just as effective as the permanent charge of the soils of the temperate regions in adsorbing and preventing the loss of Ca^{++} by leaching. The concentration of Ca^{++} in the aqueous extract (Ca^{++}) followed the relation:

$$(Ca^{++}) = K \frac{\Theta}{1-\Theta}$$

in which Θ is the degree of Ca^{++} saturation of the soil and K is the hydrolysis constant. On the other hand, the degree of hydrolysis of Ca^{++}-saturated soil, x, varied with the volume of dilution, v, according to the following equation:

$$\frac{x}{\sqrt{1-x}} = \sqrt{K}\,\sqrt{v}$$

in which K is the hydrolysis constant. In general, the two methods yielded essentially the same value for the hydrolysis constant.

The difference between the amounts of Ca^{++} recovered by extraction of the soils with 1N HCl from the limed and the corresponding unlimed soil, following exhaustive extraction of the soils with water and 1N KCl, was taken as the amount of Ca^{++} "fixed" by the limed soils. In most instances, this difference was insignificantly small, indicating little, if any, fixation of Ca^{++} into nonexchangeable forms by soils of the humid tropics.

As a side observation, the color of the aqueous extracts upon successive extraction of the fully Ca^{++}-saturated soils with water became increasingly more yellow due to the presence of Fe(111), especially in the limed surface soils indicating mobilization of Fe(111) in the limed soils in the presence of organic matter after complete removal of the soluble salts present in the soil. The exact mechanism of this mobilization of Fe(111) in limed surface soils is not known, but it is suggested that it may be due to release of some organo-Fe(111) complex adsorbed on surfaces of iron oxides and/or kaolinite as a result of the increase of the negative charge on the organo-Fe(111) surface complex at the higher pH values of the limed soils.

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