

EXCHANGEABLE HYDROGEN IN SOILS AND  
ITS RELATION TO LIME REQUIREMENT

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By

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## Introduction

The harmful effect of soil acidity on plant development was recognized in the United States by Wheeler (66) in 1895. He observed that certain crops are benefited by liming, while others are not, and pointed out the need of a satisfactory method for determining the relative acidity of soils. A majority of the earlier investigators assumed that soil acidity was confined to muck soils, peat, or very wet lands and the reason for the failure of certain crops on upland acid soils was attributed to winter-killing, poor germination of seeds, drought, excessive moisture, or attacks by insects or fungi. A divergence of opinion still exists concerning the cause of the toxic effect of acid soils on the growth of certain species of plants.

Soil acidity is associated with soils occurring in humid regions of the temperate zone. The practice of liming acid soil has become conventional since early investigators showed a positive need for it, and is now recognized as essential by those attempting to develop a more permanent system of agriculture. Along with an increased use of limestone as a soil amendment there has developed a need for accurate methods of determining the lime requirements of soils. The main object of liming, as now conceived, is to attempt to make the reaction of the soil optimum for the specific crop. Soil neutrality is not always essential. The regulation of soil acidity rather than its complete elimination is the important objective. Since liming may exert an optimum effect on plant development by the elimination of harmful constituents in the soil, or by improving conditions for the growth of desirable micro-organisms, it is important to know more about the

lime requirement of a soil as it may be affected by acidity present,  
and the relation between exchangeable hydrogen, total exchangeable bases,  
and the pH value.

### Review of Literature

Problems connected with soil acidity and related phenomena constitute an important phase of soil science since the area of agricultural land affected by acid conditions is quite extensive.

Some early investigators (20) supported the adsorption theory as an explanation of soil acidity. They assumed that selective adsorption by the soil of the cations from a neutral salt solution would leave the anions free to form acids. Other investigators (49) believed the adsorption theory because they found decreases in the pH value with decreased soil-water ratios, and because the relation between H-ion concentration and the soil water ratio seemed to follow an adsorption curve.

The mineral acid theory of soil acidity, rather than selective adsorption, has received the greatest support in the last few years as a result of the work of Truog, Bradfield, Puri, Sharp and Hoagland, and Gillespie. Some investigators (7, 58) believed that actual acids are involved in soil acidity. They held that in acid mineral soils there are present not only the so-called humic acids, which appear to be derived largely from lignin (30,35) but also insoluble mineral acids derived from the weathering of various silicates, the bases being removed by leaching. Truog (59) attributed soil acidity to an aluminosilicic acid which was isolated from soils. When the compound exists as the free acid, or as the sodium salt, it disperses readily and goes into a colloidal solution when in contact with water. Under either condition soil particles may be carried downward by gravitational water to form a B layer in the soil profile. Miller (34), working with



charcoal, found that anions formed by the hydrolysis of soluble salts are adsorbed more than cations. This work, together with Bradfield (8), who observed that acetic acid shows the same adsorption curve as that between H-ion concentration and the soil water ratio, tends to disprove the adsorption theory of soil acidity. Bradfield (7) also pointed out a close analogy between soil acidoids and true acids based on the general similarity of titration curves of weak acids, in which he used clay suspensions that were gradually added to alkali, and in later studies (9) electrolyzed clays were used. Recently Anderson and Byers (3) have published data on the neutralization curves of soil colloids representative of the great soil groups occurring in the United States. Puri and Asghar (47) and Puri and Puri (48) have shown that titration curves of soil acidoids closely resemble those of weak dibasic acids.

Several forms of soil acidity are now recognized. According to Kappen (25) there are three kinds: (a) free or active, (b) exchange, and (c) hydrolytic acidity. Exchange acidity, also known as potential acidity or exchangeable hydrogen, is defined by Puri and Uppal (49) as that acidity produced when a neutral salt is shaken with an acid soil. The production of a free acid on the addition of a salt to an acid soil is governed by the distribution of a base between two acids of unequal strength, i.e. the stronger acid combining with the larger proportion of the base. When the salt of a weak acid and a strong base, like calcium acetate (24) is added to an acid soil, the amount of titrable acidity produced is much larger than in the case of a neutral salt (22) and is known as hydrolytic acidity.

The more exact nature of soil acidity can best be explained by

studying the phenomenon of base exchange. Not all basic elements in soil are associated with the exchange complex as Kelley and Brown (26) show that soils may contain bases in four forms: (a) replaceable, (b) water-soluble such as chloride, nitrate, and sulphate, (c) carbonates, and (d) crystalline silicates and phosphates such as orthoclase, plagioclase, biotite, hornblende, apatite, and many other distinguishable silicates. The replaceable bases in soils are readily displaced by hydrogen ions, the replacing activity of these ions, when combined with a strong anion, being much greater than that of other cations under similar conditions.

The fact that base exchange compounds are universally distributed in soils and are of colloidal nature led Truog and Chueka (61) to suggest that the inorganic exchange material is formed in the weathering of silicate minerals, possibly the feldspars or micas, and the organic exchange material is formed from plant residues.

The work of several investigators (27, 42, 39) prove conclusively that the nature of base exchange reactions in the soil whereby one cation is exchanged for another is a true chemical reaction associated with soil colloids, and that the difference between the chemical behavior of materials in the colloidal state and those in true solution is one of degree only and not of kind. The colloidal material may take part in reactions governed by the stoichiometric laws for metathetical reactions and may be regarded as displaying ionization phenomena in a manner quite analogous to that of dissolved substances. Conner (14) observed that acid soils which have a high colloidal content are capable of producing good crops even though several tons of lime per acre are required to bring them to neutrality, and that soils high in colloids have a high

total exchange capacity. In a similar type of study Pierre (43) noted that there is a positive correlation between the total exchange capacity of the soils and their crop producing power. He explains this as why fertile soils are able to withstand greater degrees of acidity than poorer soils, and the failure to get response from liming on soils that are quite acid may be due to the fact that such soils have a high degree of saturation. In a study of a Clermont silt loam profile, Schollenberger (51) has shown an excellent correlation between percentage of total base absorbent capacity satisfied by neutral salt-forming bases and soil reaction. This soil represents an extreme example of weathering in situ of a very old (Illinoian glaciation) calcareous till, the highly eluviated surface and subsurface horizons being acid and practically all carbonates leached out to the depth of eight or nine feet. The relation is shown graphically in figure 1, degree of saturation being plotted against pH determined on 1:1 suspensions of dried soil and water, after three days standing for equilibrium to become established. The points are numbered according to order in sampling, 1 being surface soil and 10 the parent material, 108-120 inches, with over 25 per cent carbonate. The figure shows that the first two horizons are less acid and more saturated than the third, and that beginning with the fourth horizon acidity decreases and degree of saturation increases as the parent material is approached. From the first to the third horizon the points are on a straight line, but points corresponding to lower horizons are all near a smooth curve with slope different from that of the line. The difference in slopes may indicate that there is a difference between base absorbents at the surface and below, perhaps due to the presence of organic matter.

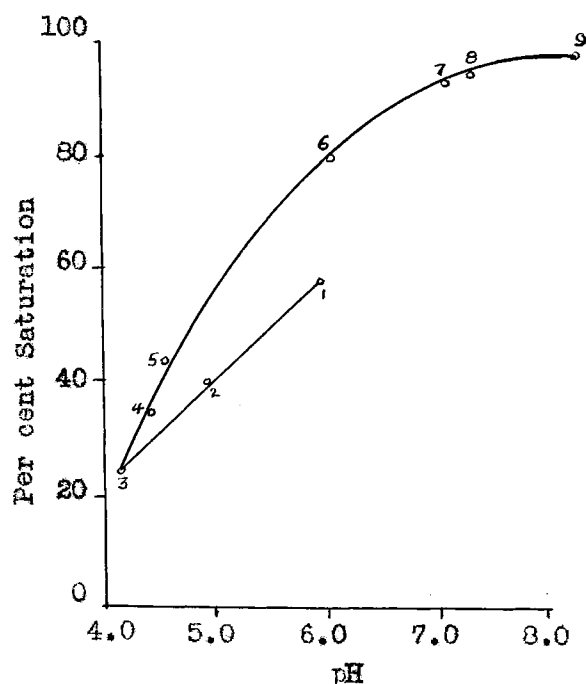


Fig. 1. The relation of degree of saturation to pH. The numbers refer to the various horizons.

It is well known that acids have a quantity factor as well as an intensity factor. The former is determined by the total hydrogen capable of being replaced by a base; and the latter by the number of hydrogen ions present, i.e., the dissociation or activity coefficient of the acid. Thus, to get at the total soil acidity, both the quantity and intensity factors are important.

The measurement of the intensity of acidity in a soil is obtained by a determination of the hydrogen ion concentration by electrometric or colorimetric methods. The hydrogen ion concentration of the soil may be determined electrometrically by the use of the quinhydrone, hydrogen, or glass electrode methods, the values being expressed in units of pH. The pH of the soil usually ranges from 3.5 to 8.5, but the extremes are

not suited for cultivatable crops. The pH value, however, does not give the total acidity; it only measures the intensity of the hydrogen ion, i.e.,

0.1 molar Hydrochloric acid    pH = 1.03

0.1 molar Acetic acid            pH = 2.85

The total titrable acidity of the two acids are the same (18).

Along with a number of methods (13, 17, 19, 22, 24, 56, 60, 61, 63) that were designed for the practical measurement of soil acidity, several methods have been used to determine the total quantity of exchangeable hydrogen in a soil. One method is to replace the hydrogen with a neutral solution of normal barium acetate, and then titrate the acetic acid in the filtrate. Another method is essentially indirect, namely, to determine the total cation-exchange capacity of a soil using a neutral solution of normal ammonium acetate, the capacity being determined by the  $\text{NH}_4$  absorbed in the process, then by analyzing the acetate extract whereby the absorbed bases are determined. The replaceable hydrogen can be calculated by difference; that is, by subtracting the sum of the bases present from the exchange capacity, all quantities being expressed in chemical equivalents. Still another method is that of titration curves. Various increments of a standard solution of calcium hydroxide corresponding to known amounts of calcium carbonate are added to a soil and the pH values are measured with the glass electrode. The data thus obtained can be plotted in the form of a titration curve and the lime requirement of a soil at any desired pH value may be estimated from the graph.

Morgan (37), and others (36), believed that lime requirements could be estimated with reasonable accuracy for all practical purposes

from determination of pH values, using appropriate factors depending upon the texture and organic content of the soil, and the soil reaction preferences of the crop.

A similar type of correlation between pH values and lime requirement was attempted by Arrhenius (4), reported by Morgan (36), who gives the following table as the amount of hydrated lime in kilograms per hectare (approximately the same as pounds per acre) to change the soil reaction one pH unit in the alkaline direction.

Table 1 - Organic matter and texture lime requirement table

Soils	Poor in humus	Average humus	Rich in humus
Sandy	500	1000	1500-3000
Fine sandy	500-1000	1000-1500	2000-3000
Light clay	1500	2500	3500
Average clay	2500	3500	4000
Heavy clay	3000	4000	4500
Humus soils with 15 per cent organic matter - 4000-8000			

The work of Jones (24), Pierre and Worley (45), Crowther (15), Hissink (21), and Christensen and Jensen (12), may also be quoted in support of the "liming factor" theory, which indicates that lime requirement as obtained in a laboratory procedure must be multiplied by a factor to get field lime requirement. Pierre and Worley (45) designated the relation between the amounts of base required in a laboratory procedure and the amounts of lime required in the field to bring soils to similar pH values as the "liming factor" and showed that this factor was 1.5 for 77 soils of different texture and acidity. They believed

the reason why soils to which have been added amounts of lime equivalent to their content of exchangeable hydrogen, do not reach a pH of 7.0 but only of about 6.5, to be because the lime reacts with compounds other than the exchange complex in the soil.

It is necessary to have a favorable soil reaction for several reasons. First, because the susceptibility of different plants to hydrogen ion toxicity varies. Many crops grow poorly if the soil reactions fall below a critical point whereas they thrive above it within their growth range. Slipher (55) states minima soil reactions for several forage crops, expressed as pH, as follows:

Alfalfa	6.5	Soybeans	5.2
Red clover	5.7	Redtop	4.5
Alsike clover	5.5		

McCall (28) has reviewed the work of several investigators showing that many crop plants grow best in solution and sand culture at acidities of pH 5 and above pH 6. He concludes that a soil does not always need to be limed to neutrality since many crops make satisfactory growth on acid soils. Numerous workers have studied the effects of the reaction of the medium upon plant development. A summary of these observations is tabulated in the following table (33).

Table 2 - Summary of optimum soil reactions for agricultural crops

Investigator	Plants	Optimum pH
Wherry (1924)	Alfalfa, barley, and orchard grass	8.0
	Alsike clover and beets	7.5
	Radish, rutabaga and wheat	7.0
	Lupine, peas and red clover	6.0
	Oats	5.0
	Flax and turnips	4.0

(Table 2 - continued)

Investigator	Plants	Optimum pH
Powers (1927)	Alfalfa and alsike clover	5.6-6.0
	Hungarian vetch	5.3
Arrhenius (1929)	Rye, oats, potatoes, and timothy	5.0
	Beets, barley and alfalfa	7.0-7.2
Katchioni and Walther (1930)	Buckwheat	5.0-6.5
Wilson (1930)	Onions	6.0-7.0
Emmert (1931)	Tomatoes	8.4
	Lettuce	7.5
Wessels (1932)	Cauliflower	5.5-6.6
	Potatoes	4.8-5.4
Olsen (1923)	Potatoes	5.0-5.5
	Barley	6.4
	Oats	5.3-5.8
	Wheat	5.2-7.0
	Rye	6.2
	Grasses	7.0
	Lucerne	6.0

An acid condition is unfavorable for the optimum development of a desirable physical and biological condition in a soil. Magistad (32) has shown the solubility of aluminum to be lowest between pH 5 and 7, and that below pH 5 crops suffer from aluminum and hydrogen ion toxicity, whereas above pH 5 most crops do not suffer injury from either cause. Abbott, Conner, and Smalley (1), Burgess (10), Pierre (43), and Eisenmeyer (16), have also shown that aluminum may become toxic to plants in strongly acid soils.

Injury from certain plant diseases can be reduced by regulating the soil reaction. Diseases like potato scab and root rot of tobacco and cotton (57) are more serious when the pH rises above 5.3 and 5.9



respectively, while finger-and-toe disease and fusarium wilt of tomatoes develop only in acid soils.

A favorable soil reaction is further important in that the availability of all the essential elements obtained by plants from the soil, (23, 31), the activity of many soil microorganisms (11), and the physical properties of the soil (5, 29), are affected in one way or another. Numerous workers (2, 21, 38, 46) have shown that fertilizers may exert an acid or alkaline residual effect upon the soil, and that continued use of acid fertilizers should be paralleled by an equivalent amount of neutralizing materials. By examining the exchangeable bases in the soil, an estimate of the effect of the addition of a mineral fertilizer and the amount of neutralizing material needed may be obtained.

## EXPERIMENTAL DATA

The relation between exchangeable hydrogen, total exchangeable bases, and the pH value of twenty-one soils from different regions was studied. The location from which each soil sample was secured, the soil type, and the depth at which the sample was taken is given in table 3. Different soil types were used so as to include a wide range of soil characteristics on organic matter content, pH value, texture, exchangeable hydrogen, and total exchangeable bases.

Bowie, Kirvin, and Clarksville are forest soils, Miller and Osage are bottom soils, and the remainder are upland prairie soils. The samples ranged from slight to very strongly acid and from those with relatively high content of organic matter to those relatively low in this substance. Two profile samples from the Bowie and Kirvin series of soils were included so as to present data showing the relation between pH and base saturation in the lower horizons.

The experimental data in table 4 were obtained as follows: The per cent organic matter was determined by the chromic acid method (51, 52), pH with the glass electrode, using a 1:2 soil-water ratio, and the base exchange capacity and total exchangeable bases using a variation of the method as proposed by Kelley and Brown (26). Table 4 shows that soils may have a low pH value, yet have a high degree of base saturation. This is especially noticeable with surface samples of Vanoss silt loam and Bowie fine sandy loam. The Clarksville loam, a forest soil, is the only sample showing a comparatively low amount of exchangeable bases and also a low per cent of base saturation.

Table 3 - Description of soils used

Sample No.	Location	Soil Type	Depth of Sample
1	Garber, Okla.	Kirkland silt loam	0-6"
2	Stillwater, Okla.	Kirkland very fine sandy loam	0-6
3	Inola, Okla.	Parsons silt loam	0-6
4	Vinita, Okla. (Holman)	Parsons silt loam	0-6
5	Dustin, Okla.	Parsons silt loam	0-6
6	Vinita, Okla.	Parsons silt loam	0-6
7	Blackwell, Okla.	Vanoss silt loam	0-6
8	Garber, Okla.	Tabler silt loam	0-6
9	Sumner, Okla.	Polo loam	0-6
10	Stillwater, Okla.	Miller clay	0-6
11	Stillwater, Okla.	Bates fine sandy loam	0-6
12	Skiatook, Okla.	Osage silty clay	0-6
13	Vernon, Mo.	Clarksville loam	0-6
14	Savoy, Tex.	Bowie fine sandy loam	0-5
15	"	"	5-18
16	"	"	18-34
17	"	"	34-53
18	Savoy, Tex.	Kirvin fine sandy loam	0-3
19	"	"	3-28
20	"	"	28-48
21	"	"	48-74

Table 4 - Comparative data on base exchange studies.

Sample Number	% Organic Matter	pH	Base Exchange Capacity	Total Exchangeable Bases	% Base Saturation
1	2.21	6.0	12.19 **	8.59 **	70
2	1.82	5.4	13.46	9.36	69
3	1.75	5.4	9.49	6.19*	65
4	1.87	5.0	9.9	7.1	71
5	1.06	4.6	8.82	6.32*	71
6	1.85	4.5	12.05	8.35*	70
7	2.98	4.7	15.10	10.65*	70
8	1.32	5.5	10.62	7.82	73
9	2.34	5.5	11.29	7.79*	68
10	1.60	6.0	12.04	9.14	76
11	1.24	5.3	12.54	8.74	70
12	1.14	5.3	11.51	7.81	68
13	1.68	5.5	7.63	4.03*	53
14	2.11	5.7	18.05	15.55	85
15	1.06	6.2	17.7	15.60	88
16	0.53	6.4	19.42	17.42	89
17	0.31	6.6	21.16	19.16	90
18	1.22	5.1	12.36	9.26	75
19	0.89	4.7	11.26	9.26	81
20	0.70	4.5	8.43	5.43	63
21	0.62	4.0	1.18	2.45	--

\*Iron oxide was present in the exchange material of these samples.

\*\*m. e. per 100 grams of soil.

Base exchange studies have brought several definitions into soil literature. Kelley and Brown (26) state that "when the total content of the several bases present in the replaceable form has been substituted by some other base, or when all of the replaceable bases except one have been replaced by a salt of that base, the soil is said to be saturated with respect to that base." In replacement reactions with ammonium salts, the amount of ammonia absorbed by the soil is a measure of the total cations replaced and is known as the base-exchange capacity of a soil. The ratio between the exchangeable bases, exclusive of acid hydrogen, and the base-exchange capacity of a soil is known as the degree of base saturation of a soil.

The total exchangeable bases and the base exchange capacity was not correlated with the crop producing power of the soils in this study except in a general way. It may be noted, however, that the Kirkland and Vanoss soils are recognized as fairly productive and have a relatively higher base exchange capacity than less productive soils such as Parsons and Clarksville.

Lime requirement of the soils studied has been determined by treatment with barium acetate or  $\text{Ca}(\text{OH})_2$ . The  $\text{Ca}(\text{OH})_2$  titration method, which was a modification of the Vietch procedure (64), also known as a buffer method, gives both the quantity and intensity factors of soil acidity and seems desirable for several reasons. Since the result of many investigations shows that the optimum pH for the development of most crop plants is approximately 6.0 to 6.5, it would seem desirable to bring the soil reaction to these values, and theoretically this could be done by obtaining the lime requirement by this method in the laboratory and then using a "liming factor" to correct for any coarse material

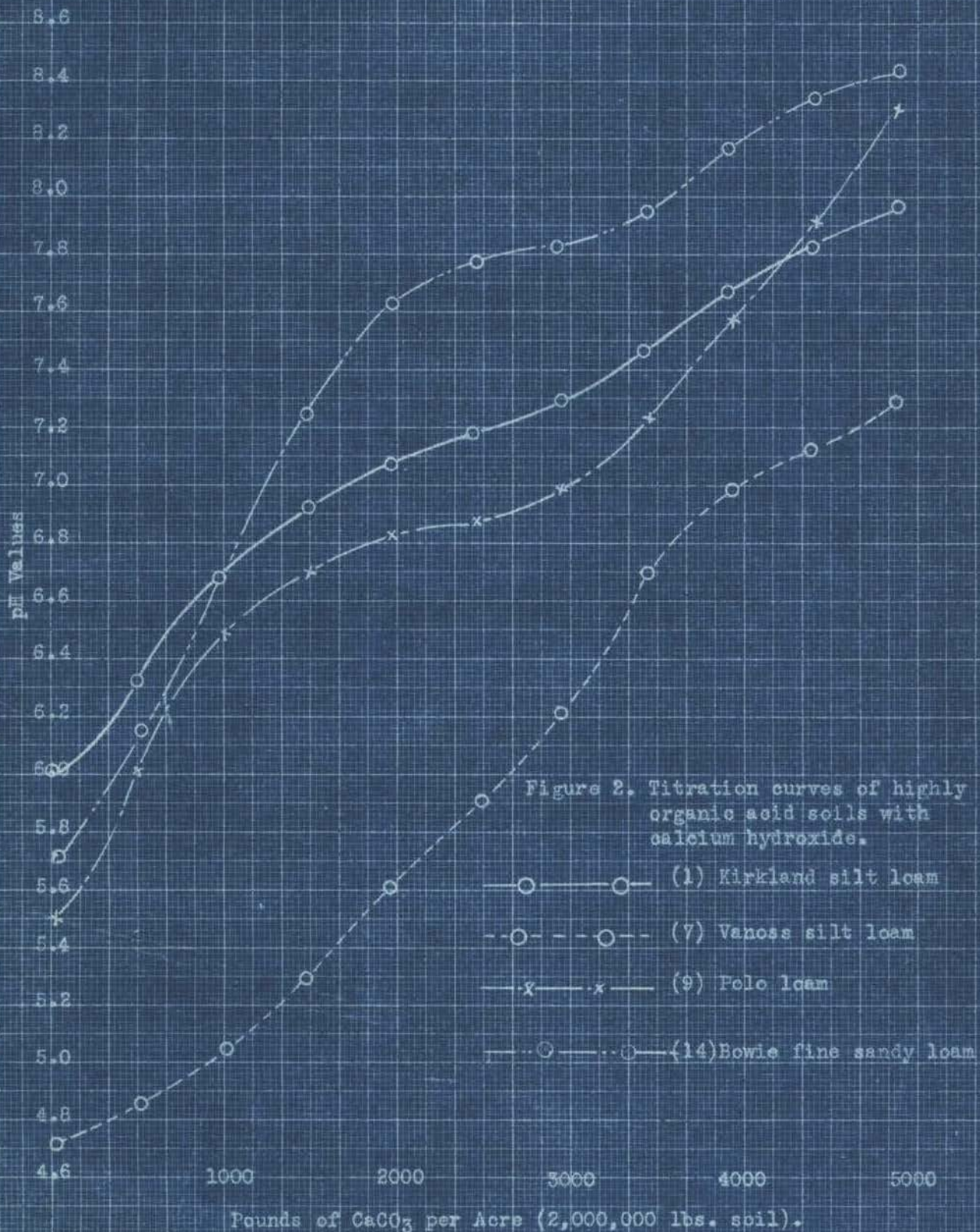
in the limestone applied.

Table 5 - Removal of exchangeable hydrogen from soil by successive extractions with neutral normal barium acetate solution.

Sample	First Extraction	Second Extraction	Third Extraction
Kirkland (2)	2.7*	1.0*	0
Parsons (3)	3.5	0.1	0
Parsons (4)	2.4	0.1	0
Parsons (5)	2.0	0.1	0
Parsons (6)	3.7	0.3	0
Vanoss (7)	4.0	0.4	0
Tabler (8)	2.25	0.65	0
Polo (9)	3.0	0.9	0
Clarksville	3.3	0.4	0

\*Exchangeable hydrogen expressed as m.e. per 100 grams of soil. All other samples gave no exchange hydrogen in the second extraction.

It may be noted from the titration curves of several soil suspensions (figures 2, 3, and 4) that the buffer action varies at different points on the curve. This may be due to varying amounts of organic matter and the character of the clay minerals in the soil. Hissink and van der Spek's (21a) studies reveal that the titration curves of soil suspensions show buffer action between pH 6.0 and 8.0. Figure 2 is a group of soils all containing more than 2% organic matter and presenting buffered and more or less gradual curves. Figure 3 represents soils of relatively low organic matter and which show less buffering action and steeper curves, thus less lime requirement.

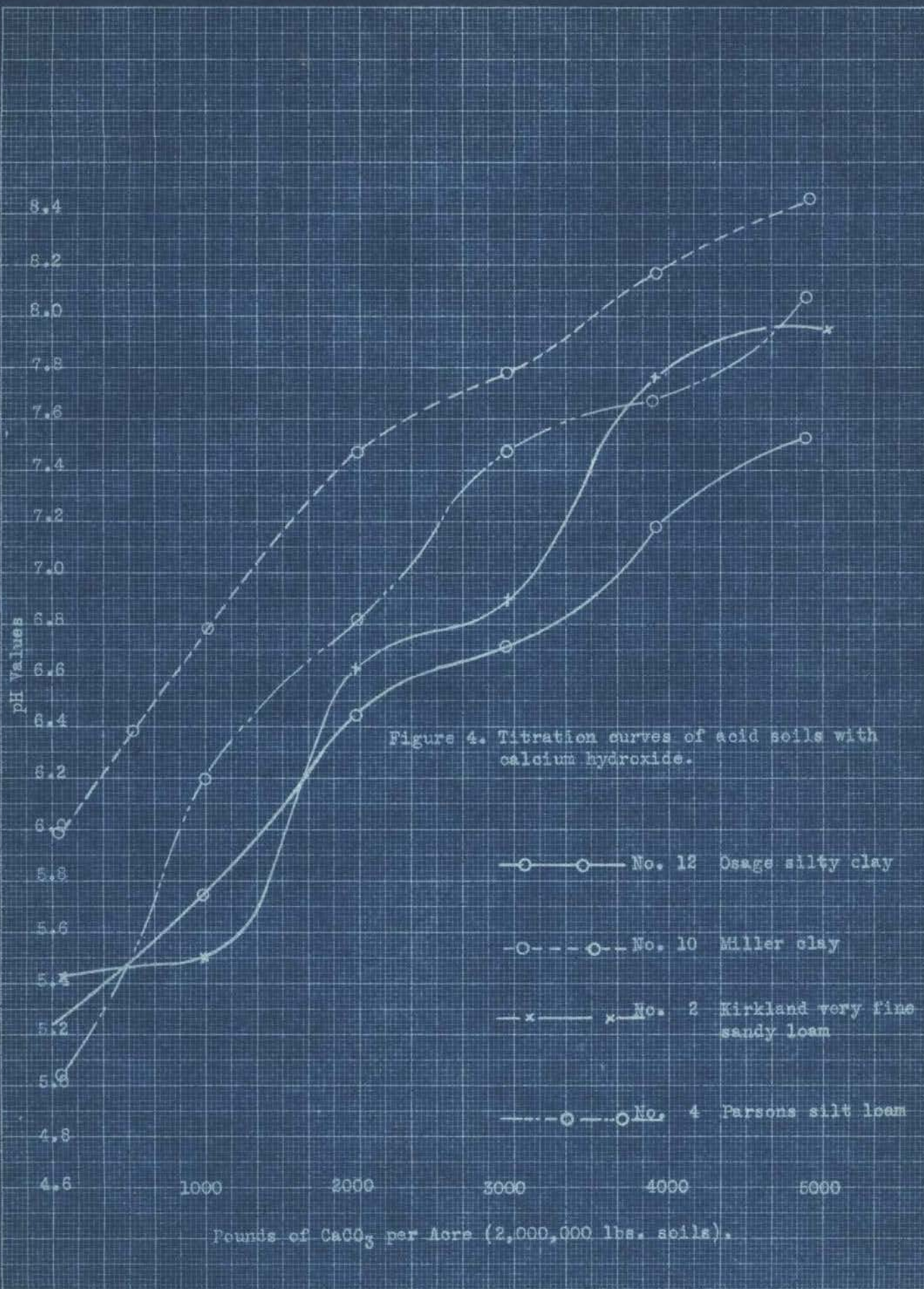


Figures 2, 3, and 4 present two general types of curves. Soil samples 4, 7, 10, 14, and 18 all show low buffer capacity below pH 7.6 as indicated by the steepness of slope and the absence of a sharp break at any point. All other samples indicate a well buffered condition between pH 6.0 and 7.2, the curves flattening out over this pH range. Kirkland very fine sandy loam (figure 3, sample 2) exhibits a strong buffer capacity at pH 5.4, thus indicating that buffer action is not caused by organic matter alone but is more likely due to variations in the clay minerals that are present in these samples.

These curves show that the soil acids in all soils are not the same. The curves have two general shapes, the flat portions indicating increased buffer capacity which may be due to the neutralization of a specific acid at that point, or one of the hydrogens in a polybasic compound. Baver and Scarseth (6) state that the buffering is a function of the extent of weathering and not parent material, and that well weathered soils have higher buffer capacities.

By studying the curves (figures 2, 3, and 4) obtained by titrating a soil suspension with  $\text{Ca}(\text{OH})_2$ , it may be seen that only a part of the soil acids are represented by these titrations. The fact that some of these samples show an acid condition with a high base saturation, and that the titration curves are not complete because the acidoid is partly saturated as it exists in the soil, it would indicate that titrations of this nature should be carried out on samples free of exchangeable bases as suggested by Puri and Uppal (49). They have shown that  $\text{Ca}(\text{OH})_2$  titration curves are not complete since they start at pH values above the pH of the hydrogen saturated form of the clay minerals present in the soil.





The barium acetate method for exchangeable hydrogen, as used in these studies, is essentially that of Parker's (41) except that extraction of the soil for one hour at 50°C. is used instead of Parker's leaching method over a longer period of time. As shown in table 5, more than one extraction of the same sample was necessary to remove all the exchangeable hydrogen, or until the last filtrate was equivalent to a blank sample. This study indicated that a single extraction multiplied by the factor 1.12 was equivalent to all the exchangeable hydrogen that could be extracted by this method.

The exchangeable hydrogen obtained in extracts has been found by various investigators (28, 46) to be closely correlated with the pH of the solution in contact with the soil. As shown in table 6 the barium acetate method for lime requirement gives only one value, namely, lime requirement of a soil at a pH of 7.0. Determination of the total amount of exchangeable hydrogen of a soil, therefore, cannot serve as a measure of plant response to liming, because most plants can make optimum growth on soils that are not completely neutralized. As compared to the  $\text{Ca}(\text{OH})_2$  method which gives the lime requirement at any pH value, the barium acetate procedure is inferior when only partial neutralization of the soil is necessary for acid tolerant crops.

Table 6 also indicates that the barium acetate procedure usually produces a higher lime requirement value than the  $\text{Ca}(\text{OH})_2$  titration method to pH 7.0, but is equivalent at about 7.5.

Table 6 - Experimental data showing comparison of lime requirement and exchangeable hydrogen by two methods.

Sample No.	Exchangeable Hydrogen Ba(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	Exchangeable Hydrogen by Difference Method	Lime pH 7.0 Requirement Ba(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	Lime Requirement pH 7.6 Ca(OH) <sub>2</sub>	Lime Requirement pH 7.0 Ca(OH) <sub>2</sub>	pH Value at which Ca(OH) <sub>2</sub> and Ba(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> are Equivalent
1	3.5**	3.7**	3500†	3700†	1800†	7.5
2	3.7	4.1	3700	3600	3100	7.6
3	3.6	3.3	3600	5000	4000	6.8
4	2.5	2.8	2500	3100	2260	7.2
5	2.1	2.5	2100	3500	2900	6.3
6	4.0	3.7	4000	6000	5500	6.7
7	5.3	4.4	5300	5700	4000	7.4
8	2.9	2.8	2900	2700	2000	7.7
9	3.9	3.5	3900	4000	3000	7.55
10	2.3	2.9	2300	2300	1300	7.6
11	3.8	3.8	3800	3700	2400	7.7
12	5.0	3.7	5000	5250	3650	7.55
13	3.7	3.6	3700	3500	2350	7.7
14	2.0	2.5	2000	1900	1300	7.65
15	1.9	2.1	*	*	*	*
16	1.5	2.0	*	*	*	*
17	1.5	2.0	*	*	*	*
18	2.8	3.1	2800	2700	1800	7.7
19	3.5	3.0	*	*	*	*
20	3.8	3.0	*	*	*	*
21	3.8	---	*	*	*	*

\*\* m.e. per 100 grams soil

† CaCO<sub>3</sub> per acre (2,000,000 lbs. soil)

\* Not determined

The values presented in tables 4 and 6 indicate a general relationship between the degree of saturation of the base exchange material, lime requirement, and response to liming. Generally, the higher the degree of saturation, the more feeble will be the response from liming. Highly saturated base exchange material can neutralize the soil acids, but poorly saturated base exchange material may itself become acid by the action of excess soil acids. Pierre (43) and Scarseth's (44) studies give reason to believe that the percentage base saturation of soils and probably the proportion of the various bases present in the exchange complex and in the soil solution, are primary factors which directly influence plant growth on acid soils. They found that soils of the same reaction may vary considerably in their percentage base saturation and gave the following factors as influencing this: Presence of soluble acids, strength of soil acids, nature of the bases in the exchange complex, nature of the exchange complex, as might be revealed by (a) organic matter content of the soil, (b) silica-sesquioxide ratio of soil colloid, (c) total exchange capacity of soil colloid.

The fact that exchange capacity increased with liming was attributed by some investigators (54, 65) to a slight breakdown or destruction of the minerals present and to a build up of the exchange complex in the alkaline medium, while Naftel (40) said that increases in organic matter resulting from a greater amount of roots caused the increase in exchange capacity. The presence of organic matter is important in the soil exchange complex when it is not saturated with bases because it affects the lime requirement of soils.

### Methods of Analysis

#### 1. Determination of replaceable bases (26).

Add 100 ml of neutral normal ammonium acetate to 10 gram sample of soil, shake 2 to 3 seconds, and let stand one hour or longer, agitating every 15 minutes. Filter on Buchner filter and leach soil with the ammonium acetate solution to total value of 250 ml. Save residue for determination of exchange capacity. Evaporate filtrate, ignite organic matter, and dissolve residue with excess of 0.2 normal HCl. Back titrate with 0.05 normal NaOH, using phenolphthalein as an indicator.

#### 2. Exchange Capacity (26).

Wash soil residue from determination of replaceable bases with ethanol in portions of 15 ml to total of 250 ml. Transfer to distillation flask, add excess MgO, and determine the total  $\text{NH}_4$ .

Replaceable hydrogen was obtained by subtracting the replaceable bases from the absorbed  $\text{NH}_4$ .

#### 3. Exchangeable hydrogen by barium acetate extraction (41).

Add 250 ml of neutral normal barium acetate to 10 gram sample of soil in Erlenmeyer flask, cork and set in constant temperature water bath of 50°C. for one hour. Filter on suction using a large Buchner funnel. Titrate 200 cc. of filtrate with 0.1 normal NaOH using phenolphthalein as an indicator. Successive extractions are carried out until the last filtrate is equivalent to a blank sample.

Lime requirement was obtained by this method by calculation: 1 cc. of N/10 NaOH = 1,000 lbs. of  $\text{CaCO}_3$  per acre of soil (2,000,000 lbs. per acre).

#### 4. Lime requirement by $\text{Ca}(\text{OH})_2$ titration (64).

Weigh out six samples of soil of 5 grams each and then add various

increments of calcium hydroxide corresponding to calcium carbonate applications of 1, 2, 3, 4, and 5 tons respectively. Make a 1:2 soil-water ratio by additions of distilled water, cork samples in test tubes, and set in constant temperature water bath of 50°C. for one hour. Measure the pH value with the glass electrode, and plot the data in the form of a titration curve. Lime requirement to any pH value is read from the graph.

### Summary

The relation between exchangeable hydrogen, total exchangeable bases, and the pH value of twenty-one soils from different regions has been studied in their relation to lime requirement. Experiments were conducted in the laboratory which indicated that these soils showed no relation between pH and degree of base saturation. In general, high base exchange capacities were correlated with productiveness and associated with soils that would not show any response to liming.

The titration of several soil suspensions with  $\text{Ca}(\text{OH})_2$  presented curves which give evidence that there are several kinds of acid in the soil. These titration curves show that organic matter and the type of clay mineral present effect the buffer capacity of a soil at different pH values.

Exchangeable hydrogen was determined by two methods and the values obtained were comparable within 0.8 m. e. per 100 grams of soil.

A comparison of a barium acetate and a  $\text{Ca}(\text{OH})_2$  method for the determination of lime requirement was made. In general, a higher lime requirement was obtained by the barium acetate procedure. An average of fifteen soils showed that the lime requirement by the barium acetate method was equivalent to the lime requirement of the  $\text{Ca}(\text{OH})_2$  titration method, when the end point was read at pH 7.5. The desirable features of a simple  $\text{Ca}(\text{OH})_2$  titration method that will give the lime requirement for any pH was emphasized.

It is shown that all the exchangeable hydrogen in a soil may not be obtained with a single barium acetate extraction. Three-fifths of all the samples studied showed that two extractions of the same soil sample were necessary to remove all the exchangeable hydrogen. A factor was

calculated which indicated that exchangeable hydrogen from a single extraction, multiplied by 1.12, would give actual lime requirement for the soils used in this study.



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