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To the Graduate Council:

I am submitting herewith a thesis written by Wilbur Wayne Frye entitled "Evaluation of Buffer Methods for Determining Lime Requirement of Soils." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agronomy.

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Major Professor

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EVALUATION OF BUFFER METHODS FOR DETERMINING LIME REQUIREMENT OF SOILS

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

---

by

Wilbur Wayne Frye

August 1964

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CHAPTER I

INTRODUCTION

In the humid regions of the world, bases are leached from soils and are replaced by acid forming elements such as hydrogen and aluminum, and the soils become acid in reaction. In order to maintain these soils at a high level of productivity, lime must be added. Although this principle has been known for many years and economical liming materials are available in most of the humid regions, many farmers do not use as much lime as needed.

Crop response to lime is often not so striking as that obtained from some other practices such as the use of commercial fertilizers, irrigation, or hybrid varieties. This may be one reason why some farmers have failed to realize the importance of liming and have failed to adopt proper liming procedures as one of their soil management practices. Another probable reason is that only in relatively recent years have methods been developed which adequately predict lime needs.

Much work has been done during the past half century regarding liming and its effects on plant growth. A considerable amount of progress has also been made in methods of determining lime needs and numerous methods have been developed, but no one method has been widely accepted. Some of the methods were based on sound chemical principles and were, or still are, adequate but others were not based

on sound chemical principles and were, of course, inadequate. Some methods, although quite precise, are not adaptable for soil testing on a mass basis because of the time involved in the procedure. These methods are usually restricted to laboratory research and often serve as standards of comparison for the development and evaluation of more rapid methods. Rapidity is demanded in any method adapted to mass testing. A compromise between speed and accuracy must be accepted, because those methods which are precise are usually long, somewhat tedious operations and those which are rapid are usually lacking in accuracy to varying extents.

Those methods which are precise enough today in predicting or estimating the lime needs for soils may be wholly inadequate in the near future because of increased technology and intensification of practices in other areas of soil management. With an increasing population farmers will have to produce more and more food on less and less land which means that they will have to manage intensively each acre of land so as to maintain it in a highly productive condition over a long period of time. As a result, more precise measurements of lime needs will be required in order that farmers may obtain maximum production and efficiency in land use. More farmers probably will be using the services of the state soil testing laboratories, thus increasing the demand for rapidity in the method or methods used.

The soil properties that affect the lime requirement of soils are varied and complex. Like methods of determining lime needs, these properties have been studied quite intensively, yet the exact nature of

their influence on liming is not fully understood. As a result, continued study of these properties as well as methods of determining the amount of lime needed to cause a desired change in soil reaction is essential. With an awareness of these problems, the objectives of this investigation were to study the various soil properties affecting the lime requirement and to evaluate certain methods of determining the lime requirement of some Tennessee soils to designated pH values.

CHAPTER II

REVIEW OF LITERATURE

I. DEFINITION OF LIME REQUIREMENT

In the early history of the study of lime requirement, no clear meaning of the term had been established. Consequently, each worker had his own concept of lime requirement and conducted his research and interpreted his findings accordingly. This resulted in numerous definitions of the term and considerable controversy over what connotation the term should have.

Some workers have defined lime requirement in terms of the soils only, while others maintained that it must be defined according to the plants that are to be grown on the soils. Veitch (59), recognizing that crops enter into lime requirement, proposed two possible definitions. One, the amount of lime required to neutralize the soil to the point that it shows a faintly alkaline reaction. The other, the amount of lime needed for a soil to grow acid susceptible plants, such as red clover. He concluded that the former "furnishes the best conditions for the economic production of crops" and that "the lime requirement of soils should be based on this hypothesis". MacIntire (25) defined lime requirement as "the soil's maximum capacity to decompose $CaCO_3$ in the laboratory". Pierre and Worley (41) stated that lime requirement meant the amount of lime necessary to neutralize the total acidity of the soil. They pointed out that various methods of determination gave widely

differing values and that lime requirement must be stated as lime requirement by a certain method. Shaw (49) stated that Bradfield and Allison had defined a fully base saturated soil as one which had reached equilibrium with an excess of calcium carbonate at the partial pressure of carbon dioxide of the atmosphere and at a temperature of 25° C. He interpreted this to mean the same as lime requirement for he considered a base saturated soil to be one that was in equilibrium with an excess of calcium carbonate. He pointed out that concepts of Veitch and MacIntire were in agreement with this definition of lime requirement. He also considered the meanings of exchangeable hydrogen, soil acidity, and lime requirement to be essentially the same. He stated that "exchangeable hydrogen has come to be recognized as the cause of soil acidity and lime requirement".

A definite, common meaning of the term lime requirement has not yet been formulated. However, the term does not carry the ambiguity that it once did. In recent years, it has been defined mainly in terms of the pH of the soil, usually as the amount of lime needed to increase the pH of a given soil to a predetermined value, usually 6.5 or 6.8 (44).

With a better understanding of the relationships between soil pH and plant growth that has been accomplished in recent years, it seems likely that an agreement could be reached among investigators in the various fields of crops and soils on an acceptable meaning. Shaw (51) proposed defining lime requirement in terms of percentage base saturation, 60, 80, or 100 per cent as deemed needed. Bray and

DeTurk (4) proposed a method of titration to approximately 80 per cent base saturation rather than neutral. Pierre and Worley (41) proposed that it should mean the amount of lime necessary to raise the soil pH to any chosen pH value. All methods of determining lime requirement are aimed at accomplishing the same end result; a statement of the amount of lime needed to produce a desired reaction in a particular soil for the growth of crops.

II. METHODS OF DETERMINING LIME REQUIREMENT

Peech (37) stated that there is a need for well defined methods of determining the lime requirement of soils in order that the results could be better understood and properly interpreted. Several investigators (25, 39, 51) recognized that the difficult task was the interpretation of tests results into lime requirement values. Peech and Bradfield (39) claimed that this could be remedied somewhat by a better understanding of all the beneficial effects of liming different acid soils.

There has been no common agreement reached by investigators on a laboratory method best suited for determining the lime requirement of soils (44). As a result, many varied methods have been developed. Peech and Bradfield (39) in 1948 stated that the methods varied from simple, qualitative and indirect tests to more direct quantative methods involving the determination of exchangeable hydrogen, exchangeable calcium, degree of calcium saturation, soil reaction, or the amount of readily soluble aluminum, iron, and manganese present in the soil.

Coleman et al. (9) in 1958 indicated that the methods of determining lime requirement used by various states ranged from the use of the pH of a soil-water suspension to the measurement of exchangeable acidity with buffer solutions. Peech and Bradfield (39) pointed out that the best methods were based on sound chemical principles and were capable of determining accurately the amount of lime needed to bring the soil reaction to some arbitrary pH value.

With the realization of the similar connotation of the terms exchangeable acidity, soil acidity, and lime requirement (49); and, since in most cases the reason for determining soil acidity and exchangeable hydrogen was to determine the lime requirement (37, 39); methods designated in the literature as procedures for the determination of either of these are herein considered as methods of determining lime requirement. The various methods reviewed are divided into four groups according to the chemical principles involved in determining the lime requirement. These groups are colorimetric, titration, pH, and buffer methods.

Colorimetric Methods

Colorimetric methods are those which involve the determination of the soil reaction and lime needs by producing color changes in various solutions and materials. These methods are mainly qualitative in nature but some are attempts to measure relative amounts of acidity.

Prior to about 1915, when interest in liming and lime requirement methods became widespread, the methods used mainly for determining the lime status of soils were the effervescence test for free carbonate to determine the presence of adequate lime and the litmus paper test

for soil acidity (18, 58). A variation of the litmus paper test was developed, probably around 1915, and was called the potassium nitrate litmus test (60). It made use of the phenomenon of displacing exchangeable acidity with the cation of a neutral salt solution. The soil was moistened with a potassium nitrate solution rather than with distilled water as in the case of the litmus paper test. Troug (58) criticized litmus paper because it often gave indistinct color changes in acid soils due to poor quality or deterioration of the paper.

Around 1900, Wheeler made extensive use of the ammonium hydroxide test at the Rhode Island Experiment Station. This method made use of the fact that humus is more soluble in an acid soil than in a base saturated soil. The soil was shaken in dilute ammonium hydroxide and the humus produced a yellow or brown color in the solution. The intensity of the color indicated the degree of soil acidity and lime needs (33).

In 1915, Troug (58) developed a test known as the sulfide test which was designed for field use and was supposed to distinguish five degrees of acidity plus neutrality and alkalinity. According to this procedure, the soil was placed in a flask with water, calcium or barium chloride, and zinc sulfide and boiled over an alcohol lamp. If the soil was acid, the calcium or barium displaced the exchangeable acidity forming hydrocholoric acid which in turn reacted with the zinc sulfide releasing hydrogen sulfide gas. The hydrogen sulfide produced blackening of a piece of filter paper which had been impregnated with lead acetate and placed over the mouth of the flask. The intensity of blackening was

compared to a standard chart and was taken as a measure of the degree of acidity. Lime recommendations were made according to the degree of acidity. This test was widely used in the United States.

Comber (13) in 1920 devised a thiocyanate color method for determining soil reaction. The method was based on the theory that iron and aluminum are associated with acid soils and the more acid the soils, the greater the amount of adsorbed iron and aluminum contained in them. An alcohol solution of potassium thiocyanate was added to the soil and the potassium displaced the adsorbed iron which reacted with thiocyanate giving a red color. The greater the amount of iron that reacted, the redder the color became, consequently, the higher the soil acidity and lime needs. Peech (37) criticized this method stating that several factors besides soil pH influenced the solubility of iron in the soil.

Pierre and Worley (41), 1928, proposed a dialysis-colorimetric method in which several samples of the same soil were placed in collodian sacks to obtain clear extracts and the sacks were placed inside flasks. Barium hydroxide was used as the extracting agent and the acidity was determined colorimetrically and plotted as a titration curve. This was one of the early efforts directed toward quantitative acidity determination. Apparently it did not become widely accepted because very little, if any, attention was given to it by subsequent writers.

During the early part of this century from about 1915 to the early 1930's, several qualitative colorimetric methods were developed which employed an indicator or a series of indicator dyes to estimate

the degree of soil acidity. Some of these involved extraction of the acidity prior to the addition of the indicators, while in others, the indicators were added directly to the soil. Among these were the Hellige and Indiana methods (27); Spurway's method sold under the trade name Soiltex (58); the LaMotte-Hester and LaMotte-Morgan (27), both commercial methods; and the modification of Comber's method sold as the Rich-or-Poor Test (58).

These colorimetric tests left much to be desired as methods of determining the lime needs of soils, but they served a very useful purpose during the early years of the development of lime requirement methods.

Titration Methods

Three main types of titration methods for soil acidity and lime requirement have been developed. One involved treating the soil with an excess of an alkaline hydroxide, carbonate, or bicarbonate and determining, in various ways, the excess after reaction with the soil was completed. Another involved displacing the exchangeable acidity and titrating it with a standard base. The third type was direct titration whereby the soil was treated directly with varying quantities of $CaCO_3$ or $Ca(OH)_2$ and the pH of the soil was determined, usually with a glass electrode, after the lime had reacted fully with the soil.

Probably the first attempt to develop a quantitative method for determining soil acidity was made by Tacke in 1897 (58). It was not truly a titration method, however, it was somewhat similar to the

titration methods that were developed later. Calcium carbonate was mixed with the soil and the soil acidity was determined by the amount of carbon dioxide evolved. The method was objectionable because the reaction involved was slow and indefinite (58).

In 1902, Veitch (59) developed a method which consisted of titrating the soil acidity with standard calcium hydroxide solution to the phenolphthalein end point, and was, according to Shaw (52), a modification of Tacke's method. The smallest amount of lime water required to give a slight pink color was taken as the acidity of the soil. The lime requirement was then calculated from this value using a factor. Peech (37) and Peech and Bradfield (39) reported that the method gave high results. This method received considerable attention by various workers as evidenced by the numerous times it has been discussed, evaluated, and other methods compared to it.

The Hopkins method proposed in 1908 used a normal solution of potassium nitrate to displace the exchangeable hydrogen which was then titrated to the phenolphthalein end point using standard sodium hydroxide (33, 37, 58, 60). Peech (37) pointed out that the potassium nitrate did not give complete replacement of the exchangeable acidity, consequently, the results were always low.

The calcium acetate method recommended by Jones (20) in 1915 involved mixing calcium acetate with the soil using a mortar and pestle. Water was added and the mixture was allowed to stand for a period of time before filtering. The filtrate was then titrated with standard sodium hydroxide and the value converted to pounds of lime per acre-furrow-

slice. According to Peech (37), it was more satisfactory than the Hopkins method and was widely accepted by American investigators.

Hutchinson and MacLennan (18) suggested a method of lime requirement in 1915 in which a small quantity of soil was suspended with a known amount of calcium bicarbonate and the amount of calcium adsorbed by the soil was determined by titration with standard acid.

In 1929, a method was published by Hardy and Lewis (17) in which the acidity was exchanged with calcium chloride and titrated with standard calcium hydroxide using the quinhydrone electrode to determine the end point. The results of the titration were plotted and the lime requirement to pH 7.0 was determined from the curve. This procedure was reportedly more reliable than some other methods, and was rapid, less tedious, and the results could be reproduced.

The method of Bray and DeTurk (4), 1931, used potassium chloride to remove the exchangeable soil acidity which was then titrated with sodium carbonate. They suggested that liming according to this procedure would raise the base saturation of a soil to about 80 per cent, which was the definition they suggested for lime requirement. Peech (37) stated that this method gave higher, more empirical results than did the method of Veitch and other methods involving titrations with calcium hydroxide.

Dunn (14) described a potentiometric method for determining lime requirement by means of titration curves in 1943. The procedures of Dunn's method involved shaking samples of the soil twice daily over a period of four days in varying amounts of standard calcium hydroxide.

The pH values were determined with the glass electrode. The pH values for each different soil were plotted against lime rates and the amount of calcium hydroxide needed to reach any desired pH value was read from the appropriate titration curve. Five ml. of 0.04N $Ca(OH)_2$ represented 1 ton of ground limestone per acre. Shaw (49) pointed out that Dunn's method is similar to that of Veitch except for the longer contact period and the use of pH instead of phenolphthalein. The method was found to be reliable (14). Peech and Bradfield (39) stated that it was the best method that had been developed involving the use of hydroxides.

Although the procedures of this method are rather easily performed, it is not well adapted to routine soil testing because of the length of time involved and the large number of operations which must be performed on one soil sample. Advantage has been taken of its high reliability in using it as a standard of comparison for other methods.

Mehlich (28), 1938, proposed a titration method which was the forerunner of the $BaCl_2$-triethanolamine (TEA) method described by Peech, et al. (38), and was based on the same principles as an earlier method proposed by Schofield (45) in 1933. Mehlich's method used a buffered triethanolamine acetate and barium hydroxide solution which was shaken in a flask with the soil. The soil adsorbed some barium, the amount being equal to the amount of exchangeable acidity. This value was determined by titration with standard acid.

The method for direct determination of exchangeable acidity outlined by Peech et al. (38) in 1947 was a modification of Mehlich's method. They recommended a buffered solution which consisted of

barium chloride and triethanolamine adjusted to pH 8.1 or 8.2 with HCl to extract the exchangeable acidity. After filtration and thorough leaching, the extract was titrated to the brom cresol green-methyl red indicator end point with standard hydrochloric acid.

The TEA method has been evaluated and compared to other methods by various workers (16, 37, 39, 43, 54, 56). The work of Hanna and Reed (16), in comparing the TEA method and the ammonium acetate method of Peech et al. (38), showed that the TEA method gave higher results for all soils tested. Pratt and Holowaychuk (43) found comparable results for exchangeable acidity when the TEA method was compared to neutralization curves to pH 7.6.

Shaw (48, 50, 51, 52, 53) and Shaw and MacIntire (54), recognizing the inadequacy of pH for making lime requirement recommendations, developed, recommended, and tested the calcium acetate method which involved replacement of the soil acidity with neutral normal calcium acetate and the subsequent titration with barium hydroxide to pH 8.8. Shaw (51) proposed that exchangeable acidity determined by this method and exchangeable bases be used to determine the cation exchange capacity of soils which would then be used in making lime recommendations to some desired per cent base saturation. In comparing this method to the ammonium acetate method of Peech et al. (38), Shaw and MacIntire (54) found that the two methods gave results that agreed. They reported that, like the ammonium acetate method, the calcium acetate method gave lower results on soils with 1:1 type clay and organic soils than did the TEA method. Shaw (50) showed that when calcium carbonate was added to soils

in the laboratory in amounts indicated as needed by the calcium acetate method, widely differing soils were brought to near pH 7.0. Shaw and MacIntire (54) concluded that the calcium acetate method was the method best suited to raise the pH of soils to near neutral.

Yuan (64) reported on a simple titration method whereby the total exchangeable acidity, exchangeable hydrogen, and exchangeable aluminum can be determined rather rapidly and easily using a single neutral salt extract of the soil. The extraction was made with 1N KCl and the leachate was titrated to the phenolphthalein end point with standard sodium hydroxide to obtain a value for total exchangeable acidity. Sodium fluoride was then added to the titrated leachate to form a complex, stable sodium fluoaluminate which caused the solution to become alkaline due to the release of sodium hydroxide. The amount of alkalinity developed was equal to the amount of aluminum present in the extract. This value was determined by titrating back to the phenolphthalein end point with standard hydrochloric acid. The exchangeable hydrogen was then determined by subtracting exchangeable aluminum from the total exchangeable acidity.

Yuan (64) pointed out that exchangealbe hydrogen could be determined by this method without interference from the hydrolysis of displaced exchangeable aluminum which normally occurs in the titration of a soil extract.

Coleman et al. (11) made use of this principle in separating permanent cation exchange capacity and pH dependent cation exchange capacity. They leached the soil with neutral normal potassium chloride

and determined the exchangeable hydrogen and aluminum by a procedure similar to that of Yuan except that potassium fluoride was used as a complexing agent. This value along with exchangeable bases was taken as the cations countering the permanent change of the soil. The pH dependent cation exchange capacity was determined by further leaching with barium chloride triethanolamine buffered at pH 8.2.

Direct determination of lime requirement by various periods of moist incubation of soils with calcium carbonate, calcium hydroxide, ground limestone, or some other liming material has been used rather extensively in research laboratories and greenhouses mainly as a standard of comparison (1, 22, 44, 51, 56). The procedure involves treating several samples of a soil with some liming material and keeping the soil moist in the laboratory or greenhouse for a period of time ranging from a few weeks to several months to allow equilibration to occur. After the lime has fully reacted with the soil, pH of the soil plotted against the various levels of lime forms a titration curve for that particular soil. The lime requirement can then be read directly from the curve for any desired pH value.

Some methods have been devised which cannot be readily classified into one of the groups of methods previously mentioned. One such method is the ammonium acetate method for exchangeable acidity described by Peech et al. (38) in which the soil is extracted with neutral normal ammonium acetate for simultaneous determination of exchangeable bases and cation exchange capacity. The exchangeable acidity is determined by the difference between the two. Peech et al.

(38) and others (39, 43, 54) criticized the method because it gave low values for 1:1 type clays and for organic soils.

pH as a Method for Lime Requirement

The pH of a soil is a measure of the active acidity and does not indicate the total amount of soil acidity, but it has been recognized that there is a relationship between the pH and the degree of base saturation of a soil, and this relationship can be used in estimating the lime requirement of soils (10, 15, 29, 30, 37, 57, 62). Although it can be shown that a relationship exists between the per cent base saturation and pH for a given soil or for given soil types, the relationship is not the same for all soils (1, 30, 32, 34, 40, 49). Adams and Evans (1) stated that any general application of this relationship must be made with caution.

The soil pH has probably been the most widely used method of assessing the condition of the soil with respect to lime. Many workers have indicated its widespread use (15, 37, 39, 49, 57). There are limitations, however, to the use of pH as a lime requirement method mainly because of variation caused by the nature of the soil colloidal matter, the presence of electrolytes, soil-water ratio, and concentration of carbon dioxide (10, 15, 37, 57). Shaw (49) indicated that variations may be as much as a few hundred to several thousand pounds of calcium carbonate per acre. He concluded that pH without detailed consideration of the physical and chemical properties of a soil did not give a complete picture of the lime requirement of that soil. Shaw (51) stated that the

cation exchange capacity of a soil must be known in order to translate its lime requirement as calculated from a pH-base unsaturation curve into pounds of calcium carbonate per acre. Several workers have suggested that the use of pH along with other soil properties such as cation exchange capacity, texture, exchangeable calcium, exchangeable hydrogen, and organic matter would be a more desirable method (10, 22, 39, 44, 49, 51). The procedures involved in determining these properties would require considerable time and eliminate rapidity, the major advantage of the use of pH as an estimate of lime requirement.

It is well known that when the electrodes of a pH meter are in the supernatant liquid of a soil-water suspension, the pH reading is usually higher than if the electrodes are in the solid phase of the suspension. This phenomenon has been attributed to various causes by various investigators and has been recognized as a limitation to the validity of soil pH. Coleman et al. (12) attributed this to a junction potential arising at the junction between the potassium chloride bridge of the reference electrode and the medium in which the electrodes are placed. The potential was theorized to be due to differential mobility of ions within the soil-water mixture. They found that when the pH was measured in a 1N KCl solution the junction potential was negligible. Therefore, they recommended that soil pH be measured in the presence of 1N KCl.

Schofield and Taylor (47) recognized that soil pH varied with electrolyte concentration and that the pH value of soil sediments was different from the liquid phase of a soil-water suspension. They

proposed a method for determining a value that they called the "lime potential" and expressed it as pH-1/2p(Ca+Mg). The method involved the measurement of soil pH in 0.01M calcium chloride solution. The electrolyte content of the soil is very small compared to the calcium chloride solution, allowing the pH determination to be made in a practically constant electrolyte concentration. They found that the pH value with the electrodes in the soil suspension was the same as with the electrodes in the supernatant liquid when using this method. This, then, eliminated variations due to what was believed to be junction potential as well as variations caused by different electrolyte concentration.

Buffer Methods

In buffer methods, the exchangeable acidity of the soil is extracted directly into the buffer solution by one of the components of the solution. The solution is buffered within some pH range, such as between pH 6.0 and 7.0. The extracted acidity depresses the pH of the buffer solution, the amount of depression being proportional to the amount of acidity extracted. The quantity of exchangeable acidity or the lime requirement of the soil can be determined from titration curves or tables prepared for use with a particular buffer solution. These procedures are simple, rapid, and well suited for routine soil testing.

Probably the first attempt to use a buffer method was made by Schofield (45) in England in 1933. The procedures of his method were somewhat different from the procedures of the buffer methods developed

later but the underlying principles were similar and probably formed the basis for the development of other buffer methods. Schofield's solution consisted of p-nitrophenol which was partially neutralized by calcium hydroxide and at approximately pH 7.0. When an acid soil was mixed with the solution, calcium hydroxide from the solution neutralized the acidity of the soil and the solution pH was depressed to some extent depending on the amount of lime taken from the solution. The amount of lime taken up was then determined by titration with 0.2N HCl to neutrality using brom cresol green indicator. This value was considered to be the lime requirement of the soil. Schofield evaluated the method stating that it was rapid, simple, used cheap reagents and apparatus, and personal factors were absent. However, Innes and Birch (19) found that it gave lower results for exchangeable hydrogen than did Mehlich's method (28).

Brown (5) described a method in 1943 in which an extraction of the soil was made with a buffered neutral normal ammonium acetate solution and the pH of the extract was determined by the glass electrode. To determine the amount of exchangeable acidity, the pH of the extract was compared to a calibration curve prepared by plotting the pH of an ammonium acetate solution to which varying amounts of acetic acid had been added. This method was described by Peech (37) as rapid and quite suitable for routine determinations of lime requirement.

In 1948, Woodruff (61, 62) recommended and outlined the procedures for a lime requirement test which made use of a buffer solution and the glass electrode to measure exchangeable acidity. It involved the same

principles as the earlier method devised by Brown (5), that is, the depression of the pH of a buffered solution as a measure of exchangeable acidity. The Woodruff buffer was composed of a mixture of calcium acetate, p-nitrophenol, and magnesium oxide or sodium hydroxide and had a pH of 7.0. The solution was buffered between pH 6.0 and 7.0 and, upon titration, gave a smooth curve within this range. Each 0.1 unit pH depression of the soil-buffer solution mixture was taken as 1 me. of exchangeable acidity per 100 g. of soil or 1,000 pounds of lime per acre. Woodruff (62) stated that this method was relatively simple, rapid, accurate, and adaptable to soils of differing cation exchange capacities. Shaw and MacIntire (54) obtained lower results with this method than with several others tested.

Shoemaker et al. (56) in 1961 reported on a buffer method which they had developed after observations by McLean et al. (26) indicated that the Woodruff buffer method did not accurately measure the lime requirement of certain Ohio soils. It was indicated that these soils were high in extractable aluminum. One of the purposes of the investigation was to develop a method which would be suitable for soils either high or low in extractable aluminum.

The buffer mixture consisted of p-nitrophenol, triethanolamine, potassium chromate, calcium acetate, and calcium chloride, adjusted to pH 7.5 with sodium hydroxide. The procedure described for soil testing involved the determination of pH using the glass electrode first in water and again after the addition of the buffer. The lime requirement to selected pH values based on the depression of the buffer pH by the

soil was determined from a prepared table.

Shoemaker et al. (56) compared the lime requirement by this method with actual values obtained by calcium carbonate incubation for 14 soils and obtained a correlation coefficient of 0.97. When compared to calcium hydroxide titration of 100 soils, the correlation coefficient was 0.93. They indicated that this method was sufficiently rapid for use in routine soil testing laboratories.

Adams and Evans (1) recognized the need for a rapid and reliable method for determining the lime requirement of Red-Yellow Podzolic soils which usually have low cation exchange capacities, consequently low lime requirements and the possibility of over-liming. In 1962, they reported on a newly developed buffer method for the purpose of evaluating these soils for lime requirement. The buffer solution consisted of p-nitrophenol, boric acid, potassium chloride, and potassium hydroxide at pH 8.0. Exchangeable acidity was measured by the pH depression of the buffer caused by the soil (0.1 pH unit change equals 0.8 me. exchangeable acidity per 100 g. of soil). Base unsaturation was calculated from exchangeable bases and exchangeable acidity by dividing exchangeable acidity by bases plus exchangeable acidity. The soil pH values for 1:1 soil-water mixtures were plotted against base unsaturation for a large number of soils and the equation for the curve determined by the method of least squares. Base unsaturation values as determined using the equation and exchangeable acidity measured by the buffer solution were used to calculate the amount of soil acidity to be neutralized to give some desired change in base unsaturation.

These values were converted to pounds of lime per acre-furrow-slice of soil and arranged in table form with soil pH in water along one axis and soil pH in the buffer solution along the other.

The recommended laboratory procedure for lime requirement involves the measurement of soil pH in a 1:1 soil-water suspension followed by the addition of the buffer solution and determination of pH of the soil-buffer solution after a period of intermittent stirring. The lime requirement to any desired pH is read directly from the appropriate table.

Adams and Evans (1) compared the exchangeable acidity as measured by the buffer solution with that determined by the ammonium acetate method and obtained a correlation coefficient value of 0.94. The buffer method tended to indicate more acidity than did the ammonium acetate method. The lime requirements to 25 per cent base unsaturation as determined by the buffer method and that calculated using base unsaturation and cation exchange capacity were compared and found to agree satisfactorily.

Further evaluation of the method was made by comparing the lime requirement predicted by the buffer method with the lime requirement determined from titration curves obtained by 4 weeks moist incubation of several soil samples with calcium hydroxide. The buffer method predicted lower lime requirements than the titration curves indicated, but the method appeared to be satisfactory for lime recommendations.

Recently Wright (63) at Mississippi State University has developed a buffer method which has not been published. The buffer solution consisted of p-nitrophenol, calcium chloride, and sodium hydroxide adjusted to pH 7.2. The procedures involve determination of buffer pH depression caused by the soil and each 0.1 pH unit depression indicates 1,000 pounds of lime per acre. Preliminary work with this method at Mississippi State indicated high correlations with several other methods tested.

III. SOIL PROPERTIES THAT INFLUENCE THE LIME REQUIREMENT

The lime requirement of soils has been found to vary with variations in several soil properties (4, 9, 10, 22, 39, 44, 56, 57). It is well known that soils may have the same pH value, but have very different lime requirements. Soils may be similar with respect to base status yet vary greatly in lime requirements. Several investigators have reported poor or no correlation between methods of lime requirement using soils with widely varying properties, but found a much closer correlation between methods when using soils of the same type or soils that were similar in certain properties (2, 6, 34, 62). Mehlich (29, 30) noted that there was a wide difference in per cent base saturation-pH relationship for soils of different types. These results indicate that there are soil factors or properties which affect lime requirement other than the acidity measured by ordinary methods such as pH, and that those properties are likely related to soil type.

Probably the factors which cause the greatest variation between soils in their lime requirements are the amount and kind of colloidal matter in the soil (29, 30, 31, 40). Mehlich (29, 30, 31) stated that the wide variation in per cent base saturation-pH relationship found in soils of different types was associated with the nature of the exchange colloids of the soils. Several writers have indicated that soils in which the exchange complex is dominated by 2:1 type clay minerals have higher lime requirements than those in which 1:1 type clays predominate; that is, 2:1 type requires more lime to effect a given pH change (10, 21, 29, 30, 39).

That variations in the amount of clay and organic matter in soils causes variations in lime requirements is shown by the fact that a relatively high degree of correlation exists between these values (22, 44).

The variations in lime requirement noted with variations in clay and organic matter content and, at least in part, the type of clay minerals may be due to their effect on the cation-exchange capacity of the soil. The lime requirement of soils has been shown to vary closely with their cation-exchange capacities (21, 22, 24, 44). Variations in cation-exchange capacity have often been accompanied by a corresponding variation in one or more of these properties; type of clay minerals, clay content, or organic matter content (10, 21, 35).

According to Keeney and Corey (22), several workers have related the pH dependent charge of soil cation-exchange colloids to

lime requirement. Clay minerals have a permanent charge which is constant to pH 5.0 or 6.0 (10, 11, 42, 46). When the pH is increased above this point, an additional charge, the pH dependent charge is developed, due to dissociation of hydrogen ions from SiOH groups at the edges of the crystals, dissociation of hydrogen ions from carboxyl groups of organic colloids, the adsorption of hydroxyl groups by clays, and possibly others (10, 11, 46). The entire cation-exchange capacity of organic colloids is probably due to the pH dependent charge (10). Pratt (42) limed eight acid soils to the point where no further increase in pH could be obtained with further additions of lime and found this amount of calcium carbonate to be closely related to the cation-exchange capacity resulting from the pH dependent charge.

As would be expected, lime requirement has been shown to be closely correlated with exchangeable acidity (1, 22, 44, 56). Of greater significance is the effect of exchangeable or extractable aluminum on the lime requirement of soils and its measurement by lime requirement methods. McLean et al. (26) stated that soils in which the actual lime needs exceeded that indicated by soil tests were found to be high in aluminum. They concluded that aluminum may be the major portion of acidity in some soils. Coleman et al. (11) found evidence that indicated that the exchangeable acidity resulted almost entirely from the hydrolysis of trivalent aluminum. Yuan (64) reported similar findings. Chernov (7) stated that the titratable acidity in neutral salt extracts from unsaturated soils

was equal to the aluminum content of those soils. He also found that aluminum ions were much more effective in displacing calcium in soils than were hydrogen ions.

McLean et al. (26), in 1958, stated that the present methods of measuring exchangeable acidity may not take into account extractable aluminum. Shoemaker et al. (56) obtained data which tended to substantiate this. Their evidence indicated that the aluminum was reacting with lime added to the soil but was not reacting with the Mehlich TEA buffer. They postulated that this might be due to the fact that the lime reacted with the soil slowly causing a gradual pH change and allowed complete reaction between the lime and exchangeable aluminum whereas the buffer solution changed the soil pH instantly causing some of the aluminum to be trapped inside the clay crystal lattice by insoluble aluminum hydroxide. They developed and recommended a buffer method for lime requirement which they found to be effective in measuring the lime requirement of soils high in exchangeable aluminum content.

The main purpose for the laboratory study of lime requirement is to successfully interpret laboratory measurements of lime needs into lime recommendations in the field. In order to fulfill this purpose, factors other than soil properties and methods of determination must also be considered. It is well recognized that difficulty arises in relating laboratory determined lime requirements to the amount of lime needed to properly adjust the soil reaction in the field (1, 8, 9, 14, 37, 39, 41, 52, 57). Observations have shown

that the values obtained in the laboratory often do not produce the desired change in soil reaction when applied to field use. This has led to the use of lime factors, numbers by which the laboratory values for lime requirement are multiplied to arrive at field recommendations for lime. Various lime factors have been used, but factors of 1.5, 2, or 3 are most commonly accepted (1, 8, 9, 41). The need for lime factors is not associated with the nature of the soil or the method of lime requirement determination but is associated with such factors as fineness and purity of the liming material, leaching and erosion losses after application in the field, and the depth and manner in which the lime is mixed with the soil.

CHAPTER III

MATERIALS AND METHODS

Three buffer methods for determining lime requirement were evaluated using several selected Tennessee soils. Lime requirements by the buffer methods were compared to lime requirements by incubation with pure calcium carbonate. The buffer methods were compared with one another and with the ammonium acetate method of Peech et al.

The physical and chemical properties believed to have an influence on lime requirement were studied in relation to the soils' lime requirements.

I. SOIL SAMPLES

Ninety-two soil samples from 47 sites representing 24 different soil types and 20 different soil series were used. The sites were located at various points across Tennessee, from the Smoky Mountains on the east to the Mississippi River on the west. The 20 series represent 6 types of parent material, 5 of which are common and agriculturally important in Tennessee. Parent materials were metamorphic rocks, limestone, sandstone, shale, loess, and alluvium. Samples ranged in textural classes from loamy sand to clay, with the largest number being silt loams. Some of the sites were represented by samples from more than one horizon. At other sites, only the surface layer was sampled.

II. LABORATORY METHODS

Mechanical analyses were made according to the procedures of Kilmer and Alexander (23).

The cation-exchange capacity and easily oxidizable organic matter were determined following the procedures outlined by Peech et al. (38). Exchangeable bases were determined with the Beckman Model DU flame photometer after extraction with neutral normal ammonium acetate according to the method of Shaw and Veal (55).

The three buffer solution methods for predicting lime requirement that were evaluated were those of Adams and Evans (1), Shoemaker et al. (56), and Mississippi State (63). These methods will hereafter be referred to as the Auburn, Ohio, and Mississippi buffers respectively. Detailed procedures for these methods are outlined in the appendix. A portion of each buffer solution equal to the volume and in the concentration recommended for use with soils was titrated with increments of standard hydrochloric acid to the point of rapid deflection using the glass electrode to measure the pH depression. A titration curve was plotted for each buffer solution and was used in connection with the soil-buffer solution pH values to determine the exchangeable soil acidity as measured by each buffer solution. The soil-buffer solution pH values and the soil pH values in a 1:1 water suspension were determined using a Beckman Model H2 pH meter.

The Auburn buffer and the Ohio buffer procedures as outlined by the authors involved the determination of soil pH in a 1:1 soil-

water mixture followed by the addition of the buffer solution and subsequent determination of the soil-water pH value. These procedures were modified slightly in that the soil-water pH values were determined on separate sub samples. The soil-buffer solution pH values were determined using buffer solutions diluted with distilled water to give the recommended concentration when added directly to the soil without prior addition of water to the soil. In this manner, the buffer solution concentrations for all soil samples were constant, eliminating any error which might arise when the water and buffer solutions were added in separate operations to the same soil sample.

Lime requirement values for all samples were determined from the equation:

$$\text{me. acid to be neutralized} = \frac{\text{me. exchangeable acidity}}{\text{initial base unsaturation}} \times \text{desired change in base unsaturation.}$$

The exchangeable acidity values used in the equation were those obtained by each of the buffer solutions. The initial base unsaturation and the desired change in base unsaturation were estimated from the equation of Adams and Evans (1), $y = 7.79 - 5.55x + 2.27x^2$ where y = soil pH and x = base unsaturation. These values were multiplied by 1,000 to convert to pounds of calcium carbonate per acre-furrow-slice. The original procedures for determination of lime requirement by the Ohio and Mississippi buffer solutions were not used because those procedures gave predictions which were, in many cases particularly the Ohio buffer method, extremely high as compared to

calcium carbonate incubation. Also, in order to effectively evaluate each buffer solution, the procedures had to be the same for all three. Lime requirements were also calculated to prescribed base unsaturation percentages by the ammonium acetate method and were estimated by the pH method.

Exchangeable acidity was determined by the ammonium acetate method as described by Peech et al. (38) whereby the total bases were subtracted from the cation exchange capacity to obtain the exchangeable acidity values. Total exchangeable acidity, exchangeable aluminum, and exchangeable hydrogen were determined by the procedures of the Yuan titration method (64). According to this method, the soils were leached with a normal potassium chloride solution, and the total acidity was titrated to the phenolphthalein end point with sodium hydroxide. Sodium fluoride was used to complex the aluminum and the alkaninity developed upon complexing the aluminum was titrated with hydrochloric acid and this value was taken as the exchangeable aluminum. The exchangeable hydrogen was determined by subtracting the exchangeable aluminum from the total exchangeable acidity.

III. INCUBATION WITH CALCIUM CARBONATE

Twenty-one surface soil samples and one subsoil sample were selected for determination of the lime requirement by incubation with reagent grade precipitated calcium carbonate. One hundred-gram samples of each soil were mixed thoroughly with calcium carbonate at rates equivalent to 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 tons per acre-furrow-

slice (2,000,000 pounds of soil) and placed in paper cups. Each treatment was duplicated. The samples were then placed in the greenhouse and kept moist for two weeks after which they were allowed to air-dry, thoroughly mixed, and returned to the greenhouse for further moist incubation. This procedure was repeated again at the end of six weeks. At the end of six months moist incubation the samples were weighed out for pH determination in water. The incubation period was concluded after six months because it was believed that the calcium carbonate had reacted fully with the soils.

The pH values of the 1:1 soil-water mixtures were plotted against the various rates of calcium carbonate to produce titration curves for each soil in the incubation study.

CHAPTER IV

RESULTS AND DISCUSSION

I. PROPERTIES OF 22 SOILS USED IN INCUBATION STUDY

The physical and chemical properties for the 22 soils used in the incubation study are presented in tables 1 and 2. These soils represent the major parent materials of Tennessee and give a representation of the soils of the state as far as geographical distribution is concerned. All the samples were from surface horizons except one, the Maury B_{23}, which was chosen for the incubation study because preliminary tests indicated that it was highly buffered and had a high lime requirement. Textures ranged from loams to clays with the largest number of soils being silt loams. The soils varied widely in clay content, ranging from a low of 8.4 per cent for the Dickson to 48.9 per cent for the Maury B_{23}.

These soils represent a relatively wide range in organic matter content. The range was from 0.18 per cent in the Maury B_{23} to 5.33 per cent in the Halewood. The greatest number of soils had less than 2.0 per cent organic matter.

The cation exchange capacities determined by the neutral normal ammonium acetate method ranged from 3.3 to 33.0 me. per 100 g. of soil. Two soils had cation exchange capacities at the high end of this range but all the others were less than 14 me. per 100 g. of soil. Both these high cation exchange capacity soils, Bowdre and Tunica, were relatively

Table 1.--Selected physical properties of 22 Tennessee soils used in $CaCO_3$ incubation study.

Sample No.	Soil Series	Horizon	Inches Depth	Texture	Per Cent Clay	Per Cent Organic Matter
91	Dickson	A_p	0-6	Silt loam	8.4	0.98
4	Clarksville	A_2^p	1-4	Loam	9.5	1.75
76	Loring	A_p^2	0-6	Silt loam	10.2	1.05
81	Loring	A_p	0-6	Silt loam	10.8	0.87
52	Baxter	A_2	1-10	Silt loam	12.5	1.29
58	Cookeville	A_2	2-5	Silt loam	14.5	1.75
83	Hatchie	A^2	0-6	Loam	14.5	1.75
1	Clarksville	A_2^p	1-7	Silt loam	15.2	1.04
49	Hartsells	A^2	0-9	Loam	15.6	2.89
68	Baxter	A^p	0-6	Silt loam	16.5	1.38
88	Vicksburg	A^p	0-6	Silt loam	16.9	0.70
40	Dewey	A^p	0-10	Silt loam	17.2	1.90
66	Baxter	A^p	0-6	Loam	18.4	1.50
92	Grenada	A^p	0-6	Silt loam	19.5	1.38
7	Sequoia	A^p	2-5	Silt loam	20.4	1.86
89	Falaya	A^p	0-6	Silt loam	20.5	1.21
86	Olivier	A^p	0-6	Loam	23.7	1.05
28	Halewood	A_2^p	1-4	Clay loam or loam	26.6	5.33
13	Decatur	A^2	1-4	Clay loam	30.9	2.08
78	Bowdre	A^p	0-6	Clay loam	34.6	2.84
79	Tunica	A^p	0-6	Clay	42.4	3.70
39	Maury B_{23}	B_{23}^p	53-67	Clay	48.9	0.18

Table 2.--Selected chemical properties of 22 Tennessee soils used in $CaCO_3$ incubation study.

Sample No.	Soil Series	C.E.C. me./100g.	Total bases me./100g.	Per Cent Base saturation	Soil pH	Exch. Al me./100g.	Exch. H me./100g.
91	Dickson	7.7	3.6	46.8	5.1	1.02	0.23
4	Clarksville	3.6	0.2	5.6	4.8	1.41	0.23
76	Loring	7.0	4.7	67.1	5.9	0.10	0.18
81	Loring	7.0	4.7	67.1	6.4	0.00	0.08
52	Baxter	4.9	0.8	16.3	5.1	1.30	0.27
58	Cookeville	7.2	2.0	27.8	5.1	0.94	0.32
83	Hatchie	10.0	9.1	91.0	5.7	0.19	0.09
1	Clarksville	3.3	0.3	9.1	5.1	0.84	0.19
49	Hartsells	9.8	5.4	55.1	5.7	0.49	0.03
68	Baxter	10.8	6.6	61.1	5.3	0.89	0.25
88	Vicksburg	7.4	9.6	129.7	6.4	0.00	0.06
40	Dewey	6.8	2.4	35.3	5.8	0.00	0.14
66	Baxter	11.4	11.0	96.5	5.9	0.00	0.11
92	Grenada	10.5	5.5	52.4	5.2	3.19	0.00
7	Sequoia	8.6	2.7	31.4	5.9	0.05	0.10
89	Falaya	12.2	13.4	109.8	6.5	0.00	0.09
86	Olivier	11.2	7.5	67.0	5.2	0.81	0.21
28	Halewood	12.9	1.3	10.1	4.7	3.58	0.54
13	Decatur	9.4	7.5	79.8	6.1	0.00	0.18
78	Bowdre	32.7	20.0	61.2	6.2	0.00	0.06
79	Tunica	33.0	19.5	59.1	6.4	0.00	0.13
39	Maury B_{23}	13.6	1.8	13.2	4.8	6.19	0.12

high in clay content and organic matter content, 34.6 and 42.4 per cent clay and 2.8 and 3.7 per cent organic matter respectively. These two constituents together probably accounted for the high cation exchange capacities of these soils.

The total bases ranged between 0.2 me. per 100 g. of soil for the Clarksville, sample 4, and 20.0 me. per 100 g. of soil for Bowdre. The Clarksville, sample 4, also had the lowest per cent base saturation. This soil was very acid as evidenced by its low pH value of 4.8 and its relatively high exchangeable acidity. Vicksburg had the highest per cent base saturation, 129.7, and Falaya was the next highest with 109.8. Theoretically soils with base saturation percentages greater than 100 should have pH values above 7.0 since the cation exchange capacities and exchangeable bases were determined using neutral ammonium acetate. However, their pH values were 6.4 and 6.5 respectively. This inconsistency may be due to errors in the determination of cation exchange capacity or exchangeable bases. These extremely high per cent base saturation values indicate the probability of a liming history for these soils, however, available information did not indicate such.

A moderately wide range of pH values was represented, ranging from 4.7 to 6.5. Exchangeable aluminum by the Yuan titration method ranged from 0 to 6.19 me. per 100 g. of soil. Exchangeable hydrogen by the same method was less than 1 me. per 100 g. in all cases and less than 0.25 me. per 100 g. in most cases. The exchangeable aluminum accounted for nearly all the exchangeable acidity extracted by neutral normal potassium chloride where appreciable quantities of exchangeable

acidity were measured. This is consistent with the results presented by Coleman et al. (11), Yuan (64), and Chernov (7).

II. EXCHANGEABLE ACIDITY BY FIVE DIFFERENT METHODS

Exchangeable acidity values measured by the buffer solutions, the Yuan titration, and the ammonium acetate method are shown in table 3. The Yuan titration measured the least amount of exchangeable acidity, however, those soils which had the highest exchangeable acidity as measured by the buffer solutions also had the highest by the Yuan titration indicating that a relative portion of the exchangeable acidity was being measured by the Yuan titration but not in as great a quantity as by the buffer solutions. The ammonium acetate method, in most cases, gave the highest values for exchangeable acidity. In general, the soils that gave high values by the buffer solution methods also gave high values by the ammonium acetate method. Some exceptions to this can be noted, however, particularly with the soils which were highly base saturated. Some soils showed high exchangeable acidity contents by the buffer solutions and the ammonium acetate method although they had relatively high pH values. Bowdre and Tunica had pH values of 6.2 and 6.4 respectively but had high exchangeable acidity values by the buffer solutions and by the ammonium acetate method. These soils are relatively high in both clay and organic matter content, and are highly buffered, illustrating the relationship between soil buffering and the amount of exchangeable acidity.

Table 3.--Exchangeable acidity of 22 Tennessee soils used in $CaCO_3$ incubation study by Yuan titration, Auburn buffer, Ohio buffer, Mississippi buffer, and NH_4OAc methods.*

Sample No.	Soil Series	me. per 100 grams of soil				
		Yuan titration	Auburn buffer	Ohio buffer	Miss. buffer	NH_4OAc
91	Dickson	1.25	4.0	2.9	3.33	4.0
4	Clarksville	1.63	1.6	2.3	3.33	3.4
76	Loring	0.28	3.2	1.4	2.00	2.2
81	Loring	0.08	1.6	1.6	2.00	2.2
52	Baxter	1.57	3.6	2.3	2.67	4.1
58	Cookeville	1.26	4.0	2.9	3.33	5.3
83	Hatchie	0.28	4.0	2.9	3.33	0.9
1	Clarksville	1.03	1.6	2.0	2.67	3.0
49	Hartsells	0.52	3.2	2.3	2.00	4.4
68	Baxter	1.14	4.0	3.2	4.00	4.2
88	Vicksburg	0.06	0.8	1.1	1.33	0.0
40	Dewey	0.14	4.0	2.6	4.00	4.4
66	Baxter	0.11	4.0	2.3	2.00	0.4
92	Grenada	3.19	5.2	3.7	4.67	5.1
7	Sequoia	0.15	3.2	2.6	5.34	5.9
89	Falaya	0.09	1.6	1.4	0.67	0.0
86	Olivier	1.02	4.8	2.9	4.00	3.7
28	Halewood	4.12	8.0	4.6	8.00	11.6
13	Decatur	0.18	3.2	2.0	4.00	1.8
78	Bowdre	0.06	4.8	2.6	3.33	12.7
79	Tunica	0.13	5.6	2.9	4.00	13.5
39	Maury B_{23}	6.31	9.6	6.1	9.34	11.9

*Determined by subtracting total bases from C.E.C.

Of the three buffers, the Auburn buffer solution measured the highest amount of exchangeable acidity for most soils. The Ohio buffer measured the lowest amount and the values for the Mississippi buffer were intermediate in most cases but closer to the Auburn buffer values than to the Ohio buffer values. Results of the titration of the buffer solutions shown in figure 1 reveal that, in general, the higher the buffering capacity of the solutions, the higher amount of exchangeable acidity measured. Also, the higher the pH of the solution over its effective buffering range, the higher the amount of exchangeable soil acidity measured by that buffer solution. There are two possible explanations for these relationships. One is that the buffer solution measuring the greatest amount of acidity may be more effective in extracting the acidity from the soil particles. This would be determined by the composition of the buffer solution and, of course, the composition determines the buffering capacity. The other, and more probable explanation, is that the higher pH value at the equilibrium point between the soil and the buffer solution causes the release of acidity, probably hydrogen ions, held by the pH dependent charge of the soil. This could also account for the exchangeable acidity measured by the buffer solutions being higher than that measured by the Yuan titration. Coleman et al. (11) found that after extraction of the soil with neutral normal potassium chloride, as was the case in the Yuan titration, other exchangeable acidity was measured by a buffered barium chloride triethanolamine solution. They indicated that the pH of the soil after leaching was about 6.0 and the

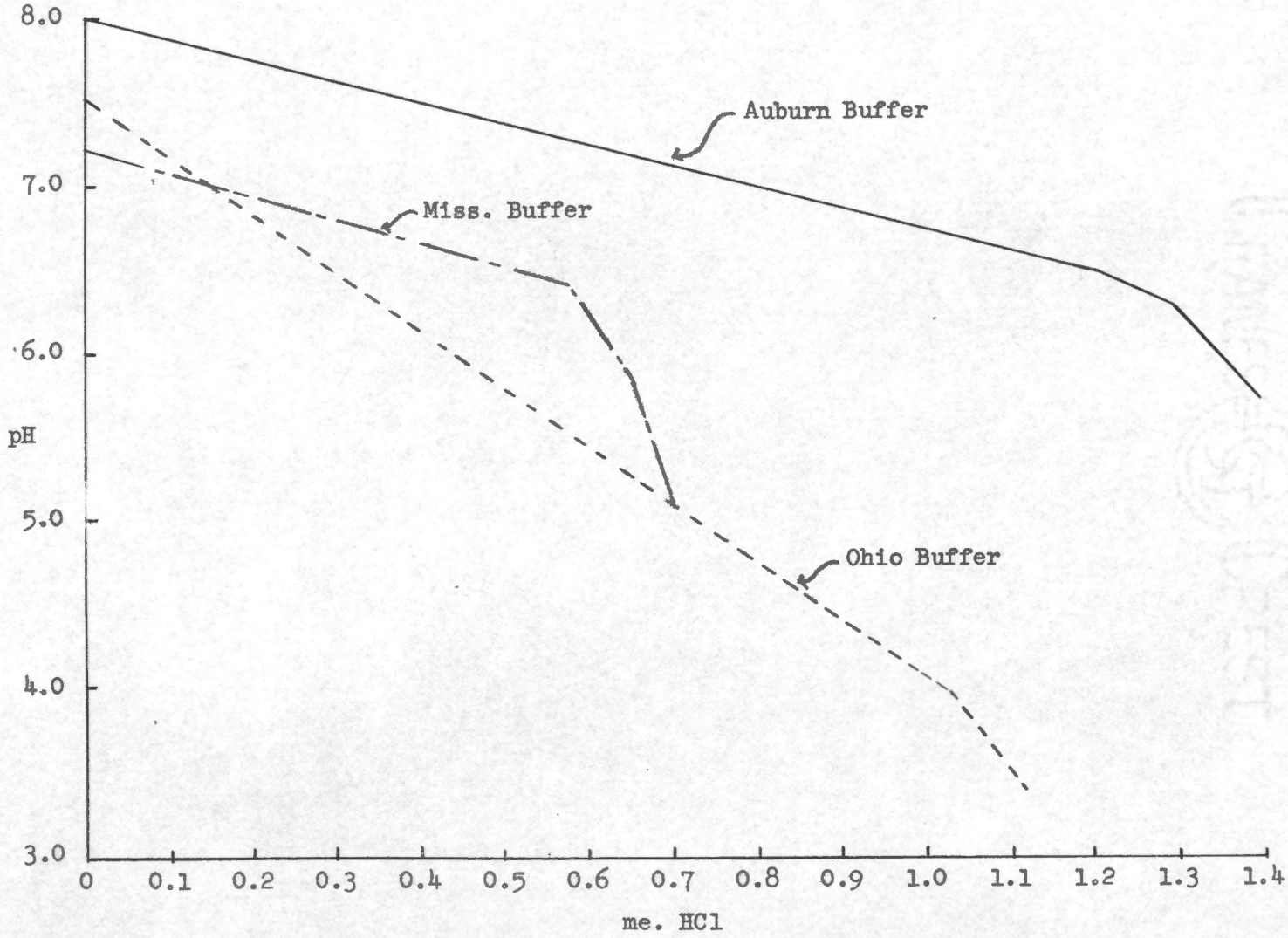


Fig. 1.--Titration curves for 20 ml. of dilute Auburn buffer solution, 30 ml. of dilute Ohio buffer solution, and 20 ml. of dilute Mississippi buffer solution.

acidity displaced by potassium chloride at that pH was considered as that held by the permanent charge of the soil. Acidity measured by barium chloride triethanolamine after the potassium chloride leaching was considered as that held by the pH dependent charge and released when the pH of the soil was raised to about 8.2 in the buffered solution. If pH dependent charges were responsible for the differences observed in the capacity of the buffer solutions to measure the exchangeable acidity, the buffer solution with the highest pH values at the equilibrium point of the soil-buffer mixture would be expected to measure the highest amount of exchangeable acidity. This was, in general, the case.

III. LIME REQUIREMENT BY CALCIUM CARBONATE INCUBATION

Lime requirements to pH 6.5, 6.8, and 7.0 by calcium carbonate incubation are presented in tables 4 through 6. Lime requirement values to the desired pH levels by incubation were taken from the titration curves plotted for each of the 22 soils used in the incubation. These titration curves are shown in figures 2 through 6. These curves were grouped and plotted according to their similarity of form. The shape of a particular titration curve was determined by two characteristics of the soil. First, the over-all buffering capacity of the soil, which determined whether or not the pH of the soil increased sharply with increments of calcium carbonate, and secondly, the amount of increased buffering with increased pH. Some soils were evenly buffered throughout the range of calcium carbonate additions and produced titration curves

Table 4.--Lime requirement to pH 6.5 for 22 Tennessee soils used in incubation study.

Sample No.	Soil Series	$CaCO_3$, lbs./A.*					
		$CaCO_3$ incubation	Auburn buffer	Ohio buffer	Miss. buffer	NH_4OAc#	pH/
91	Dickson	1,800	2,400	1,800	2,000	2,100	2,800
4	Clarksville	1,700	1,100	1,600	2,300	2,500	3,400
76	Loring	1,200	1,200	500	700	500	1,200
81	Loring	100	100	100	300	500	200
52	Baxter	1,900	2,200	1,400	1,600	2,900	2,800
58	Cookeville	2,400	2,400	1,800	2,000	3,500	2,800
83	Hatchie	800	1,800	1,300	1,500	0	1,600
1	Clarksville	1,400	1,000	1,200	1,600	2,200	2,800
49	Hartsells	1,000	1,400	1,000	900	2,000	1,600
68	Baxter	2,300	2,200	1,800	2,200	1,500	2,400
88	Vicksburg	100	100	100	100	0	200
40	Dewey	1,500	1,600	1,000	1,600	2,700	1,400
66	Baxter	700	1,500	800	700	0	1,200
92	Grenada	3,000	3,000	2,200	2,700	2,400	2,600
7	Sequoia	900	1,200	900	1,900	3,700	1,200
89	Falaya	0	0	0	0	0	0
86	Olivier	2,800	2,800	1,700	2,300	900	2,600
28	Halewood	4,900	5,600	3,200	5,600	8,400	3,600
13	Decatur	600	900	500	1,100	0	800
78	Bowdre	600	1,000	600	700	4,500	600
79	Tunica	600	500	200	300	5,300	200
39	Maury B_{23}	8,600	6,500	4,100	6,300	8,500	3,400

*2,000,000 pounds of soil.

#to 25% base unsaturation of the cation exchange capacity.

/2,000 pounds per acre of $CaCO_3$ per unit desired change in soil pH.

Table 5.--Lime requirement to pH 6.8 for 22 Tennessee soils used in incubation study.

Sample No.	Soil Series	$CaCO_3$, lbs./A.*					
		$CaCO_3$ incubation	Auburn buffer	Ohio buffer	Miss. buffer	NH_4OAc#	pH/
91	Dickson	2,400	2,800	2,100	2,400	2,500	3,400
4	Clarksville	2,200	1,200	1,700	2,500	2,700	4,000
76	Loring	1,600	1,700	700	1,100	800	1,800
81	Loring	500	500	500	600	800	800
52	Baxter	2,600	2,600	1,600	1,900	3,100	3,400
58	Cookeville	3,000	2,800	2,100	2,400	3,800	3,400
83	Hatchie	1,400	2,300	1,700	1,900	0	2,200
1	Clarksville	1,800	1,100	1,400	1,900	2,300	3,400
49	Hartsells	1,900	1,900	1,300	1,200	2,500	2,200
68	Baxter	3,500	2,700	2,200	2,700	2,000	3,000
88	Vicksburg	400	300	300	400	0	800
40	Dewey	2,200	2,200	1,400	2,200	3,000	2,000
66	Baxter	1,000	2,100	1,200	1,100	0	1,800
92	Grenada	4,200	3,600	2,600	3,200	3,000	3,200
7	Sequoia	1,600	1,700	1,400	2,800	4,200	1,800
89	Falaya	200	400	400	200	0	600
86	Olivier	4,400	3,300	2,000	2,800	1,500	3,200
28	Halewood	7,200	6,200	3,600	7,100	9,000	4,200
13	Decatur	900	1,500	900	1,800	0	1,400
78	Bowdre	1,200	2,000	1,100	1,400	6,100	1,200
79	Tunica	3,000	1,800	900	1,300	6,900	800
39	Maury B_{23}	10,300	7,300	4,600	7,100	9,100	4,000

*2,000,000 pounds of soil.

#to 20 per cent base unsaturation of the cation exchange capacity.

/2,000 pounds per acre of $CaCO_3$ per unit desired change in soil pH.

Table 6.--Lime requirement to pH 7.0 for 22 Tennessee soils used in incubation study.

Sample No.	Soil Series	$CaCO_3$, lbs./A.*					
		$CaCO_3$ incubation	Auburn buffer	Ohio buffer	Miss. buffer	NH_4OAc#	pH/
91	Dickson	2,800	3,100	2,200	2,800	2,900	3,800
4	Clarksville	2,800	1,300	1,900	2,700	2,900	4,400
76	Loring	1,900	2,000	900	1,300	1,200	2,200
81	Loring	800	700	700	900	1,200	1,200
52	Baxter	3,000	2,800	1,800	2,100	3,400	3,800
58	Cookeville	4,000	3,100	2,200	2,600	4,200	3,800
83	Hatchie	2,000	2,700	2,000	2,200	0	2,600
1	Clarksville	2,200	1,200	1,500	2,100	2,500	3,800
49	Hartsells	2,600	2,200	1,600	1,400	3,000	2,600
68	Baxter	4,600	3,000	2,400	3,000	2,500	3,400
88	Vicksburg	600	400	500	600	0	1,200
40	Dewey	3,000	2,600	1,700	2,600	3,400	2,400
66	Baxter	1,600	2,500	1,400	1,300	0	2,200
92	Grenada	5,000	3,900	2,800	3,500	3,500	3,600
7	Sequoia	2,200	2,000	1,600	3,400	4,600	2,200
89	Falaya	400	700	600	400	0	1,000
86	Olivier	5,400	3,600	2,200	3,000	2,100	3,600
28	Halewood	8,800	6,600	3,800	6,600	9,700	4,600
13	Decatur	1,400	1,800	1,100	2,300	400	1,800
78	Bowdre	2,000	2,600	1,400	1,800	7,700	1,600
79	Tunica	4,000	2,600	1,300	1,900	8,600	1,200
39	Maury B_{23}	11,400	7,800	4,900	7,600	9,800	4,400

*2,000,000 pounds of soil.

#to 15 per cent unsaturation of the cation exchange capacity.

/2,000 pounds per acre of $CaCO_3$ per unit desired change in soil pH.

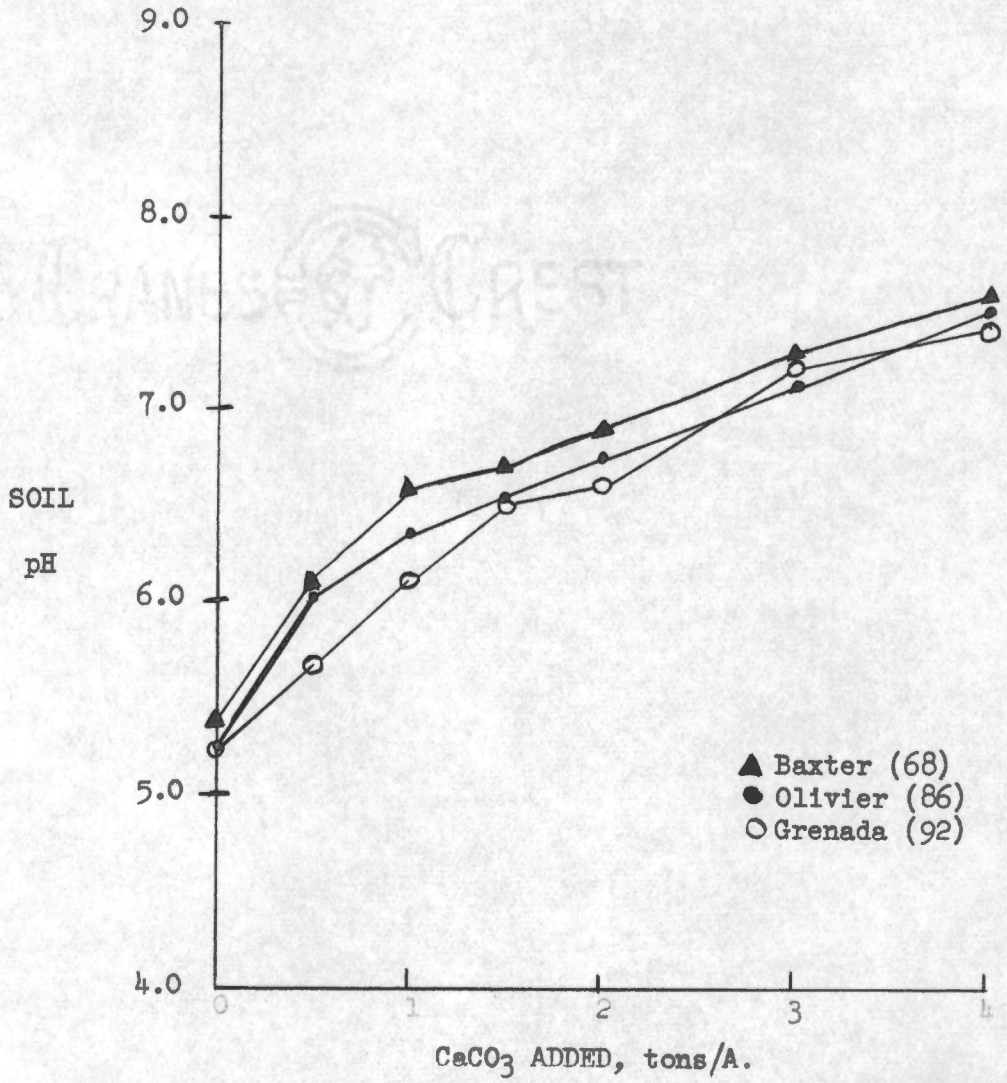


Fig. 2.--Titration curves for 3 Tennessee soils determined by moist incubation with $CaCO_3$.

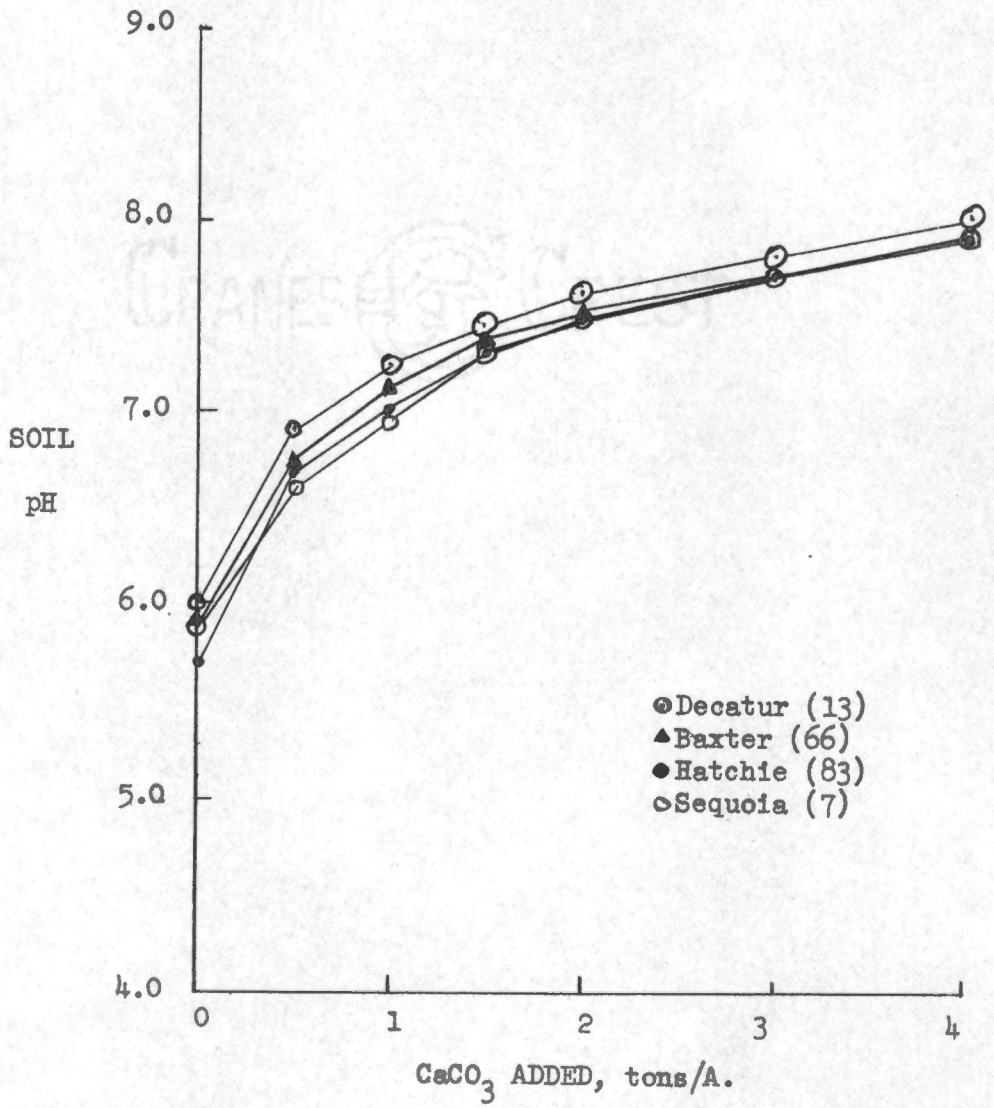


Fig. 3.--Titration curves for 4 Tennessee soils determined by moist incubation with $CaCO_3$.

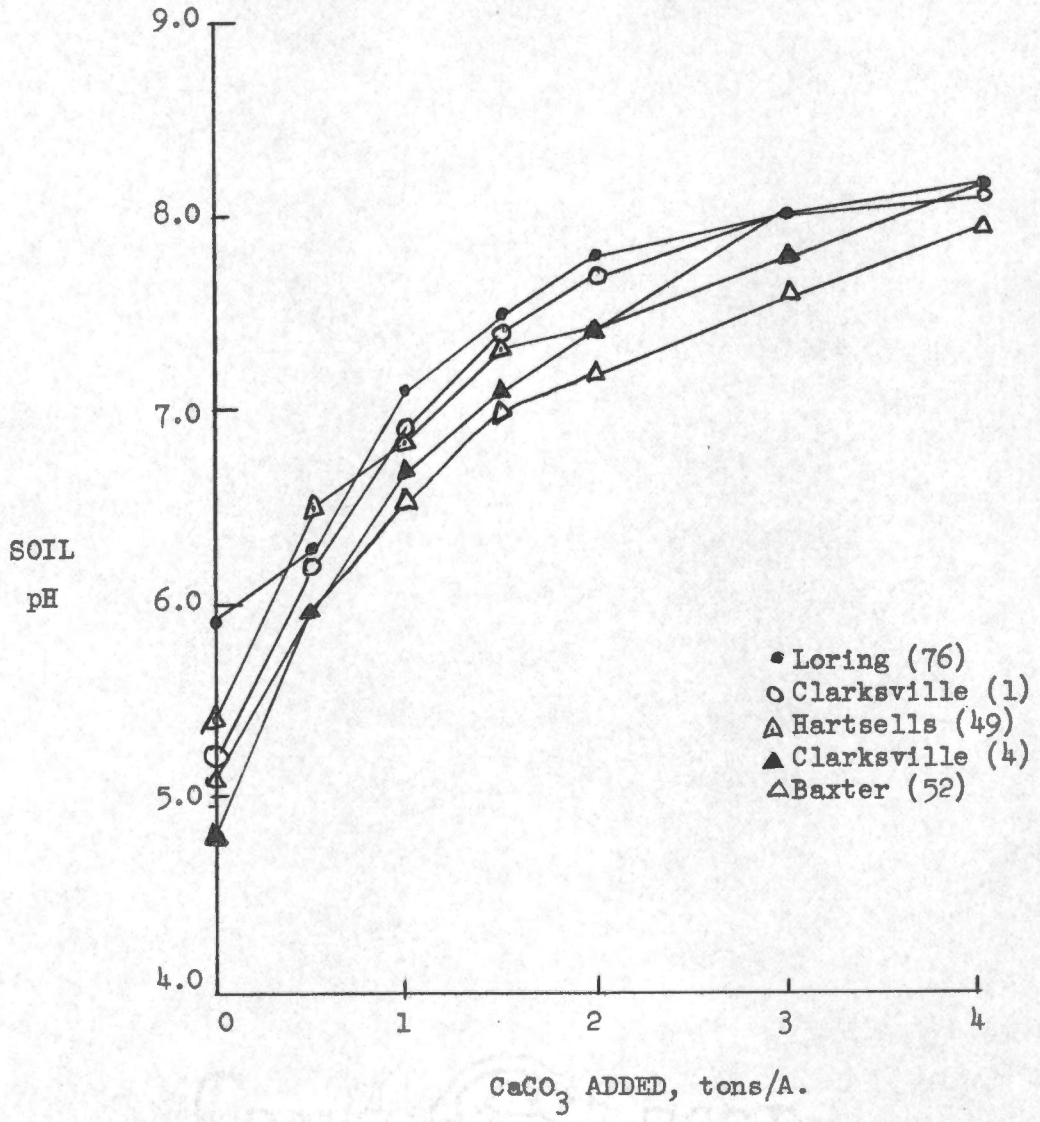


Fig. 4.--Titration curves for 5 Tennessee soils determined by moist incubation with $CaCO_3$.

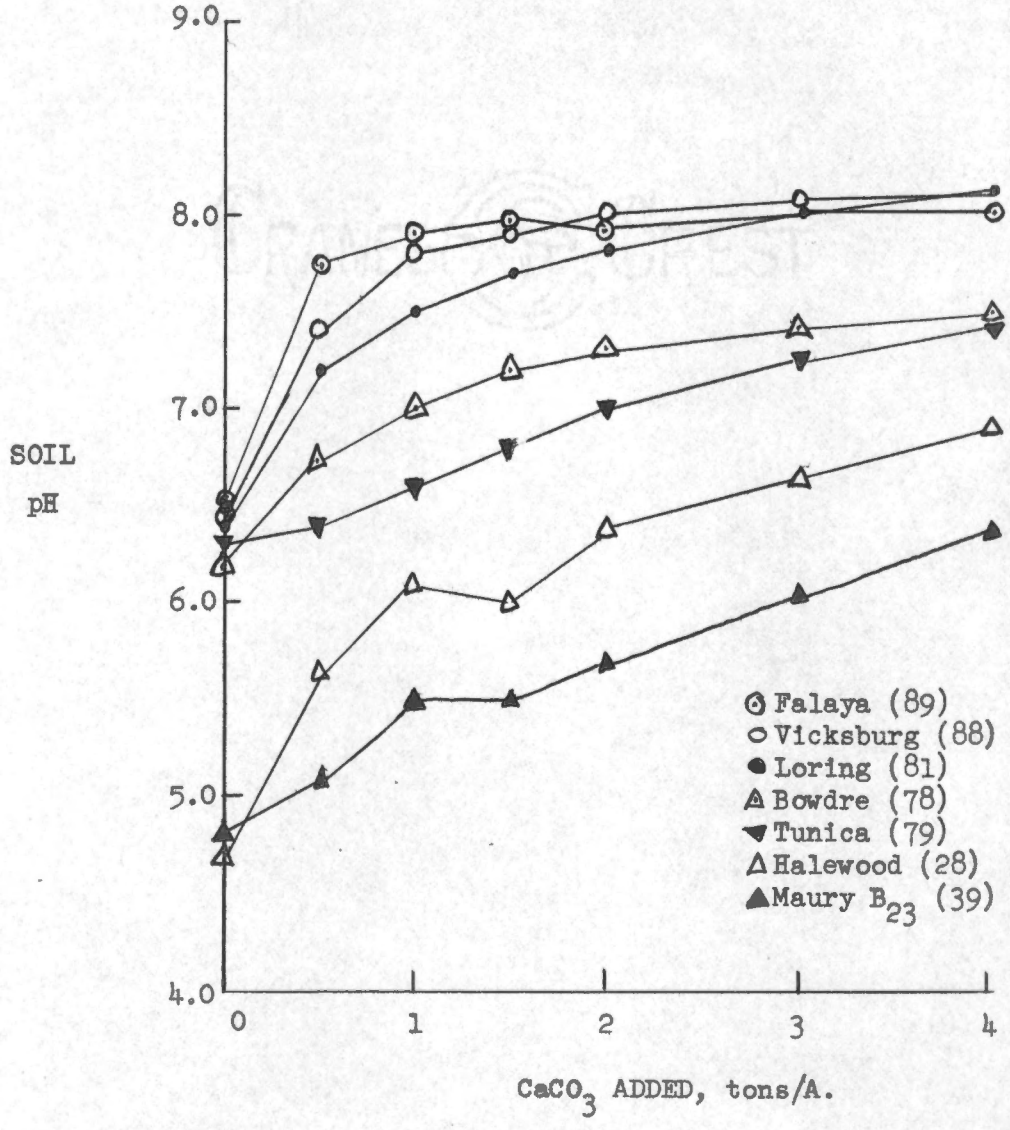


Fig. 5.--Titration curves for 7 Tennessee soils determined by moist incubation with $CaCO_3$.

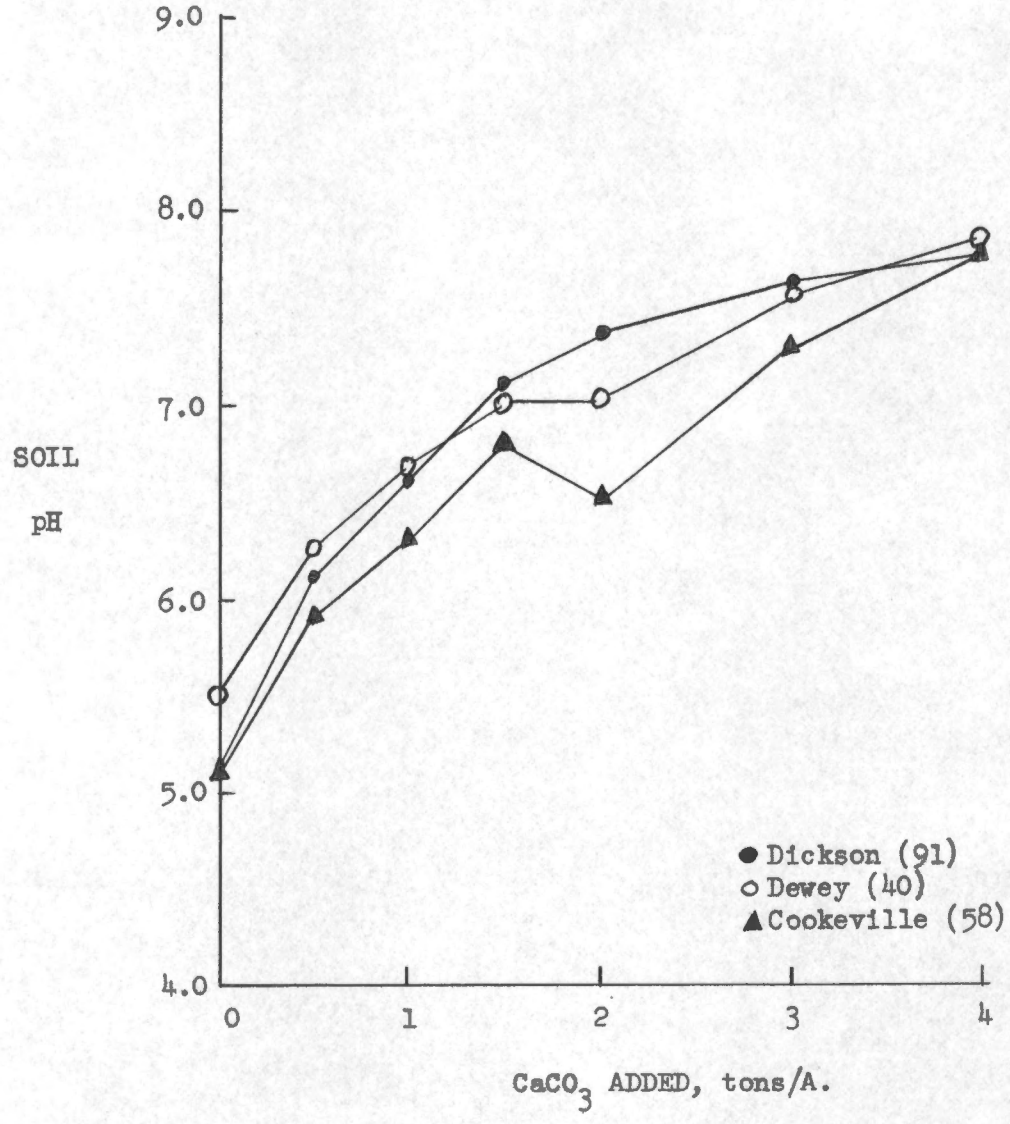


Fig. 6.-- Titration curves for 3 Tennessee soils determined by moist incubation with $CaCO_3$.

which were essentially straight lines. Increased buffering with increased soil pH was apparent with most soils as evidenced by the curved lines produced. This indicates that as the pH of most soils increased, their buffering capacity also increased requiring more calcium carbonate to effect a given pH change at the higher calcium carbonate levels than at the lower levels. This was attributed to pH dependent charge effect. Coleman and Mehlich (10) stated that as the pH increased the pH dependent charge increased and was at its maximum at about pH 10.0.

The shape of a particular titration curve would, of course, determine the lime requirement of the soil as determined from that curve. Any soils with similar titration curves would have correspondingly similar lime requirements. Since field applications of lime are made to adjust the soil reaction to some point within the range of the initial soil pH and pH 7.0, consideration should be restricted to this region of the titration curves. Those soils which were weakly buffered within this pH range had low cation exchange capacities and those which were strongly buffered had high cation exchange capacities. Furthermore, those with intermediate buffering capacities had medium cation exchange capacities. Soils which were base saturated tended to display lower buffering effects between the initial pH values and pH 7.0 than did soils with comparable cation exchange capacities but with lower base saturation values. This is shown by the Vicksburg, Falaya, and Baxter, sample 66.

Those soils which were high in clay and/or organic matter content displayed the highest buffering capacities. This effect was probably

though the effect of these constituents on the cation exchange capacity. Ross et al. (44) obtained a correlation coefficient of 0.906 between clay content and cation exchange capacity and 0.941 between organic matter content and cation exchange capacity. They stated that the relationship between cation exchange capacity and lime requirement was indicated by the effect of clay and organic matter content on the cation exchange capacity.

The titration curve of the Maury B_{23}, shown in figure 5, was essentially a straight line, being evenly buffered throughout the entire range of calcium carbonate additions, and that of the Halewood indicated that its buffering capacity increased considerably as the pH was increased by higher increments of calcium carbonate. This may have been an effect of organic matter. The Maury B_{23} was high in clay and low in organic matter content. The Halewood was high in organic matter content but lower in clay than the Maury B_{23}. Baver (2) stated that organic matter exhibited buffering effects at higher pH values than inorganic materials. It is recognized that this one observation is insufficient evidence for any such definite relationship to be established. However, the Bowdre and Tunica, soils fairly high in clay and organic matter content, had titration curves (figure 5) similar in shape to those of the Maury B_{23} and the Halewood. These curves did not show the low buffering effect at the lower ends of the curves which was shown by the Halewood curve. However, these soils were much higher in base saturation percentage and had much higher pH values. Possibly the organic fractions of these soils were responsible for the high buffering

effect throughout the entire range of the titration, whereas, in the case of the Halewood, the effect of the organic matter did not become apparent until the pH was increased somewhat. Another possible explanation for the different buffering capacities of these soils is the type of clay minerals.

Per cent base saturation, soil pH, and exchangeable aluminum apparently were not closely related to the buffering capacity. Soils with similar titration curves had widely different values for these properties in several cases. Those soils with pH values above about 5.2 or 5.3 had little or no exchangeable aluminum although some had high buffering capacities. The absence of exchangeable aluminum at the higher pH values is likely due to the formation of insoluble $Al(OH)_3$ which is believed to occur within the range of pH 5.0 to 5.5. Exchangeable aluminum may have affected the buffering of those soils in which appreciable amounts occurred but its effect would be difficult if not impossible to assess from these data.

To further study the relationships between soil properties and lime requirement, ten soils were selected from the incubation study for the determination of linear correlation between lime requirement by incubation and certain soil properties. These soils were selected on the basis of their similarity in pH values. The pH values ranged from 4.7 to 5.3. The range is wide considering that the lime requirement values were the amounts of calcium carbonate to raise the soil pH values from the initial points to the desired levels. This, of course, tended to cause some inconsistency in values for lime

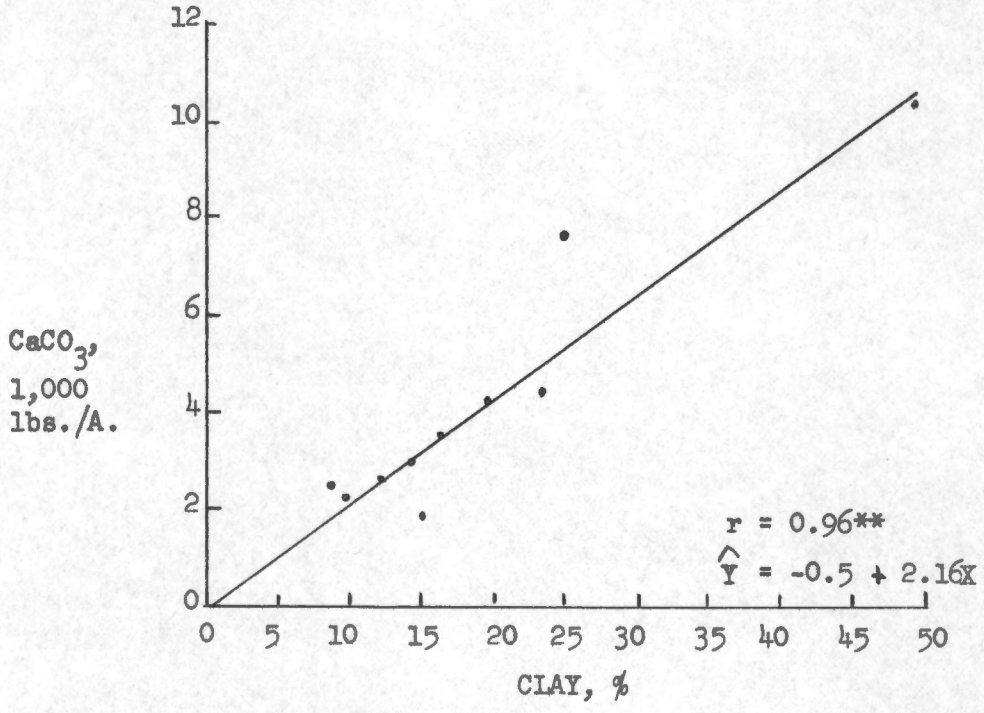
requirement in terms of the amount required to cause a given change in pH.

The linear correlation coefficients for soil properties compared to lime requirement by incubation are shown in table 7. Clay content gave the highest correlation coefficient, 0.96, 0.96, and 0.94 to pH 6.5, 6.8, and 7.0 respectively. Figure 7 shows the relationship between clay content and lime requirement to pH 6.8 by incubation. This was not consistent with the findings of Keeney and Corey (22) who reported insignificant correlations between clay content and lime requirement. However, they used soils which were considerably higher in organic matter than most of the soils used in this study. Morgan (35) stated that the organic matter content often masks the effect of clay content on the cation exchange capacity of soils because of the greater influence of organic matter on this property. This being true one would expect the lime requirement of soils high in organic matter to vary more with variations in the organic matter content than with variations in clay content. This was probably the case in the report of Keeney and Corey. Ross et al. (44), on the other hand, obtained a relatively high correlation between lime requirement by incubation and clay content of nine Michigan soils. They indicated that clay content was an important factor affecting the buffering capacity and lime requirement of soils. Clay would be expected to be the constituent having the greatest influence on cation exchange capacity, buffering capacity, and lime requirement of soils low in organic matter.

Table 7.--Correlation of lime requirement by $CaCO_3$ incubation with selected soil properties of 10 highly acid Tennessee soils.

Soil Property	to pH 6.5	to pH 6.8	to pH 7.0
% Clay	0.96**	0.96**	0.94**
Exchangeable Al	0.94**	0.92**	0.89**
C.E.C.	0.75*	0.83**	0.85**
% Organic matter	0.04	0.15	0.69*
% Base saturation	-0.09	-0.06	-0.06

*Significant at 5 per cent level. **Significant at 1 per cent level.



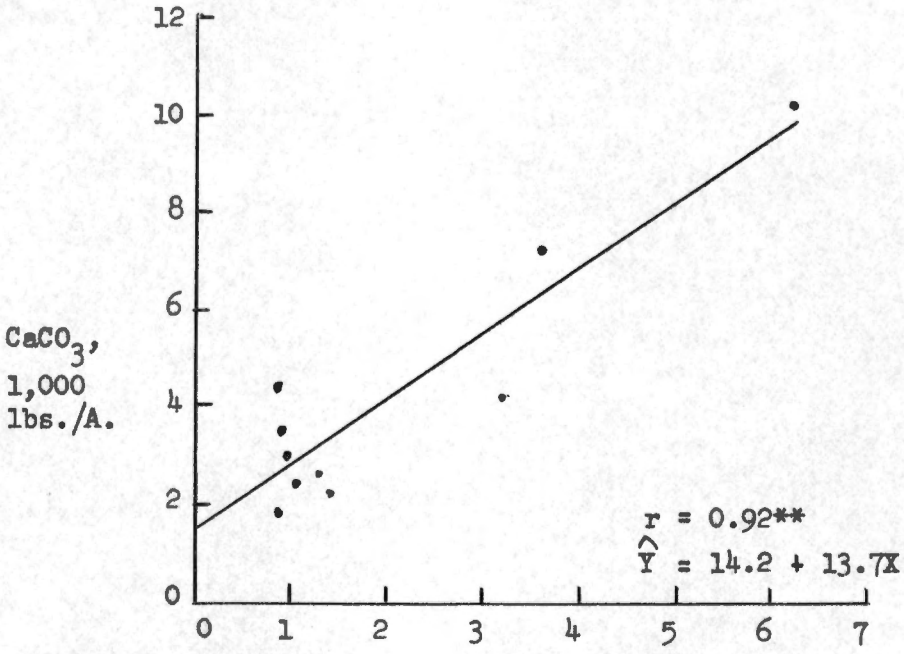
** Significant at the 1 per cent level.

Fig. 7.--Relationship between lime requirement by $CaCO_3$ incubation to pH 6.8 and per cent clay for 10 Tennessee soils.

Exchangeable aluminum gave a high correlation with lime requirement to all three pH levels for these 10 acid soils. Figure 8 shows the relationship between exchangeable aluminum and lime requirement to pH 6.8. The correlation coefficient decreased from 0.94 for pH 6.5 to 0.89 for pH 7.0. This was as expected since aluminum is effective as a buffer against lime only at the lower pH values. This may appear in contrast to the previous statements regarding the relationship between exchangeable aluminum and buffering of the soil, however, it should be pointed out that in the case of the 22 soils under discussion previously, the soil pH values varied widely. In the case of the 10 acid soils, the pH values were low and exchangeable aluminum would be expected to have considerable influence on the lime requirement.

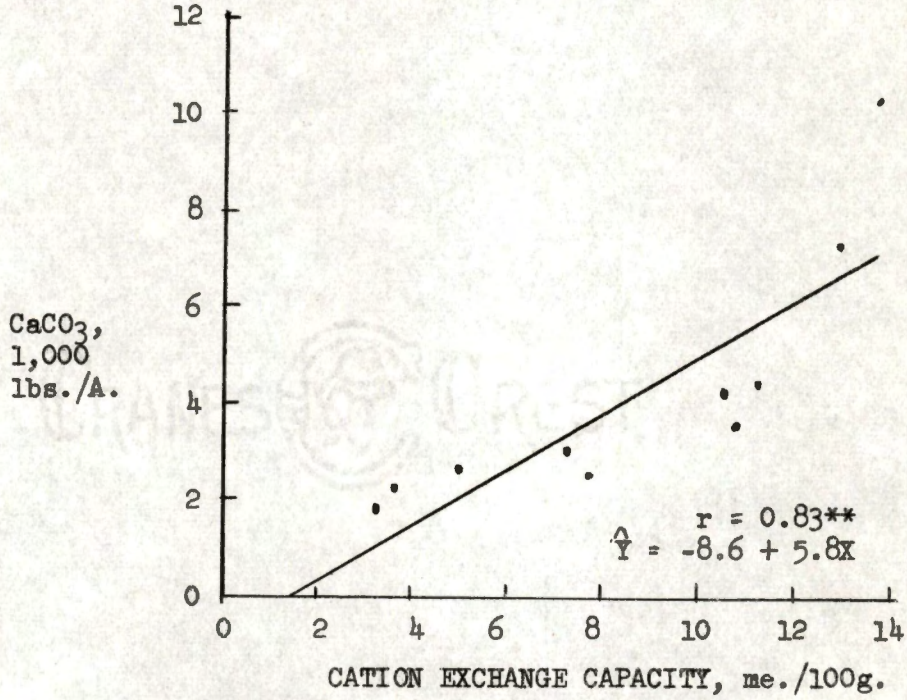
Cation exchange capacity gave a lower correlation coefficient than either clay content or exchangeable aluminum. The values were 0.75, 0.83, and 0.85 for pH 6.5, 6.8, and 7.0. The relationship between cation exchange capacity and lime requirement to pH 6.8 is shown in figure 9.

Organic matter content was not significantly correlated with lime requirement to pH 6.5 or 6.8 but was significant at the five per cent level to pH 7.0. This was probably due to the relationship discussed earlier between organic matter and the buffering capacity of soils as the pH was increased. The low correlation between organic matter content and lime requirement was not surprising in view of the fact that most of these soils were low in organic matter, thus clay



** Significant at the 1 per cent level.

Fig. 8.--Relationship between lime requirement by $CaCO_3$ incubation to pH 6.8 and exchangeable aluminum for 10 Tennessee soils.



**Significant at the 1 per cent level.

Fig. 9.--Relationship between lime requirement by $CaCO_3$ incubation to pH 6.8 and cation exchange capacity for 10 Tennessee soils.

content was expected to have the greater influence on lime requirement.

Per cent base saturation by the ammonium acetate method was not significantly correlated with lime requirement to either pH level.

IV. EVALUATION OF METHODS OF PREDICTING LIME REQUIREMENT AS COMPARED TO LIME REQUIREMENT BY CALCIUM CARBONATE INCUBATION

Predicted lime requirement values to pH 6.5, 6.8, and 7.0 by the Auburn buffer, Ohio buffer, Mississippi buffer, the pH method, and to 25, 20, and 15 per cent base unsaturation of the cation exchange capacity by the ammonium acetate method are shown in tables 4 through 6 along with the incubation lime requirement values. Predicted lime requirement values by the buffer solutions were calculated using the equations of Adams and Evans (1) and according to the procedure outlined in the appendix. Estimated lime requirement values to 25, 20, and 15 per cent base unsaturation were calculated from the results of the neutral normal ammonium acetate determination of the cation exchange capacity and base status of the soils. These values of base unsaturation were chosen because they closely approximate the base unsaturation values obtained for soils with pH values of 6.5, 6.8, and 7.0 as determined by the equation of Adams and Evans (1). The lime requirement values by the pH method were estimated using a "rule of thumb", whereby 2,000 pounds per acre of calcium carbonate is recommended for each pH unit increase desired. This is the procedure used by the Tennessee Soil Testing Laboratory with the use of a lime factor of about 3.

Lime requirements predicted by the buffer solutions were closely related to exchangeable acidity measured by the buffer solutions. This was as expected since the exchangeable acidity values measured by the buffer solutions were used in calculating the predicted lime requirement values. It should be pointed out that the two sets of values were not directly proportional to one another because different pH values gave different base unsaturation values and both base unsaturation and exchangeable acidity are involved in calculating the predicted lime requirements. The equation used in calculating the lime requirement values by the buffer solutions has an inherent compensating feature. As explained by Adams and Evans (1), the equation compensates for errors caused by variations in base unsaturation at the same pH values. If, at a given pH value, the equation for pH-base unsaturation relationship overestimates the actual base unsaturation, the first part of the equation will be too small but the other part will be too large, because, when the initial base unsaturation is overestimated the desired change in base unsaturation is also overestimated. An example of this is the Cookeville and Dickson. Both had pH values of 5.1 and similar cation exchange capacities, 7.3 and 7.7 me. per 100 g. of soil; but their base saturation percentages were 27.0 and 47.0 respectively. The predicted lime requirements to all three pH levels by each buffer solution were about the same for both soils.

The exchangeable acidity of a soil may be high and the soil pH be near the desired level, yet the predicted lime requirements will be low. For example, the Tunica had exchangeable acidity values of 5.6,

2.9, and 4.0 me. per 100 g. of soil by the Auburn, Ohio, and Mississippi buffers and a pH of 6.4; but the lime requirement values predicted by each of the three buffers were 500, 200, and 300 pounds per acre to pH 6.5. The compensating feature was involved also in the case of soils with low pH values and low exchangeable acidity. Although the low pH values tended to cause high lime requirement predictions due to high base unsaturation values, the low exchangeable acidity values reduced the requirement. An example of this was the Clarksville, sample 1.

Correlation coefficients for the relationships between lime requirement by calcium carbonate incubation and the predicted lime requirements by the Auburn, Ohio, and Mississippi buffers, the ammonium acetate method, and the pH method for the 22 soils used in the incubation study are presented in table 8. All were significant at the one per cent level. The Auburn buffer predictions gave the highest correlation coefficients when compared to the lime requirement by calcium carbonate incubation, being 0.95, 0.96, and 0.95 to pH 6.5, 6.8, and 7.0 respectively. The Ohio buffer gave 0.94, 0.94, and 0.95 correlation coefficients respectively to the three pH levels. The values for the Mississippi buffer were 0.95, 0.93, and 0.94.

Predictions by the three buffers were all highly correlated with lime requirement by incubation to the three pH levels indicating that where there were variations in incubation lime requirements between soils there were proportinate variations in the predicted lime requirements by the buffer solutions. This, however, does not give an indication of the amount of predicted variation corresponding to a given variation in the

Table 8.--Correlation of lime requirement by $CaCO_3$ incubation with various lime requirement methods and between methods for 22 Tennessee soils.

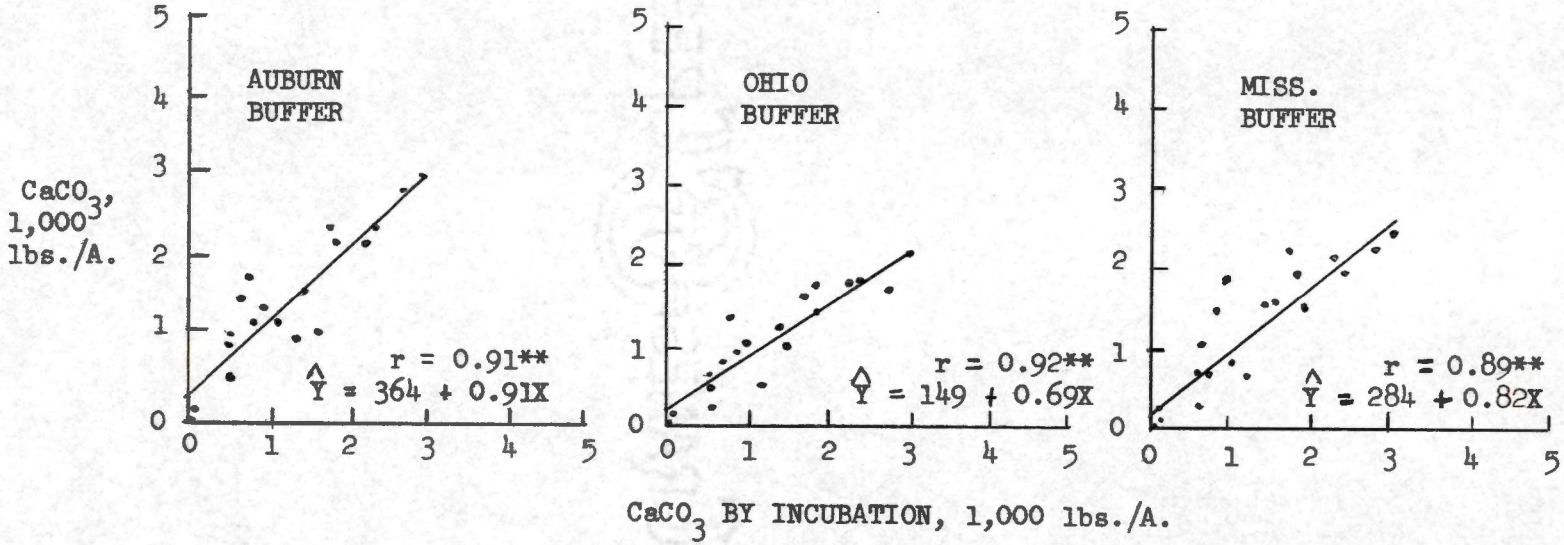
Correlation between:	to pH 6.5	to pH 6.8	to pH 7.0
$CaCO_3$ incubation and Auburn buffer	0.95**	0.96**	0.95**
$CaCO_3$ incubation and Ohio buffer	0.94**	0.94**	0.95**
$CaCO_3$ incubation and Miss. buffer	0.95**	0.93**	0.94**
$CaCO_3$ incubation and NH_4OAc	0.73**	0.76**	0.75**
$CaCO_3$ incubation and pH method	0.72**	0.68**	0.68**
Auburn buffer and Ohio buffer	0.96**	0.95**	0.95**
Auburn buffer and Miss. buffer	0.96**	0.94**	0.92**
Auburn buffer and NH_4OAc	0.72**	0.72**	0.68**
Ohio buffer and Miss. buffer	0.97**	0.95**	0.95**
Ohio buffer and NH_4OAc	0.69**	0.68**	0.61**
Miss. buffer and NH_4OAc	0.75**	0.75**	0.87**

**significant at the 1 per cent level.

incubation lime requirement. Figures 10 through 12 show the relationships between the amounts of calcium carbonate required to pH 6.5, 6.8, and 7.0 as determined by incubation and that predicted by each of the buffer solutions. In order to facilitate graphic presentation of the relationships, values for two very high lime requirement soils were omitted. These were the Maury B_{23} and the Halewood. The correlation coefficients shown in the figures are those obtained from correlation analyses of the remaining 20 soils of the incubation study. These were also significant at the one per cent level. The values omitted were, in all cases, relatively close to the lines determined by linear regression analyses.

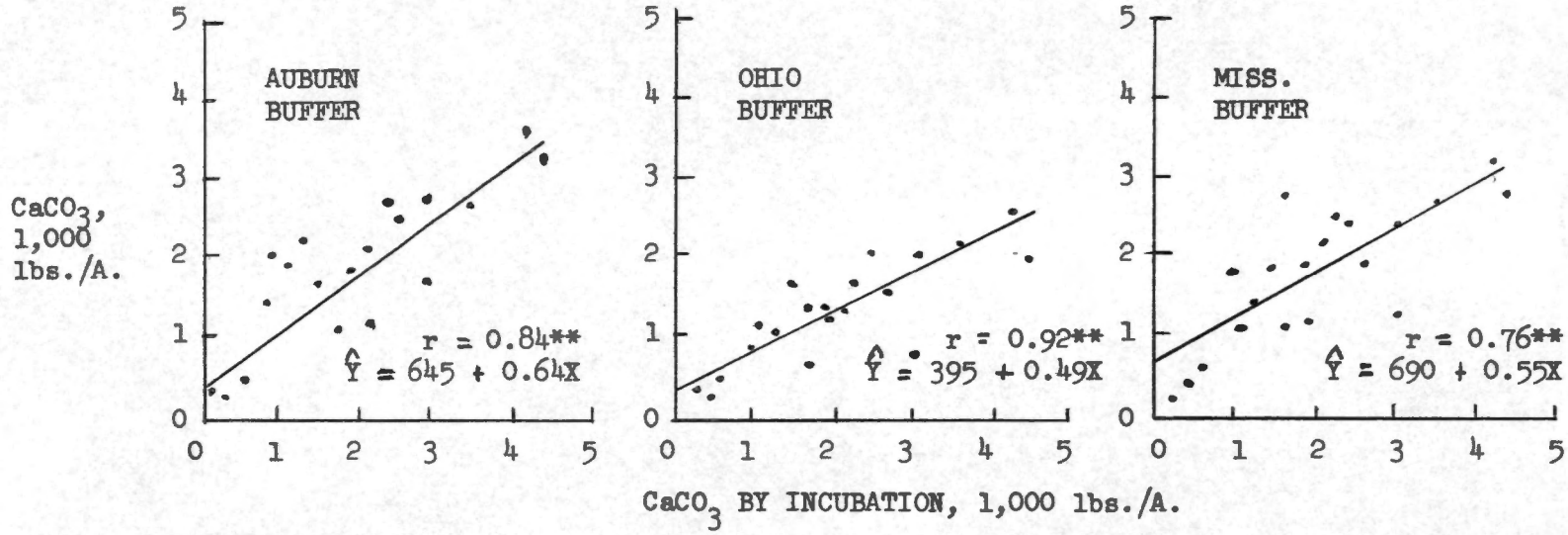
All the linear regression lines had slopes less than 1.0. However, considering the entire range of lime requirements, the Auburn buffer gave predictions which were closer to the incubation values at all three pH levels than did the Ohio or the Mississippi buffers. The Mississippi buffer predictions were closer to the incubation values than the Ohio buffer. The slopes of the lines and their junctions with the axes indicate that there was a region, evident in each case, at the higher lime requirement levels where the buffer solutions were underestimating the lime requirement. The effects were more apparent to pH 6.8 than to pH 6.5, and even more apparent to pH 7.0. At the low lime requirement levels, the buffer solutions predicted values which were very near the incubation values. These observations indicate that probably a line which best fits the points would be a curve rather than a straight line.

In the intermediate lime requirement range, the points spread out considerably, but, if a line with a slope of 1.0 is superimposed on the



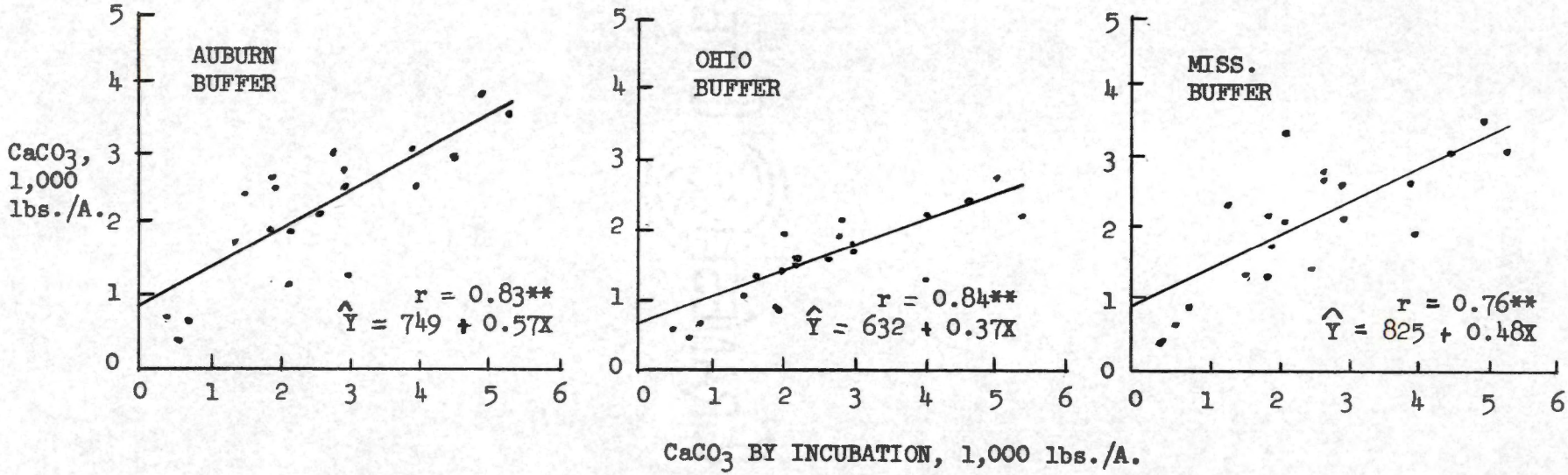
**Significant at the 1 per cent level.

Fig. 10.--Lime requirement by $CaCO_3$ incubation compared to lime requirement predicted by buffer methods to pH 6.5 for 20 Tennessee soils.



**Significant at the 1 per cent level.

Fig. 11.--Lime requirement by $CaCO_3$ incubation compared to lime requirement predicted by buffer methods to pH 6.8 for 20 Tennessee soils.



** Significant at the 1 per cent level.

Fig. 12.--Lime requirement by $CaCO_3$ incubation compared to lime requirement predicted by buffer methods to pH 7.0 for 20 Tennessee soils.

graphs, about as many points fall below the line as above in the cases of the Auburn and Mississippi buffers, indicating that this is probably a region of high error in predictions. The Ohio buffer predictions were consistently lower than the incubation values except at the very low lime requirement levels. Within the high range of lime requirements, all buffers consistently predicted values lower than the incubation values, and the predictions were lower relative to the incubation values in going from pH 6.5 to 6.8 and 7.0. These relationships are not surprising in view of the pH dependent charge effect. When the buffer solutions were mixed with soils having high lime requirements, the soil-buffer solution pH values at the equilibrium point were low, since the greater the lime requirements the greater the depression of the soil-buffer pH values. This then restricted the development of acidity caused by the development of pH dependent charge by the buffer solutions, but it was developed fully and measured by the calcium carbonate. The higher the soil pH was raised by additions of calcium carbonate, the greater the pH dependent charge effect became, thus accounting for the even greater differences at the higher pH levels.

If the above hypothesis be true, the buffer solution with the highest soil-buffer pH values at the point of equilibrium would be expected to be more effective in measuring lime requirement due to the effect of pH dependent charge and would give predictions at the high lime requirement levels which would be nearer to the incubation values. Furthermore, a buffer solution which was weakly buffered and gave low soil-buffer pH values throughout the range of lime requirement values

would be expected to show consistently low values throughout the entire range except at low lime requirement levels where little or no pH dependent charge is developed as apparent from the calcium carbonate titration curves shown in figures 2 through 6. The soil-Auburn buffer solution pH values were highest of the three buffers and gave lime predictions closer to the incubation values. The soil-Mississippi buffer pH values were next highest and the predictions were next in nearness to the incubation values. The soil-Ohio buffer pH values were, in general, lowest of the three and the solution itself had considerably less buffering capacity than the other two. It gave low predictions throughout most of the lime requirement range when compared to the incubation values.

The soil-buffer solution pH values with a given buffer are related to the initial buffer solution pH and its buffering capacity. In order for a buffer solution to be effective in measuring lime requirement due to pH dependent charge for high lime requirement soils, the initial pH of the buffer solution needs to be relatively high and it should be highly buffered over a wide range so that the pH is not greatly depressed when high lime requirement soils are mixed with the solution. Of the three buffers evaluated, the Auburn buffer came nearer to meeting these requirements.

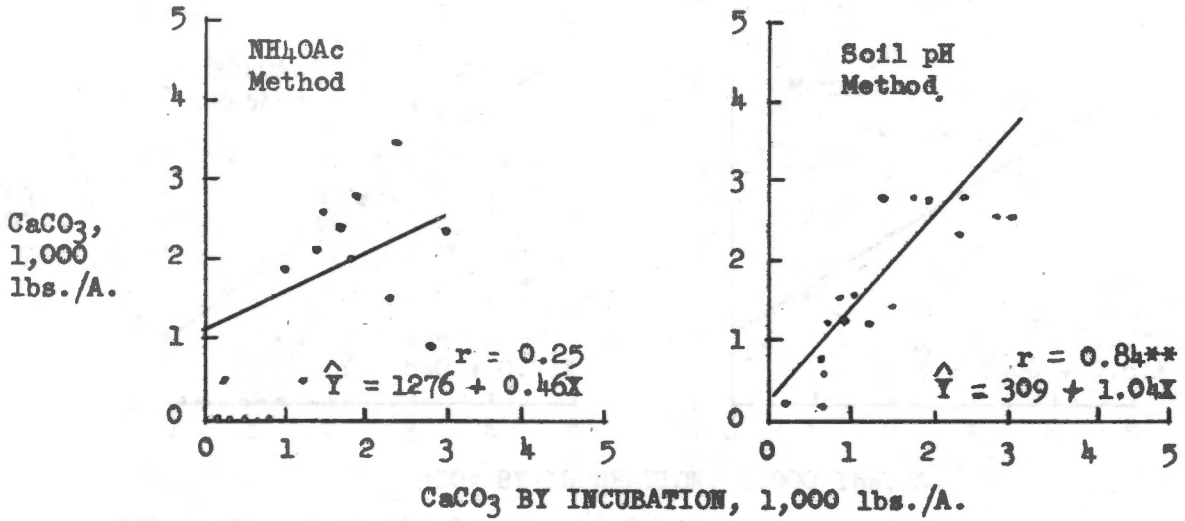
It is conceivable that a solution which allowed full development of pH dependent lime requirement at the higher lime requirement levels might develop too great a pH dependent charge in the intermediate lime requirement range, thus overestimating the lime requirements of these

soils.

No buffer solution could compensate for the increased lime requirement due to pH dependent charge when going from lower to higher pH levels except through adjustments in the equation used in calculating the predictions, in which case, the values would be based on empirical rather than actual measurements. Predictions to all pH levels are made with buffer solutions using one pH reading, therefore, a given amount of acidity due to pH dependent charge is measured and has the same amount of influence on predictions to all pH levels. With calcium carbonate incubation, as the pH is increased to the higher levels by additions of calcium carbonate, the correct amount of pH dependent charge is developed and its full influence shown.

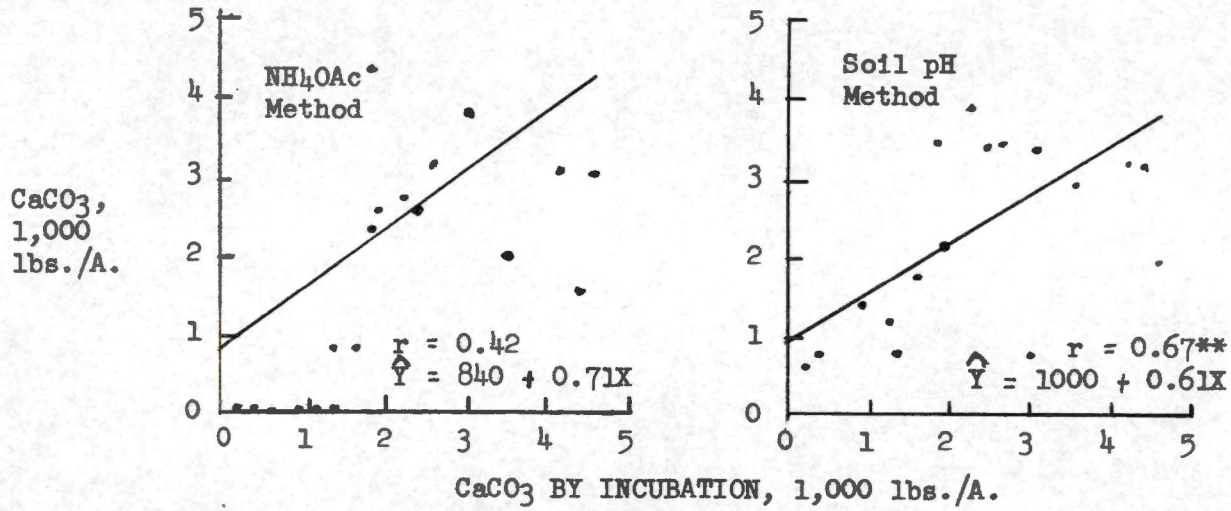
The coefficients of correlation between lime requirement by incubation and by the ammonium acetate method were significant at the one per cent level to all three pH levels, however, they were considerably lower than in the cases of the buffer solutions. When the two high lime requirement values were omitted the correlation coefficients were reduced to the extent that the two methods were significantly correlated at the five per cent level only at pH 7.0. The points of the graphs shown in figures 13 through 15 are extremely scattered and seemingly show no definite trends.

Correlations between incubation lime requirements and estimates made by the pH method were significant at the one per cent level to all three pH levels and for both the 22 sample and the 20 sample correlations. As was expected, the pH method overestimated lime requirement for those



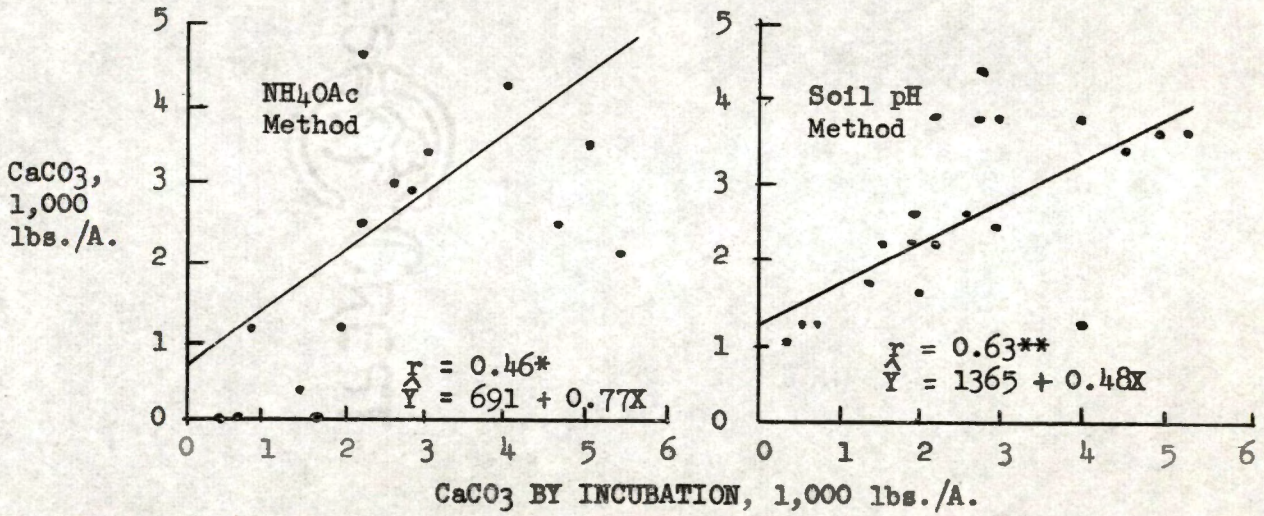
**Significant at the 1 per cent level.

Fig. 13.--Lime requirement by $CaCO_3$ incubation compared to lime requirement predicted by NH_4OAc method to 25 per cent base unsaturation and by soil pH method to pH 6.5 for 20 Tennessee soils.



**Significant at the 1 per cent level.

Fig. 14.--Lime requirement by $CaCO_3$ incubation compared to lime requirement predicted by NH_4OAc method to 20 per cent base unsaturation and by soil pH method to 6.8 for 20 Tennessee soils.



*Significant at the 5 per cent level.

**Significant at the 1 per cent level.

Fig. 15.--Lime requirement by $CaCO_3$ incubation compared to lime requirement predicted by NH_4OAc method to 15 per cent base unsaturation and by soil pH method to pH 7.0 for 20 Tennessee soils.

soils with low pH values and low buffering capacities and underestimated lime requirement in the cases involving soils with high buffering capacities. Figure 13 through 15 show the relationships between incubation lime requriement and that estimated by the pH method. Generally speaking, the estimates were most accurate for those soils which had intermediate cation exchange capacities. For soils with low cation exchange capacities and low buffering capacities, the estimate becomes more accurate when predicting to the higher pH levels. As the pH values of these soils were increased by additions of calcium carbonate, their buffering capacity increased as evidenced by their titration curves. This caused their incubation lime requirement to be increased, but the pH method does not take into account differential buffering, thus, the values were closer together at the high lime requirement levels. Examples of this relationship were the Hartsells and Hatchie.

Overton (36) reporting on a study of lime requirement of Tennessee soils concluded that soil pH alone was not a satisfactory basis for determining lime requirement but the method could be improved by a consideration of soil texture along with pH.

The lime requirement values predicted by each buffer method and by ammonium acetate to all three pH levels were compared one with the others by correlation analyses and the results shown in table 8. All were significant at the one per cent level. Predictions by the three buffer solutions gave higher correlations, ranging from 0.92 to 0.97, when compared one to the other. Lower correlation coefficients were

obtained in comparing the buffer method predictions with ammonium acetate estimates. The values ranged from 0.61 to 0.75.

V. COMPARISON OF THREE BUFFER SOLUTION METHODS FOR PREDICTING LIME REQURIEMENT ON UNTREATED SOIL SAMPLES

Seventy soil samples not involved in the incubation study were used to study the relationships between the lime requirement predictions made by the Auburn, Ohio, and Mississippi buffer solutions relative to the properties of the solutions themselves and the properties of the soils. Some of the physical and chemical properties and the exchangeable acidity values of the soils determined by various methods are shown in tables 9 through 11.

Several of the samples are from B and C horizons which causes considerable contrast in properties. Textures ranged from a loamy sand to clays with the clay content ranging from 7.8 to 70.2 per cent. Organic matter content ranged from a low of 0.07 per cent to a high of 5.80 per cent. All B and C horizons had organic matter contents less than one per cent and all but seven A horizons had less than two per cent.

Cation exchange capacities ranged from 3.1 to 33.0 me. per 100 g. of soil. Base saturation percentages varied from about 4.0 to over 100 per cent. Some total bases and base saturation values were not determined because the samples were taken from heavily limed plots at the West Tennessee Agricultural Experiment Station, Ames Plantation, and Fort Pillow Farm. The experimental plots from which these samples were taken

Table 9.--Selected physical properties of some Tennessee soils used in lime requirement study.

Sample No.	Soil Series	Horizon	Inches Depth	Texture	Per Cent Clay	Per Cent Organic Matter
2	Clarksville	B_{21}	18-24	Clay loam	38.1	0.24
3	Clarksville	C^{1}	49-57	Clay loam	35.6	0.17
5	Clarksville	B^{2}	18-25	Loam	19.4	0.22
6	Clarksville	C^{2}	34-52	Loam	13.8	0.07
8	Sequoia	B_{2}	14-17	Silty clay	46.2	0.67
9	Sequoia	C^{1}	21-24	Clay	42.6	0.39
10	Sequoia	A^{1}	2-5	Silt loam	18.6	2.74
11	Sequoia	B^{p}	20-23	Silty clay loam	37.0	0.17
12	Sequoia	C^{2}	24-27	Clay loam	38.9	0.17
14	Decatur	B^{1}_{2}	19-22	Clay	64.5	0.42
15	Decatur	B_{3}	43-46	Clay	70.2	0.15
16	Decatur	A^{3}	2-5	Silt loam	21.6	2.37
17	Decatur	B^{p}_{2}	23-26	Silty clay loam	37.2	0.42
18	Decatur	B_{3}	43-46	Clay	50.1	0.27
19	Grenada	A^{3}	1-4	Silt loam	16.2	1.09
20	Grenada	B^{p}_{22}	14-17	Silt loam	24.1	0.40
21	Grenada	B_{3m2}	29-32	Silt loam	16.2	0.40
22	Grenada	A^{3m2}	1-4	Silt loam	16.6	1.23
23	Grenada	B^{p}_{22}	14-17	Silt loam	21.7	0.66
24	Grenada	B_{3m2}	29-32	Silt loam	17.0	0.36
25	Memphis	A^{3m2}	1-4	Silt loam	20.0	1.89
26	Memphis	B^{p2}_{22}	11-14	Silt loam	25.4	0.49
27	Memphis	C^{2}_{1}	37-40	Silt loam	18.4	0.17
29	Halewood	B_{21}	12-15	Clay	50.6	1.04
30	Halewood	C^{1}_{1}	34-42	Loam	26.3	0.18
31	Halewood	A^{1}_{2}	0-3	Loam	25.9	5.80
32	Halewood	B_{2}	10-17	Clay Loam	29.4	0.74

Table 9.--continued.

Sample No.	Soil Series	Horizon	Inches Depth	Texture	Per Cent Clay	Per Cent Organic Matter
33	Halewood	C_1	27-39	Sandy loam	13.4	0.55
34	Maury	A^1	0-9	Silt loam	24.0	2.57
35	Maury	B^p_2	24-36	Silt loam	19.8	0.47
36	Maury	C^1	38-42	Loam	25.4	0.22
37	Maury	A^1	1-5	Silt Loam	17.9	1.61
38	Maury	B^p_{21}	27-32	Silty clay loam	29.7	0.32
41	Dewey	B_{22}	23-39	Clay	66.0	0.30
42	Dewey	C^1	48-58	Clay	57.4	0.30
43	Dewey	A^1	0-8	Loam	17.1	1.39
44	Dewey	B^p_{22}	22-38	Clay	53.8	0.30
45	Dewey	C^1	50-62	Clay	69.5	0.24
46	Hartsells	A^1_2	3-7	Loam	14.0	0.82
47	Hartsells	B^2	10-18	Loam	18.8	0.62
48	Hartsells	C^1_2	24-40	Sandy clay loam	21.9	0.29
50	Hartsells	B^2_1	9-18	Clay loam	28.0	0.66
51	Hartsells	C^2_1	30-33	Sandy loam	15.6	0.24
53	Baxter	B^1_2	15-18	Silt loam	26.8	0.84
54	Baxter	C^2_2	38-53	Silty clay loam	38.6	0.55
55	Baxter	A^2	0-9	Silt loam	13.1	1.78
56	Baxter	B^p_2	15-22	Silty clay loam	29.6	0.71
57	Baxter	C^1_2	30-35	Silty clay loam	33.2	0.51
59	Cookeville	B^1_2	22-27	Silty clay loam	27.8	0.74
60	Cookeville	C^2_1	31-34	Silty clay loam	41.0	0.64
61	Cookeville	A^1	0-9	Silt loam	16.2	1.33
62	Cookeville	B^p_2	18-26	Silty clay loam	32.1	0.74
63	Cookeville	C^1_2	42-62	Silty clay loam	38.9	0.66
64	Bowdre	A^1_p	0-10	Clay loam	36.6	2.91

Table 9.--continued.

Sample No.	Soil Series	Horison	Inches Depth	Texture	Per Cent Clay	Per Cent Organic Matter
65	Bowdre	D_u	20-34	Loamy sand	7.8	0.58
67	Baxter	A^p	6-12	Clay loam	30.6	0.53
69	Baxter	A^p	6-12	Silty clay loam	34.2	0.57
70	Baxter	A^p	0-6	Silt loam	12-6	1.95
71	Dexter	A^p	0-6	Silt loam	12.2	1.28
72	Dexter	A^p	0-6	Silt loam	12.8	1.28
73	Dexter	A^p	0-6	Silt loam	11.6	0.57
74	Dexter	A^p	0-6	Silt loam	12.4	0.50
75	Loring	A^p	0-6	Silt loam	9.8	0.70
77	Bowdre	A^p	0-10	Clay loam	33.4	2.72
80	Tunica	A^p	0-6	Clay loam or clay	41.8	3.52
82	Loring	A^p	0-6	Silt loam	11.4	0.63
84	Hatchie	A^p	0-6	Loam	13.1	1.50
85	Olivier	A^p	0-6	Silt loam	21.2	0.98
87	Vicksburg	A^p	0-6	Silt loam	18.8	1.29
90	Falaya	A^p_p	0-6	Silt loam	19.8	1.05

Table 10.--Selected chemical properties of some Tennessee soils used in lime requirement study.

Sample No.	Soil Series	C.E.C. me./100g.	Total bases me./100g.	Per cent Base saturation	Soil pH	Exch. Al me./100g.	Exch. H me./100g.
2	Clarksville	4.8	0.7	14.6	4.9	2.33	0.37
3	Clarksville	3.5	0.1	2.8	4.6	2.25	0.00
5	Clarksville	5.1	0.2	3.9	4.7	3.38	0.17
6	Clarksville	3.1	0.2	6.4	4.8	2.17	0.00
8	Sequoia	14.5	1.8	12.4	4.8	8.62	0.23
9	Sequoia	16.9	1.2	7.1	4.8	11.61	0.00
10	Sequoia	9.9	7.4	74.7	5.9	0.00	0.25
11	Sequoia	12.5	1.5	12.0	5.0	8.10	0.00
12	Sequoia	14.1	1.6	11.3	5.0	9.07	0.03
14	Decatur	9.8	7.2	73.5	5.3	0.15	0.12
15	Decatur	9.4	1.7	18.1	5.4	3.15	0.09
16	Decatur	9.6	7.4	77.1	6.2	0.00	0.14
17	Decatur	7.3	5.6	76.7	5.8	0.00	0.14
18	Decatur	6.9	1.4	20.3	4.8	2.99	0.03
19	Grenada	8.5	6.3	74.1	5.6	0.48	0.00
20	Grenada	13.2	7.3	55.3	5.1	3.43	0.02
21	Grenada	10.0	3.9	39.0	5.1	3.60	0.04
22	Grenada	8.2	3.8	46.3	5.2	1.46	0.04
23	Grenada	11.7	5.0	42.7	5.0	3.40	0.27
24	Grenada	9.5	4.1	43.1	5.1	3.69	0.00
25	Memphis	13.8	16.1	116.7	6.5	0.00	0.14
26	Memphis	13.6	9.5	69.8	5.1	2.02	0.12
27	Memphis	9.9	5.1	51.5	5.1	3.10	0.08
29	Halewood	11.5	1.8	15.6	5.0	3.92	0.03
30	Halewood	6.6	0.7	10.6	5.0	2.99	0.02
31	Halewood	20.8	8.8	42.3	5.4	1.05	0.25
32	Halewood	10.3	1.4	13.6	4.9	6.19	0.00

Table 10.--continued.

Sample No.	Soil Series	C.E.C. me./100g.	Total bases me./100g.	Per Cent Base saturation	Soil pH	Exch. Al me./100g.	Exch. H me./100g.
33	Halewood	8.9	1.4	15.7	5.0	5.57	0.00
34	Maury	17.5	14.9	85.1	6.0	0.00	0.19
35	Maury	16.3	13.9	85.3	6.0	0.00	0.20
36	Maury	13.4	11.7	87.3	6.0	0.00	0.16
37	Maury	10.8	10.1	93.5	6.5	0.00	0.13
38	Maury	11.1	8.8	79.3	5.8	0.10	0.11
41	Dewey	8.6	4.3	50.0	4.9	2.45	0.00
42	Dewey	7.3	1.3	17.8	4.7	4.97	0.00
43	Dewey	5.9	2.4	40.7	5.6	0.44	0.00
44	Dewey	8.2	1.2	14.6	5.0	4.19	0.00
45	Dewey	8.7	0.4	4.6	4.9	6.14	0.00
46	Hartsells	4.9	1.2	24.5	5.2	1.61	0.01
47	Hartsells	6.1	2.2	36.1	5.0	2.18	0.03
48	Hartsells	5.6	0.5	8.9	4.9	3.20	0.05
50	Hartsells	10.7	2.7	25.2	4.9	4.65	0.00
51	Hartsells	6.0	0.5	8.3	4.8	3.50	0.03
53	Baxter	8.1	2.0	24.7	4.8	3.94	0.05
54	Baxter	7.8	1.7	21.8	4.8	4.86	0.00
55	Baxter	6.9	4.0	58.0	6.0	0.17	0.11
56	Baxter	7.8	5.6	71.8	5.0	1.12	0.24
57	Baxter	9.3	6.2	66.7	5.0	1.95	0.12
59	Cookeville	8.0	3.7	46.3	4.8	2.51	0.00
60	Cookeville	10.1	4.7	46.5	4.8	3.12	0.00
61	Cookeville	8.2	10.1	123.2	6.5	0.00	0.11
62	Cookeville	9.9	7.5	75.8	4.9	0.61	0.26
63	Cookeville	9.0	2.5	27.8	5.0	1.08	0.29
64	Bowdre	32.7	20.0	61.2	5.6	0.05	0.17

Table 10.--continued.

Sample No.	Soil Series	C.E.C. me./100g.	Total bases me./100g.	Per Cent Base saturation	Soil	Exch. Al me./100g.	Exch. H me./100g.
65	Bowdre	6.0	4.2	70.0	5.4	0.46	0.17
67	Baxter	10.5	10.8	102.8	5.9	0.10	0.09
69	Baxter	11.2	7.6	67.6	5.2	1.12	0.23
70	Baxter	11.0	8.5	77.3	5.3	0.22	0.14
71	Dexter	9.0	4.0	44.4	6.2	0.00	0.08
72	Dexter	9.0	--*	--*	7.1	0.00	0.06
73	Dexter	9.0	--	--	6.7	0.00	0.06
74	Dexter	9.0	--	--	6.3	0.00	0.08
75	Loring	7.0	--	--	7.1	0.00	0.05
77	Bowdre	32.7	--	--	6.5	0.00	0.07
80	Tunica	33.0	--	--	6.7	0.00	0.11
82	Loring	7.0	--	--	7.3	0.00	0.06
84	Hatchie	10.0	--	--	7.2	0.00	0.10
85	Olivier	11.2	--	--	7.1	0.00	0.08
87	Vicksburg	7.4	--	--	7.2	0.00	0.14
90	Falaya	12.2	--	--	7.1	0.00	0.09

*Not determined.

Table 11.--Exchangeable soil acidity measured by Yuan titration, Auburn buffer, Ohio buffer, Mississippi buffer, and by the NH_4OAc methods.

Sample No.	Soil Series	me. per 100 grams of soil				
		Yuan titration	Auburn buffer	Ohio buffer	Miss. buffer	NH_4OAc
2	Clarksville	2.70	3.2	2.9	4.67	4.1
3	Clarksville	2.25	3.2	2.6	3.33	3.3
5	Clarksville	3.55	4.0	3.7	4.67	4.9
6	Clarksville	2.15	2.4	2.6	3.33	3.9
8	Sequoia	8.85	11.1	6.9	14.67	12.6
9	Sequoia	11.45	13.0	7.5	18.68	15.7
10	Sequoia	0.25	4.0	2.3	4.00	2.4
11	Sequoia	8.07	9.6	6.6	10.00	10.9
12	Sequoia	9.10	9.6	6.6	14.67	12.5
14	Decatur	0.27	4.0	2.0	3.33	2.6
15	Decatur	3.24	4.8	4.0	6.67	7.7
16	Decatur	0.14	1.6	2.0	3.33	2.2
17	Decatur	0.14	2.0	1.7	2.67	1.6
18	Decatur	3.02	2.4	3.4	5.34	5.4
19	Grenada	0.48	4.0	2.3	3.33	2.3
20	Grenada	3.45	5.6	3.7	6.00	5.8
21	Grenada	3.64	5.6	3.7	5.34	6.1
22	Grenada	1.50	4.0	2.6	4.67	4.4
23	Grenada	3.67	5.6	3.7	6.00	6.7
24	Grenada	3.66	4.0	3.4	6.00	5.4
25	Memphis	0.14	1.6	0.6	2.00	0.0
26	Memphis	2.14	4.8	3.1	4.00	4.2
27	Memphis	3.18	4.8	3.4	4.67	4.8
29	Halewood	3.95	8.0	3.7	6.67	9.7
30	Halewood	3.01	6.4	3.1	4.67	5.9

Table 11.--continued.

Sample No.	Soil Series	me. per 100 grams of soil				
		Yuan titration	Auburn buffer	Ohio buffer	Miss. buffer	NH_4OAc
31	Halewood	1.30	8.0	4.3	7.34	12.0
32	Halewood	6.19	8.0	5.2	8.00	8.8
33	Halewood	5.44	5.6	5.8	6.67	7.6
34	Maury	0.19	5.6	2.9	4.67	2.6
35	Maury	0.20	5.6	2.9	4.67	2.4
36	Maury	0.16	4.8	2.7	4.00	1.7
37	Maury	0.13	2.4	1.4	2.00	0.7
38	Maury	0.21	3.2	2.7	2.67	2.2
41	Dewey	2.42	4.8	3.1	4.67	4.3
42	Dewey	4.72	5.6	4.9	6.67	6.0
43	Dewey	0.44	4.0	2.3	2.67	2.5
44	Dewey	4.14	6.4	4.3	5.34	7.1
45	Dewey	6.12	8.0	5.8	8.67	8.3
46	Hartsells	1.62	4.0	2.6	4.00	3.7
47	Hartsells	2.21	4.4	2.9	3.33	3.8
48	Hartsells	3.25	5.2	3.1	4.00	5.1
50	Hartsells	4.64	7.2	4.9	5.34	8.1
51	Hartsells	3.53	4.8	3.7	4.00	5.4
53	Baxter	3.99	6.4	4.3	4.67	7.1
54	Baxter	4.80	6.4	4.6	6.00	6.1
55	Baxter	0.28	3.2	2.3	2.67	2.9
56	Baxter	1.36	4.0	2.3	2.67	2.3
57	Baxter	2.07	4.0	2.6	2.67	3.1
59	Cookeville	2.51	4.0	3.1	4.00	4.2
60	Cookeville	3.09	4.8	3.4	4.67	5.5
61	Cookeville	0.11	0.0	0.8	1.33	0.0
62	Cookeville	0.87	3.2	2.0	2.67	2.5

Table 11.--continued

Sample No.	Soil Series	me. per 100 grams of soil				
		Yuan titration	Auburn buffer	Ohio buffer	Miss. buffer	NH_4OAc
63	Cookeville	1.37	3.2	2.6	3.33	6.5
64	Bowdre	0.22	4.8	3.2	4.00	12.7
65	Bowdre	0.63	1.6	1.4	1.33	1.8
67	Baxter	0.19	4.0	2.0	2.67	0.0
69	Baxter	1.35	4.8	2.9	3.33	3.6
70	Baxter	0.36	4.8	2.9	4.00	2.5
71	Dexter	0.08	1.6	1.4	1.33	5.0
72	Dexter	0.06	0.8	0.3	0.00	--#
73	Dexter	0.06	0.8	0.8	1.33	--
74	Dexter	0.08	2.4	1.4	2.00	--
75	Loring	0.05	0.8	0.6	0.00	--
77	Bowdre	0.07	2.4	2.0	2.67	--
80	Tunica	0.11	3.2	1.4	2.00	--
82	Loring	0.06	0.8	0.6	0.00	--
84	Hatchie	0.10	0.8	0.8	0.67	--
85	Olivier	0.08	0.8	0.8	1.33	--
87	Vicksburg	0.14	0.0	0.6	0.00	--
90	Falaya	0.09	0.0	0.3	0.67	--

*Determined by subtracting total bases from C.E.C.

#Not determined.

involved split plots on one soil type with some of the plots being limed and some unlimed. The values were determined for the unlimed samples. The cation exchange capacities obtained for the unlimed samples of a plot were taken as the cation exchange capacities of the limed plots of that particular soil type.

Soil pH values ranged from 4.6 to 7.3. Exchangeable aluminum showed a wide range from 0 to 11.61 me. per 100 g. of soil. The highest exchangeable aluminum contents were found in those soils with pH values of 5.0 or less. Exchangeable aluminum was not directly proportional to soil pH. The soils with low pH values and high cation exchange capacities had higher exchangeable aluminum contents than those soils with low pH values and low cation exchange capacities. No soils with pH values of greater than 5.5 had appreciable amounts of exchangeable aluminum. Exchangeable hydrogen by the Yuan titration was less than 0.50 me. per 100 g. of soil in all cases and less than 0.25 me. per 100 g. of soil in most.

The exchangeable acidity values by the Yuan titration were, in nearly all cases, lower than exchangeable acidity by the Auburn and Mississippi buffer solutions but were higher in some cases and lower in others than the Ohio buffer solution exchangeable acidity values. In practically all cases where the soil-Ohio buffer solution pH was below about 6.0 at the equilibrium point, the Yuan titration measured more exchangeable acidity than did the Ohio buffer solution. This was taken as evidence in support of the hypothesis regarding the effect of acidity arising from pH dependent charge on the predicted lime requirement by the buffer solutions discussed in relation to the soils of the incubation

study.

In most instances the Auburn buffer solution measured more exchangeable acidity than the Mississippi buffer solution and both, in general, measured considerably more than the Ohio buffer solution. No definite statement can be made regarding the comparison of exchangeable acidity by the ammonium acetate method and by the other methods except that the values were higher than by the Yuan titration method and, in most cases, higher than by the Ohio buffer method. The acidity was higher for some soils and lower for others than values by the Auburn and Mississippi buffer methods.

Lime requirement values to pH 6.5, 6.8, and 7.0 as predicted by the buffer solutions are shown in tables 12 through 14. For most soils, as in the case of the incubation samples, the Auburn buffer predicted the highest values, the Ohio buffer the lowest, and the Mississippi buffer intermediate.

Generally speaking, soils with high cation exchange capacities had the highest predicted lime requirement. However, some exceptions were noted. These, for the most part, were soils with high base saturation percentages, and high pH values.

As was noted with the incubation samples, per cent base saturation itself did not appear to be related to lime requirement predictions. This may be recognized as a limitation to the determination of lime requirement using the equation of Adams and Evans, since the equation makes use of base unsaturation. It has been shown that there is a definite and specific relationship between pH and base saturation of a single soil or

Table 12.--Lime requirement to pH 6.5 as predicted by the Auburn, Ohio, and Mississippi buffer solutions for 70 Tennessee soils.

Sample No.	Soil Series	$CaCO_3$, lbs./A.		
		Auburn	Ohio	Miss.
2	Clarksville	2,100	1,900	3,100
3	Clarksville	2,300	1,900	2,400
5	Clarksville	2,800	2,600	3,300
6	Clarksville	1,600	1,800	2,300
8	Sequoia	7,500	4,700	*
9	Sequoia	8,800	5,100	*
10	Sequoia	1,500	800	1,500
11	Sequoia	6,100	4,200	*
12	Sequoia	6,100	4,200	*
14	Decatur	2,200	1,100	1,900
15	Decatur	2,600	2,100	3,600
16	Decatur	300	400	700
17	Decatur	800	700	800
18	Decatur	1,600	2,300	3,600
19	Grenada	1,900	1,100	1,600
20	Grenada	3,400	2,300	3,700
21	Grenada	3,400	2,300	3,300
22	Grenada	2,300	1,500	2,700
23	Grenada	3,500	2,300	3,800
24	Grenada	2,400	2,100	3,700
25	Memphis	0	0	0
26	Memphis	2,900	1,900	2,400
27	Memphis	2,900	2,100	2,800
29	Halewood	5,100	2,300	4,200
30	Halewood	4,000	2,000	3,000
31	Halewood	4,300	2,300	3,900
32	Halewood	5,200	3,400	5,200
33	Halewood	3,500	3,700	4,200
34	Maury	1,800	900	1,500
35	Maury	1,800	900	1,500
36	Maury	1,500	900	1,300
37	Maury	0	0	0
38	Maury	1,300	1,100	1,100
41	Dewey	3,100	2,000	3,100
42	Dewey	3,900	3,400	4,600
43	Dewey	1,900	1,100	1,300
44	Dewey	4,000	2,700	3,400
45	Dewey	5,200	3,800	*
46	Hartsells	2,300	1,500	2,300

Table 12.--continued.

Sample No.	Soil Series	$CaCO_3$, lbs./A. Auburn	Ohio	Miss.
47	Hartsells	2,800	1,800	2,100
48	Hartsells	3,400	2,000	2,600
50	Hartsells	4,700	3,200	3,500
51	Hartsells	3,200	2,500	2,700
53	Baxter	4,300	2,900	3,200
54	Baxter	4,300	3,100	4,100
55	Baxter	1,000	700	900
56	Baxter	2,500	1,500	1,700
57	Baxter	2,500	1,600	1,700
59	Cookeville	2,700	2,100	2,700
60	Cookeville	3,200	2,300	3,200
61	Cookeville	0	0	0
62	Cookeville	2,100	1,300	1,700
63	Cookeville	2,000	1,600	2,100
64	Bowdre	2,300	1,500	1,900
65	Bowdre	900	700	700
67	Baxter	1,500	700	1,000
69	Baxter	2,800	1,700	2,000
70	Baxter	2,700	1,600	2,200
71	Dexter	300	300	300
72	Dexter	0	0	0
73	Dexter	0	0	0
74	Dexter	400	200	300
75	Loring	0	0	0
77	Bowdre	0	0	0
80	Tunica	0	0	0
82	Loring	0	0	0
84	Hatchie	0	0	0
85	Olivier	0	0	0
87	Vicksburg	0	0	0
90	Falaya	0	0	0

*Values not determined because exchangeable soil acidity was too high to be measured by the buffer solution.

Table 13.--Lime requirement to pH 6.8 as predicted by the Auburn, Ohio, and Mississippi buffer solutions for 70 Tennessee soils.

Sample No.	Soil Series	$CaCO_3$, lbs./A.		
		Auburn	Ohio	Miss.
2	Clarksville	2,400	2,200	3,500
3	Clarksville	2,500	2,100	2,600
5	Clarksville	3,100	2,900	3,600
6	Clarksville	1,800	2,000	2,500
8	Sequoia	8,400	5,200	*
9	Sequoia	9,900	5,700	*
10	Sequoia	2,100	1,200	2,100
11	Sequoia	7,000	4,800	*
12	Sequoia	7,000	4,800	*
14	Decatur	2,700	1,300	2,200
15	Decatur	3,100	2,600	4,300
16	Decatur	700	800	1,400
17	Decatur	1,100	900	1,500
18	Decatur	1,800	2,600	4,100
19	Grenada	2,400	1,400	2,000
20	Grenada	4,000	2,600	4,300
21	Grenada	4,000	2,600	3,800
22	Grenada	2,800	1,800	3,200
23	Grenada	4,100	2,700	4,400
24	Grenada	2,800	2,400	4,300
25	Memphis	400	200	500
26	Memphis	3,400	2,200	2,800
27	Memphis	3,400	2,400	3,300
29	Halewood	5,800	2,700	4,800
30	Halewood	4,600	2,300	3,400
31	Halewood	5,200	2,800	4,800
32	Halewood	5,900	3,900	5,900
33	Halewood	4,100	4,200	4,800
34	Maury	2,800	1,400	2,300
35	Maury	2,800	1,400	2,300
36	Maury	2,400	1,300	2,000
37	Maury	600	400	500
38	Maury	1,800	1,500	1,500
41	Dewey	3,600	2,300	3,500
42	Dewey	4,300	3,800	5,200
43	Dewey	2,400	1,400	1,600
44	Dewey	4,600	3,100	3,900
45	Dewey	5,900	4,300	*
46	Hartsells	2,800	1,800	2,800

Table 13.--continued.

Sample No.	Soil Series	$CaCO_3$, lbs./A. Auburn	Ohio	Miss.
47	Hartsells	2,800	2,100	2,400
48	Hartsells	3,900	2,300	3,000
50	Hartsells	5,300	3,600	4,000
51	Hartsells	3,600	2,800	3,000
53	Baxter	4,900	3,300	3,500
54	Baxter	4,900	3,500	4,600
55	Baxter	1,600	1,100	1,300
56	Baxter	2,900	1,700	1,900
57	Baxter	2,900	1,900	1,900
59	Cookeville	3,000	2,400	3,000
60	Cookeville	3,600	2,600	3,500
61	Cookeville	0	200	300
62	Cookeville	2,400	1,500	2,000
63	Cookeville	2,300	1,900	2,400
64	Bowdre	2,900	1,900	2,400
65	Bowdre	1,000	900	900
67	Baxter	2,100	1,100	1,400
69	Baxter	3,300	2,000	2,300
70	Baxter	3,200	2,000	2,700
71	Dexter	700	600	600
72	Dexter	0	0	0
73	Dexter	100	100	100
74	Dexter	900	500	700
75	Loring	0	0	0
77	Bowdre	600	500	700
80	Tunica	300	100	200
82	Loring	0	0	0
84	Hatchie	0	0	0
85	Olivier	0	0	0
87	Vicksburg	0	0	0
90	Falaya	0	0	0

*Values not determined because exchangeable soil acidity was too high to be measured by the buffer solution.

Table 14.--Lime requirement to pH 7.0 as predicted by the Auburn, Ohio, and Mississippi buffer solutions for 70 Tennessee soils.

Sample No.	Soil Series	$CaCO_3$, lbs./A.		
		Auburn	Ohio	Miss.
2	Clarksville	2,600	2,300	3,700
3	Clarksville	2,700	2,200	2,800
5	Clarksville	3,300	3,000	3,800
6	Clarksville	1,900	2,100	2,700
8	Sequoia	9,000	5,600	*
9	Sequoia	10,500	6,100	*
10	Sequoia	2,500	1,400	2,500
11	Sequoia	7,500	5,200	*
12	Sequoia	7,500	5,200	*
14	Decatur	3,000	1,500	2,500
15	Decatur	3,500	2,900	4,900
16	Decatur	900	1,100	1,800
17	Decatur	1,300	1,100	1,700
18	Decatur	1,900	2,800	4,300
19	Grenada	2,800	1,600	2,300
20	Grenada	4,300	2,900	4,600
21	Grenada	4,300	2,900	4,000
22	Grenada	3,000	2,000	3,500
23	Grenada	4,400	2,900	4,700
24	Grenada	3,100	2,600	4,600
25	Memphis	700	200	800
26	Memphis	3,700	2,400	3,100
27	Memphis	3,700	2,600	3,600
29	Halewood	6,300	2,900	5,200
30	Halewood	5,000	2,400	3,700
31	Halewood	5,800	3,100	5,300
32	Halewood	6,400	4,100	6,400
33	Halewood	4,400	4,600	5,200
34	Maury	3,400	1,700	2,800
35	Maury	3,400	1,700	2,800
36	Maury	2,900	1,600	2,400
37	Maury	1,000	600	800
38	Maury	2,100	1,800	1,700
41	Dewey	3,800	2,500	3,700
42	Dewey	4,600	4,000	5,500
43	Dewey	2,800	1,600	1,900
44	Dewey	5,000	3,400	4.200
45	Dewey	6,400	4,600	*
46	Hartsells	3,000	2,000	3,000

Table 14.--continued.

Sample No.	Soil Series	$CaCO_3$, lbs./A.		
		Auburn	Ohio	Miss.
47	Hartsells	3,500	2,300	2,600
48	Hartsells	4,100	2,500	3,200
50	Hartsells	5,700	3,900	4,300
51	Hartsells	3,900	3,000	3,200
53	Baxter	5,200	3,500	3,800
54	Baxter	5,200	3,700	4,900
55	Baxter	1,900	1,400	1,600
56	Baxter	3,100	1,800	2,100
57	Baxter	3,100	2,000	2,100
59	Cookeville	3,200	2,500	3,200
60	Cookeville	3,900	2,800	3,800
61	Cookeville	0	300	600
62	Cookeville	2,600	1,600	2,100
63	Cookeville	2,500	2,000	2,600
64	Bowdre	3,300	2,200	2,800
65	Bowdre	1,200	1,000	1,000
67	Baxter	2,500	1,300	1,700
69	Baxter	3,600	2,200	2,500
70	Baxter	3,600	2,200	3,000
71	Dexter	900	800	700
72	Dexter	0	0	0
73	Dexter	200	200	400
74	Dexter	1,200	700	1,000
75	Loring	0	0	0
77	Bowdre	1,000	800	1,100
80	Tunica	900	400	600
82	Loring	0	0	0
84	Hatchie	0	0	0
85	Olivier	0	0	0
87	Vicksburg	0	0	0
90	Falaya	0	0	0

*Values not determined because exchangeable soil acidity was too high to be measured by the buffer solution.

similar soils, and, for widely different soils there is a general relationship (1, 30, 32, 34, 40, 49). This can be seen from table 10. It should be pointed out, however, that the equation also makes use of exchangeable acidity in predicting lime requirement which tends to compensate for errors resulting from the use of base unsaturation.

Another limitation of the equation is that of applying to Tennessee soils the pH-base unsaturation relationship established for Alabama soils. This limitation could be remedied by the establishment of pH-base unsaturation relationships for a large number of Tennessee soils.

CHAPTER V

SUMMARY AND CONCLUSIONS

Three buffer solutions developed for rapid determination of the lime requirement of soils, the Auburn, Ohio, and Mississippi buffer solutions, were evaluated by comparing their predictions to pH 6.5, 6.8, and 7.0 with the lime requirements to these pH levels determined by six months of moist incubation with reagent grade precipitated calcium carbonate at equivalent rates of 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 tons per acre using 22 Tennessee soils with widely different properties. All predictions by the buffer solutions were calculated using equations developed by Adams and Evans (1) for use with the Auburn buffer solution. The predictions by the buffer methods were compared to one another, to the ammonium acetate method, and to the pH method.

Exchangeable acidity values determined by the three buffer solutions, the Yuan titration method, and the ammonium acetate method were compared to one another.

Mechanical analysis, easily oxidizable organic matter, cation exchange capacity, total bases, per cent base saturation, soil pH, exchangeable aluminum, exchangeable hydrogen, and total exchangeable acidity were determined for all soils. Ten low pH soils of the 22 soils used in the incubation study were selected to study the relationships between soil properties and lime requirement.

A further comparison of the three buffer solutions for predicting lime requirement was made using 70 soil samples which were not

involved in the incubation study.

The results are briefly outlined below:

1. Exchangeable acidity values measured by the buffer solutions were, in most cases, in the order Auburn > Mississippi > Ohio. The buffer solution with the highest soil-buffer pH values measured the highest amount of acidity. This was considered to be a pH dependent charge effect. Exchangeable acidity values by the Yuan titration method were proportionately lower than the Auburn and Mississippi buffer values but were higher than the Ohio values in cases where the soil-Ohio buffer pH values at the equilibrium point were less than 6.0. It was believed that in these cases the potassium chloride, in which the equilibrium point with soil is about pH 6.0, extracted more acidity held by the pH dependent charge of the soil than did the Ohio buffer solution with the lower equilibrium pH. Exchangeable acidity by the ammonium acetate method was extremely varied and definite relationships with other methods of determining exchangeable acidity and with lime requirement were difficult to establish.

2. Most soils were not evenly buffered over the entire range of calcium carbonate titration but their buffering capacities increased as the soil pH was increased by the largest additions of calcium carbonate. This was shown by the soil titration curves and was considered to be a pH dependent charge effect.

3. Clay content was highly correlated with lime requirement by incubation but organic matter content was not significantly correlated except at the five per cent level to pH 7.0. Probably the effects of

clay and organic matter content on lime requirement are through their effects on the cation exchange capacity. Clay content would be expected to have the greater effect on lime requirement of soils low in organic matter in which most of the cation exchange capacity results from the clay.

4. Soils with pH values greater than 5.5 had very little or no exchangeable aluminum. This was attributed to the formation of insoluble $Al(OH)_3$ which is believed to occur at about pH 5.0 to 5.5. Exchangeable aluminum was related to lime requirement of those soils with pH values below 5.5 as evidenced by high correlation coefficients to all three pH levels for 10 very acid soils. When all of the 22 incubation samples were considered, apparently there was little relationship between these two properties.

5. Cation exchange capacity was highly correlated with incubation lime requirement. The higher the cation exchange capacity the higher was the soil buffering capacity in most cases, thus the lime requirement in terms of the amount required to cause a given pH change was higher.

6. Base saturation was not significantly correlated with lime requirement.

7. The ammonium acetate method was unsatisfactory in predicting lime requirement.

8. The pH method was fairly accurate for soils with intermediate buffer capacities but indicated low values for highly buffered soils and high values for weakly buffered soils.

9. The Ohio buffer solution predicted low values throughout the range of lime requirements except with soils having low lime requirements. It would be an unsatisfactory method for most Tennessee soils unless an equation could be developed to compensate for the low buffering capacity of the solution and its low capacity to measure pH dependent charge effect.

10. The Mississippi buffer solution was more accurate than the Ohio buffer solution but not as accurate as the Auburn buffer. It was strongly buffered, almost as much as the Auburn buffer, but it was not buffered over a wide enough range of acidity. Some highly acid soils contained enough exchangeable acidity to surpass its rapid deflection point. It also fell below the Auburn buffer in its capacity to measure what was believed to be acidity resulting from pH dependent charge probably because of its lower soil-buffer solution pH value at the equilibrium point.

11. The Auburn buffer solution method was the most accurate method tested. Certain limitations to the method were recognized. It makes use of a pH-base unsaturation relationship, a relationship which is very general in nature for widely differing soils. Applying the pH-base unsaturation relationship established for Alabama soils to Tennessee soils was also recognized as a limitation. Further research should be conducted toward establishing pH-base unsaturations relationship for a large number of Tennessee soils. Although this method predicted lower lime requirement values than the calcium carbonate incubation values, it was found to be a rapid method which would give

satisfactory results if used for testing soils for lime requirement on a mass scale such as a state soil testing laboratory.

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APPENDIX

CRANES CREST

PROCEDURES FOR PREDICTING LIME REQUIREMENT BY AUBURN OHIO, AND MISSISSIPPI BUFFER SOLUTIONS

I. COMPOSITION OF THE DILUTE BUFFER SOLUTIONS

Auburn buffer solution

Each liter of solution contains 10.0 g. p-nitrophenol, 7.5 g. H_3BO_3, 37.0 g. KCl, and 5.25 g. KOH, adjusted to pH 8.0 with NaOH or HCl.

Ohio buffer solution

Each liter of solution contains 1.2 g. p-nitrophenol, 1.67 ml. triethanolamine, 2.0 g. K_2CrO_4, 1.34 g. $Ca(CO_2CH_3)_2$, 17.7 g. $CaCl_2 \cdot 2H_2O$, 1.9 g. NaOH, adjusted to pH 7.2 with NaOH or HCl.

Mississippi buffer solution

Each liter of solution contains 9.9 g. p-nitrophenol, 25.0 g. $CaCl_2 \cdot 2H_2O$, 1.9 g. NaOH, adjusted to pH 7.2 with NaOH or HCl.

II. PREPARATION AND TITRATION OF THE BUFFER SOLUTIONS

Dissolve the p-nitrophenol in hot distilled water, about 300 ml. for each liter of buffer solution desired. Separately dissolve the $CaCl_2 \cdot 2H_2O$ or H_3BO_3 in about the same amount of distilled water and mix the two solutions. Add the remaining reagents and allow to dissolve. Cool the solution and make up to the proper volume with distilled water. To prepare concentrated solutions, double the concentrations of the Auburn and Mississippi buffers, and increase

the concentration of the Ohio buffer by one-third. Titrate each buffer solution with increments of standard 0.1N HCl to the rapid deflection point using the glass electrode to measure the pH depression. Titrate 20 ml. of dilute Auburn buffer, 10 ml. if concentrated; 30 ml. dilute Ohio buffer, 20 ml. concentrated; and 20 ml. dilute Mississippi buffer, 10 ml. concentrated. Plot me. HCl added against buffer solution pH to form a titration curve for each buffer solution. The Auburn buffer is buffered linearly between pH 8.0 and about 6.6, with each 0.08 me. of acid resulting in a 0.1 pH unit depression. The Ohio buffer has a linear buffering effect between pH 7.5 and about pH 4.0 and each 0.1 pH unit depression requires approximately 0.03 me. of acid. The Mississippi buffer is buffered linearly between pH 7.2 and about pH 6.3 and each 0.1 pH unit depression represents 0.0667 me. of acid.

III. DETERMINATION OF LIME REQUIREMENT USING DILUTE BUFFER SOLUTIONS

When the soil-water pH values and the soil-buffer pH values are to be determined using separate samples of a soil, dilute buffer solution is added directly to the soil without prior addition of water. Lime requirement is predicted by the following procedure.

1. Weigh 10 g. of air-dry, < 2.0 mm. soil into a 3-oz. paper cup.

2. Add:

   (a) 20 ml. of dilute Auburn buffer, or

(b) 30 ml. of dilute Ohio buffer, or

(c) 20 ml. of dilute Mississippi buffer.

3. Stir intermittently with a glass rod for 1 hour.

4. Read the pH of the soil-buffer solution suspension while stirring with a glass rod.

5. Determine the acidity measured by the buffer solution using the appropriate buffer solution titration curve and convert to me. exchangeable acidity per 100 g. of soil.

6. Determine the soil-water pH by the method of Peech et al. (50) using a separate 10 g. sample of soil.

7. Determine the $CaCO_3$ equivalent lime requirement by the following equation:

$$\text{me. acid to be neutralized/100 g. soil} = \frac{\text{exchangeable acidity/100 g. soil}}{\text{initial base unsaturation}} \times \text{desired change in base unsaturation.}$$

Initial base unsaturation and desired change in base unsaturation are determined by the equation $y = 7.79 - 5.55x + 2.27x^2$, where y = soil-water pH and x = base unsaturation. The initial base unsaturation is calculated by substituting the initial soil-water pH for y and solving for x. The desired soil-water pH is then substituted for y and the value obtained subtracted from the initial base unsaturation to derive the desired change in base unsaturation. To convert to $CaCO_3$ in lbs./A. multiply the me./100 g. acid to be neutralized by 1,000. Where a large number of soil samples

are involved or for testing on a mass scale, it is convenient to prepare tables with the probable initial soil-water pH values along one axis and the probable soil-buffer pH values along the other axis, and show within the table the predicted lime requirement values for soils with any combination of soil-water pH and soil-buffer pH. A separate table is required for each desired pH, such as 6.5, 6.8, or 7.0.

IV. DETERMINATION OF LIME REQUIREMENT USING CONCENTRATED BUFFER SOLUTIONS

If it is desirable to determine both the soil-water pH and the soil-buffer pH using the same soil sample, concentrated buffer solutions are used and the determination made according to the following procedure.

1. Add 10 ml. distilled water to 10 g. of soil in a 3-oz. paper cup.
2. Stir intermittently for 30 minutes and read the pH while stirring with a glass rod.
3. Add 10 ml. concentrated Auburn buffer, or 20 ml. concentrated Ohio buffer, or 10 ml. concentrated Mississippi buffer; stir intermittently for another 30 minutes.
4. Read the pH while stirring with a glass rod.
5. Determine the lime requirement in the same manner as outlined for the dilute buffer solutions.