H-ION CONCENTRATION, BUFFER ACTION AND SOIL TYPE AS A GUIDE TO THE USE OF LIME*

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INTRODUCTION

Probably no phase of soil studies has received so much attention in recent investigations as has that of "Soil Acidity." This term has been used interchangeably with such terms as "Soil Sourness," "Lime Requirement," "Toxicity," and others, to such an extent that the literature has been somewhat confusing as to the definite meaning of the terms used.

"Soil Sourness" is a term which has been applied to conditions of the soil unfavorable to plant growth. Some of the conditions referred to have been the presence of acids, presence of toxic materials, conditions of low oxidation due to wetness or defloculation, lack of basic materials, such as calcium compounds, or other factors which may retard or inhibit plant growth.

"Lime Requirement" of soils has usually been interpreted to mean the needs of soils for calcium as indicated by the methods of analysis used. These methods have been quite variable in technique and, as might be expected, the recommendations based upon them have varied considerably.

Among the methods used for estimation of the lime needed by soils may be mentioned the following:

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A. Testing a water extract of the soil.
   1. Titration of the filtrate from the soil with a standard alkali solution and calculation of the amount of base required.
   2. Addition of indicators to the filtrate to determine the hydrogen-ion concentration.
   3. Addition of salts (calcium acetate, potassium acetate, sodium acetate, sodium chloride, potassium chloride, etc.) and titration of the filtrate to determine the resultant acidity.

B. Testing the soil in a solution of pure water.
   1. Titration with lime water or other alkali solutions.
   2. Addition of KSCN using the soluble iron as an indicator of acidity.
   3. Use of litmus paper.
   4. Use of ZnS with lead acetate paper as an indicator.
   5. Determination of the H-ion concentration electrometrically.

The above methods or modifications of them have been used quite extensively in an effort to prescribe the amount of lime needed for soils. In some instances, the recommendations have been substantiated in practice. In many others, the applications indicated have not proven to be advisable and in some cases injury to the crop has resulted. Studies have been under way for some time in an effort to overcome these difficulties. No attempt will be made to refer to the large number of articles published upon this subject.
THE FUNCTION OF LIME

Due to the complexity of the soil, lime may have several functions in the soil.

A. It may serve as an element of plant food. Plants vary in this respect, some requiring large amounts and others requiring but little in their growth.

B. Lime brings about changes in the compounds of the soil producing new combinations which affect availability and toxicity.

C. With the changes produced chemically and physically considerable effect may be noted upon the physical properties of the soil.

D. The application of lime greatly affects the organisms of the soil both in type and numbers and also in activity. Considerable success has been attained in controlling certain plant disease organisms in the soil by regulating the soil reaction.

E. The function commonly attributed to lime is that of controlling soil acidity. It is this latter function which is to be considered in this paper.

ACTIVE ACIDITY

The use of the term acidity implies that there is an acid present in the soil. There has been much discussion of this point which has given rise to the designation of soil acidity as "active acidity," "latent acidity," and "total acidity" or other similar terms.

"Active acidity" has been considered as the part of the "total" actually in the ionized form, "latent acidity" as the difference between these two quantities, and "total acidity" as the total amount of ionizable acid present in the soil mass. As previously stated, active acidity may be determined either colorimetrically by the use of indicators, or by electrometric measurements.
The colorimetric methods, although they have been widely used, cannot be relied upon in many cases because of their lack of accuracy. This is particularly true in soils well supplied with organic matter and in titration work. The electrometric methods of measurement for active acidity have been generally adopted for the more accurate research work.

Active acidity is expressed as the concentration of hydrogen ions in the soil. For convenience, the logarithmic exponent of this value, known as pH value, is generally used. pH value consists of the logarithm of the reciprocal of the hydrogen ion concentration. Neutrality is approximately pH 7.0, and acid solutions are those below pH 7.0, while alkaline solutions are those above pH 7.0. The technique of hydrogen-ion determination may be obtained from many other sources and therefore will not be given in this paper.

EFFECT OF ACIDITY UPON PLANTS

Salter and McIlvaine⁹ found that wheat, soybeans, and alfalfa seedlings made maximum growth in solutions that were maintained at a pH of 5.94 and that corn produced the greatest growth at pH 5.16.

Duggar⁴ reported injury to seedlings of wheat, corn and field peas in solutions above pH 6.

The Carlsberg Laboratory⁸ reported that the plants usually found to grow best on acid soils showed their maximum growth near pH 4, while basic soil plants gave best results between pH values of 6 to 7.

Arndt¹ reported the rate of growth of corn seedlings to be little affected by pH 3.7.

Hoagland⁶ in studying barley seedlings reported pH 5.15 as most favorable while pH 3.5 on the acid side and pH 8.5 on the alkaline were quite toxic.
McCall and Haag\textsuperscript{8} working with sand cultures found a range of pH 3.06 to pH 3.56 to be satisfactory for wheat while pH 4.02 to 7.0 gave unsatisfactory results.

Tarr and Noble\textsuperscript{11} using solutions for corn, wheat \textbf{and} soy beans with constantly maintained intervals of 1 pH from pH 3 to pH 8 found maximum growth for wheat at pH 4, a greater concentration being harmful and no ill effects until the concentration was less than pH 6.

For corn and soy beans the optimum was pH 5, with pH 4 being harmful and no ill effects experienced until the concentration became less than pH 6.

Troug\textsuperscript{12}, Atkins\textsuperscript{2}, Wherry\textsuperscript{13} and many others have also done much to aid in determining the pH values most suitable for plant growth. The results indicate that corn, wheat, soy beans, barley, alfalfa, and field peas grow well in an acidity somewhere between pH 4 to pH 6. The probabilities are that most of the other farm crops which grow well under conditions favorable to these crops will be found to have similar acidity relations.

\section*{ACIDITY AND SOIL TYPES}

Much investigation has been carried on by Soil Survey and Experimental workers in an effort to learn what relation exists between soil type and acidity. Attempts have been made to correlate active acidity, the amount of lime needed to produce neutrality, and the supposed lime requirement of the crop. In some cases it has been thought that such a correlation could be determined, in others no apparent relationship existed.

Active acidity and total acidity have been found to vary as much within some types as among all types.
However, a very important property or action of soils has been noticed in many of these studies. This has been aptly termed "buffer action". This action may be defined as a property of the soil which causes it to resist changes in active acidity or pH value. Some soils have been found to undergo very little change in pH value from the lime applications while others with the same initial concentration have been radically changed. Several theories have been advanced as to the causes of these differences in reaction.

Such action has been attributed to colloidal material, bicarbonates, phosphates, salts of strong acids and weak bases, and to organic compounds. It has been quite generally conceded that in most soils organic matter materially assists to regulate or buffer the reaction, and that excessive concentration is thus prevented. Further study is needed to reveal the physico-chemical reactions involved in this very important action of the soil.

THE PROBLEM

It was the aim of this work to find what relation, if any, could be found to exist between soil type and buffer action and whether this information could be used in determining the lime applications for soils.

EXPERIMENTAL WORK

During the past three years some 400 samples of the soil types of Delaware have been collected and studied. These soils consisted of ten series, the Sassafras, Elkton, Portsmouth, Norfolk, Woodstown, St. Johns, and Keyport of the Atlantic Coastal Plains region and Chester, Codorus, and Cecil of the Piedmont Plateau region. The
types used were gravelly loam, sand, loamy sand, sandy loam, loam, silt loam, clay loam and a mucky phase of loam.

METHOD OF TESTING

Five gram samples were used for the determinations. These samples were thoroughly broken up in a small amount of water with a rubber pestle. The suspension was poured into the beaker to be used and successive amounts of water used upon the soil in the mortar until it was practically all brought into suspension excepting the larger particles of sand. In this way the entire sample was transferred to the beaker, a total volume of 50 cc. of water being used. The apparatus consisted of the Hildebrand type with a closed vessel. A stirrer was used to secure constant agitation. The initial H-ion concentration was determined and the samples were then titrated with 1, 2, 3, 5, 7, and 10 cc. quantities respectively of hundredth normal sulphuric acid and sodium hydroxide. Frequent check readings were made with standard solutions and with soils of known reaction.

The titration curves were then plotted for each of the soils for comparison. The sodium acetate determinations for “lime requirement” were also made upon each of the soils for comparison with H-ion concentration and titration results.

EXPERIMENTAL RESULTS

Due to the large amount of data obtained, only a sufficient amount will be included in this paper to illustrate the results and to show the applications made. Figure 1 shows the typical reactions of some of the soil types. It will be noted that the initial H-ion concentration was not the same, and for the purpose of easier comparison figures II and III were formed using the same starting point upon the graph for the curves.
Figure 1

- A: Loamy Sand
- B: Loam
- C: Silt Loam
- D: Sandy Loam
- Norfolk Series
- Chester Series
- Sassarfas Series
- Portsmouth Series

cc N/100 NaOH
cc N/100 H₂SO₄
pH
Fig. II - alkali titration curves using same starting point.

Fig. III - acid titration curves using same starting point.
Soil D averages a lime requirement by the Sodium Acetate Method of about 11,000 lbs. of limestone per acre. This soil is a sandy loam with rather poor drainage and is very high in organic matter. The typical titration curve for soils of this type shows that because of its high buffer action large amounts of lime would be needed to bring it to a low degree of acidity. To attempt to lime sufficiently to grow plants other than those favorable to high acidity probably would not be an economical procedure. A type of acid agriculture is being developed upon these soils with considerable success.

Soil A is a loamy sand, usually well drained and because of its extremely porous character it is quite low in organic matter. This type usually averages about 1500 lbs. lime requirement by the sodium acetate method. However, the titration curves show that quite unfavorable pH values may be secured by such an application. The obvious deduction in this case is that if the favorable pH value for crops lies somewhere between pH 4 and pH 6 as indicated by previously mentioned studies, then the desirable soil reaction can be established with a much more economical quantity of lime than indicated by the Sodium Acetate Method.

Soils B and C average near 1700 and 2000 lbs. of lime requirement respectively. They are heavier soils and show stronger buffer actions than soil A. It seems also with these soils that a much smaller lime application would be desirable than is indicated by their total acidity.

These deductions are well substantiated in practice. Considerable difficulty has been experienced with applications indicated by the lime requirement methods, particularly upon the soils which have low buffer action. Smaller applications upon the same types of soil have proven quite satisfactory.

From the standpoint of economy the applications made by the "Lime Requirement" method upon the Experiment Station Fertility Plots have in most instances shown no profits. However, increases in production were secured and it is felt that smaller applications
based upon H-ion concentration and plant needs would have been economical. Although more work needs to be done upon the optimum pH values for crops under field conditions yet the present indications are that most of these values may fall between pH 4 and pH 6.

Since the various soil types are found to react in such very different ways to the development of acidity or alkalinity, it would seem that any method for determination of lime requirement for a soil should take into consideration what the buffer quality of that soil is and what acidity value is desired.

The information which has been secured is being applied to the solution of the lime problem upon the soils mentioned and it is believed to be a much more satisfactory guide to the use of lime than the methods formerly used.

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