pH, Soil Acidity, and Plant Growth

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When crop plants do not grow well, one of the first questions the soil scientist usually asks is, "What is the pH of the soil?" or, "Is the soil acid, neutral, or alkaline?"

The reason for these questions lies in the fact that the pH, or degree of acidity of the soil, often is a symptom of some disorder in the chemical condition of the soil as it relates to plant nutrition.

A measurement of soil acidity or alkalinity is like a doctor's measurement of a patient's temperature. It reveals that something may be wrong but it does not tell the exact nature of the trouble.

The acidity or alkalinity of every water solution or mixture of soil and water is determined by its content of hydrogen ions and hydroxyl ions. Water molecules break up, or in chemical language, ionize, into two parts—hydrogen ions and hydroxyl ions. When there are more hydrogen ions than hydroxyl ions, the solution is said to be acid. If there are more hydroxyl ions than hydrogen ions, the solution is alkaline (or basic). Solutions with equal numbers of hydrogen and hydroxyl ions are called neutral.

Only a very small percentage of the water molecules present are broken up into hydrogen and hydroxyl ions at any one time. If one attempts to express the concentration of these ions in conventional chemical ways, some cumbersome decimal fractions result. In order to avoid these cumbersome numbers, the Danish biochemist S. P. L. Sorenson devised a system called pH for expressing the acidity or alkalinity of solutions.

The pH scale goes from 0 to 14. At pH 7, the midpoint of the scale, there are equal numbers of hydrogen and hydroxyl ions, and the solution is neutral.

pH values below 7 indicate an acid solution, where there are more hydrogen ions than hydroxyl ions, with the acidity (or hydrogen ion concentration) increasing as the pH values get smaller.

pH values above 7 denote alkaline solutions, with the concentration of hydroxyl ions increasing as the pH values get larger.

The pH scale is based on logarithms of the concentration of the hydrogen and hydroxyl ions. This means that a solution of pH 5 has 10 times the hydrogen ion concentration of a solution of pH 6. A solution of pH 4 has 10 times more hydrogen ions than one of pH 5 and 10 times 10, or 100 times, the hydrogen ion concentration of a solution of pH 6.

A measurement of the pH of a solution of a strong, or highly ionized, acid measures essentially the total strength of the acid. But a pH determination of a solution of weak, or slightly ionized, acid measures only a part of the total strength of the acid, because pH is a measure of hydrogen ions only and does not measure all the acid molecules that can potentially ionize to form hydrogen ions.

In a soil, hydrogen ions exist in a number of different chemical combinations and states of adsorption on the surfaces of solid particles. The number of hydrogen ions in the soil solution at any one time is small in relation to the number held in a less active form in various nonionized molecules and on the surfaces of the solid particles.

When the soil is limed in order to bring it to neutrality, enough lime must be added to react not only with the so-called free hydrogen ions of the soil solution but also with those held

in the less active forms. This is so because as the neutralization of the soil progresses, ionization of the less active forms of hydrogen likewise progresses and new free hydrogen ions are formed as long as the supply of less active forms holds out.

Thus it is possible to think of the total acidity of a soil as being composed of two parts.

One part, often called the active acidity, is made up of the hydrogen ions in the soil solution. These are the hydrogen ions measured when the pH of the soil is determined.

The second, and much larger, part of the total soil acidity is often called potential acidity. The potential acidity is due to hydrogen ions held in various chemical combinations and adsorbed on the surfaces of solid particles. These hydrogen ions are in chemical equilibrium with the free hydrogen ions of the active part of the soil acidity, and as the free hydrogen ions of the soil solu-

tion are neutralized or removed from the soil solution in other ways, hydrogen ions from the less active (or potential acidity) source enter the solution.

Most of the hydrogen ions in the potential acidity forms are held on surfaces of solid particles of clay or soil organic matter. These clay and organic particles are very small, and consequently have a large surface area per unit weight. They make up what is called the colloidal fraction of the soil. Since most of the potential acidity of soils is due to hydrogen ions held on the clay and organic particles, it follows that fine-textured soils, which are high in clay and organic matter, can have a higher total acidity than sandy soils of low clay and organic content.

There are different kinds of clay in different soils, and these different kinds of clay can hold different amounts of hydrogen ions in the potential acidity form. Generally speaking, the clay found in soils of cool-temperate and

Approximate Amounts of Finely Ground Limestone Needed to Raise the pH of a 7-inch Layer of Soil as Indicated [1] [5]

Soil regions and textural classes	Limestone requirements		
	From pH 3.5 to pH 4.5 Tons per acre	From pH 4.5 to pH 5.5 Tons per acre	From pH 5.5 to pH 6.5 Tons per acre
Soils of warm-temperate and tropical regions: [2]			
Sand and loamy sand	0.3	0.3	0.4
Sandy loam	....	.5	.7
Loam	....	.8	1.0
Silt loam	....	1.2	1.4
Clay loam	....	1.5	2.0
Muck	[3] 2.5	3.3	3.8
Soils of cool-temperate and temperate regions: [4]			
Sand and loamy sand	.4	.5	.6
Sandy loam	....	.8	1.3
Loam	....	1.2	1.7
Silt loam	....	1.5	2.0
Clay loam	....	1.9	2.3
Muck	[3] 2.9	3.8	4.3

[1] All limestone goes through a 2-mm. mesh screen and at least ½ through a 0.15-mm. mesh screen. With coarser materials, applications need to be greater. For burned lime about ½ the amounts given are used; for hydrated lime about ¾.

[2] Red-Yellow Podzol, Red Latosol, etc.

[3] The suggestions for muck soils are for those essentially free of sand and clay. For those containing much sand or clay the amounts should be reduced to values midway between those given for muck and the corresponding class of mineral soil. If the mineral soils are unusually low in organic matter, the recommendations should be reduced about 25 percent; if unusually high, increased by about 25 percent, or even more.

[4] Podzol, Gray-Brown Podzol, Brown Forest, Brown Podzol, etc.

[5] From USDA Handbook No. 18, p. 237.

Cation Exchange Reactions When an Acid Soil Is Limed
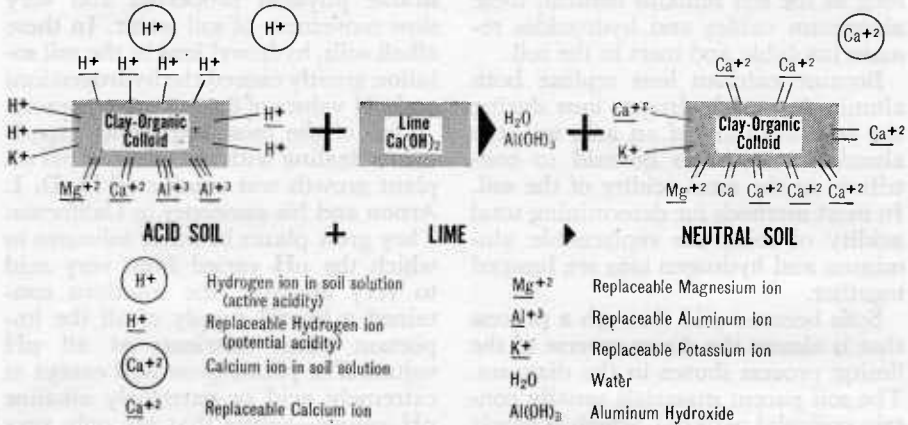
arid regions can hold a greater quantity of potential-acidity hydrogen ions than can the kind of clay found in soils of warm-temperate and tropical regions. General relationships between kind of soil, pH, and the amounts of lime required are shown in the table.

The hydrogen ions of the potential acidity form are held to the colloidal material because of their electrical charges. The colloidal material is predominantly negatively charged. The hydrogen ions are positively charged, and the attraction between the unlike charges accounts for most of the binding of hydrogen ions to the colloidal surfaces. When hydrogen ions change from the potential to the active acidity forms, their places on the clay-organic colloidal material are taken by other ions carrying positive charges. Ions of calcium, magnesium, potassium, and sodium are positively charged and may take the place of hydrogen on the colloidal complex.

Ions with positive charges are called cations. The process whereby positively charged ions of one kind are replaced on the surfaces of the clay-organic colloidal material is called cation exchange. The total amount of all kinds of cations held by the clay-organic complex at any one time is called the cation-exchange capacity. The ions held to the clay-organic surfaces are called exchangeable or replaceable cations.

The basic process involved when lime is added to an acid soil is the replacement of hydrogen ions held by the clay-organic colloidal material with calcium ions from the lime.

The diagram shows this process. The small numbers by the symbols for the different cations indicate the number of positive charges carried by that cation. Where no number appears, one positive charge is present. The numbers of different kinds of ions involved in an exchange reaction depend on the number of charges carried by each ion. Thus one calcium ion with its two positive charges will replace two singly charged hydrogen ions. Three doubly charged calcium ions are required to replace two triple charged (or, in chemical terms, trivalent) aluminum ions.

Aluminum ions have a unique role in soil acidity. In the diagram it can be seen that the replaceable aluminum ions of the acid soil have been replaced by calcium in the neutral soil. The aluminum ions thus replaced react with the soil water to form insoluble hydroxides and oxides.

Aluminum is one of the ions of positive charge that react with basic solution to form insoluble oxides and hydroxides. Aluminum occurs as a replaceable cation in acid soils in far greater quantity than any of the other

cations that show this property. So long as the soil remains neutral, these aluminum oxides and hydroxides remain insoluble and inert in the soil.

Because calcium ions replace both aluminum and hydrogen ions during the neutralization of an acid soil, the aluminum ions can be said to contribute to the total acidity of the soil. In most methods for determining total acidity of soils, the replaceable aluminum and hydrogen ions are lumped together.

Soils become acid through a process that is almost the direct reverse of the liming process shown in the diagram. The soil parent materials usually contain colloidal material, which is nearly saturated with basic cations like calcium and magnesium. But through the centuries during which soil development takes place, hydrogen ions carried by downward percolating waters gradually replace these calcium and magnesium ions. The calcium and the magnesium are carried away by the drainage waters.

The replacement of bases by hydrogen ions from the water moving through the soil profile is a slow process, but soil formation usually takes place over many centuries. The more water moving down through the soil, the faster the process. Therefore the soils of humid regions are generally more acid than the soils of subhumid regions, and acid soils are rarely found in arid regions. Also, since sandy soils can hold lesser amounts of replaceable bases, these sandy soils usually become acid more rapidly than do fine-textured soils.

Many important chemical properties of the soil are dependent on the kind of replaceable cations held by the clay-organic colloidal fraction of the soil. Calcium, potassium, and magnesium held as replaceable ions constitute the major source of these important plant nutrients in most soils.

The physical properties of the soil are often affected also by the replaceable cations. In some of the alkali soils of the West, excesses of replaceable sodium ions bring about very undesirable physical properties and very slow movement of soil water. In these alkali soils, hydroxyl ions in the soil solution greatly exceed the hydrogen ions and pH values of 8 to 10 are common.

One of the most important experiments dealing with the effect of pH on plant growth was conducted by D. I. Arnon and his associates in California. They grew plants in water solutions in which the pH varied from very acid to very alkaline; the solutions contained a liberal supply of all the important plant nutrients at all pH values. The plants grew well except at extremely acid or extremely alkaline pH values—values that are only very rarely encountered in field soils. Throughout the range of pH values common in soils—that is, from about 4 to 9—plant growth was not greatly affected by the pH of the solution.

This experiment of Dr. Arnon and his associates might well cause one to question why soil scientists so frequently measure the pH of the soil in order to diagnose troubles in crop production. One might also question the value of tables of the pH values at which various plants grow best.

The answer to these questions lies in the fact that the effects of pH on plants growing in soil are indirect, while Dr. Arnon's solution culture experiments were designed to measure the direct effects of pH. The solution cultures used contained neither deficits nor excesses of the essential plant nutrients.

In soil, however, the solubility and availability to plants of many important nutrients is closely related to the pH of the soil. It is this indirect effect of pH on the availability of plant nutrients that justifies the frequent use of pH measurements for diagnosis of soil problems, and makes tables of so-called pH preferences of plants useful under many conditions.

Changes in the acidity of soils may change the availability to plants of different nutrients in different ways. As the pH of an acid soil is increased by the addition of lime, ions such as

aluminum, iron, manganese, copper, and zinc become less soluble. In acid soils these ions may be found in dissolved form in quantities sufficient to become toxic to plants. As the soil is neutralized, these ions form inert oxides and hydroxides, and the toxicity is corrected. As the pH of the soil is increased still further, the solubility of these ions becomes so low that deficiencies of those (iron, copper, manganese, zinc) needed by plants may occur.

Bacteria and other micro-organisms living in the soil convert nitrogen, sulfur, and phosphorus from organic compounds, in which these nutrients are unavailable to plants, to simpler inorganic forms that plants can take up. Neutralizing an acid soil usually makes the soil condition more favorable to the growth of bacteria and may thus indirectly speed up processes by which important nutrients become available to plants.

The bacteria that live in association with the roots of legumes are less effective in their important role in nitrogen fixation in acid soils than in neutral or alkaline soils.

In farm practice, compounds of calcium and magnesium are the basic materials used to treat acid soils.

Along with the decrease in acidity, the addition of these materials increases the supply of calcium and magnesium for use by plants growing on the soil. In some cases, a lack of available calcium or magnesium may be the most important defect of an acid soil.

The availability to plants of the phosphorus in soils is changed in a rather complex manner when the acidity of the soil changes. Phosphate availability in many soils is highest when the soil is neutral or slightly acid, and it declines as the soil becomes either strongly acid or alkaline.

Boron and molybdenum are other plant nutrients that show changes in availability with changes in the pH of the soil. Boron deficiencies frequently occur when too much lime is added to an acid soil. On the other hand, molybdenum is most often deficient in acid soils, and becomes more available as the soil is limed.

In any discussion of the relationships between pH and nutrient availability in soils it should be emphasized that these relationships differ in different soils. In organic soils (peats and mucks), the relationships between pH and nutrient availability are not the same as for mineral soils. Copper, for example, may be deficient in acid organic soils but is rarely so in acid mineral soils.

Many soils are naturally alkaline and contain an excess of lime. The availability of plant nutrients in these naturally alkaline soils quite often differs from the availability of nutrients that results when a naturally acid soil is treated with an excess of lime. For example, many naturally alkaline soils have an adequate supply of available boron, whereas overliming of a naturally acid soil usually brings about boron deficiency.

Since the relationships between pH and the availability of plant nutrients are complex, pH measurements of soils are not easy to interpret in the solution of problems of soil fertility.

While the measurement of pH may give some valuable clues concerning the reasons for poor plant growth, it is generally necessary to follow up these clues with additional tests before an accurate diagnosis of the trouble can be made.

Among the many recent publications about chemical reactions in soils the following may be cited: *Chemistry of the Soil*, by F. E. Bear (Reinhold Publishing Corp., New York, 1955); *Clay Mineralogy*, by R. E. Grim (McGraw-Hill Book Co., Inc., New York, 1953); *Cation Exchange in Soils*, by W. P. Kelley (Reinhold Publishing Corp., New York, 1948); *Soil Conditions and Plant Growth*, by E. J. Russell and E. W. Russell (Longmans, Green and Company, New York, 1950); "Formation Constants for CU (II)—Peat Complexes," by N. T. Coleman, A. C. McClung, and D. P. Moore (Science, February 24, 1956).