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THE NATURE AND DEVELOPMENT OF SOIL ACIDITY

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THE NATURE AND DEVELOPMENT OF SOIL ACIDITY

That soil acidity has at last become recognized by soil chemists as an important factor in crop production, is made evident by the many recent articles published on the subject. This is perhaps due to the fact that the problem is becoming a more serious one each year. Large areas of sand and clay that were once alkaline or neutral have now become acid. It is a well known fact to-day, as will be explained later, that the acidity of these upland soils is due, not to the presence of organic matter, but to some other cause which is at the present time a matter of uncertainty. Whatever the cause of soil acidity may be, it is an established fact that these new areas are becoming acid through the depletion of carbonates in the soil, and that this depletion is going on at the rate of from 500 to 600[1] pounds of calcium carbonate per year from each acre of land.

Because of the increase in areas of acid sands and clay, the problems of determination and correction of soil acidity are receiving much attention at the experimental stations of Illinois, Michigan, Tennessee, and Wisconsin.

HISTORICAL

The effect of acid soils on the growth of some crops was noted as far back as the time of Aristotle,[2] although nothing was known of soil acidity. The matter was called to their attention by the increase yields on some soils treated with lime, and they naturally concluded that lime was essential in crop production. Nothing definite was known about the cause of acid soils until 1826[3] when the humic acid theory was given to the

public. Since then the whole question of soil acidity has been based upon the peculiar properties of the soil. If an acid soil be tested with blue litmus paper, the paper will in a very few minutes turn red. If, however, this soil is leached with distilled water and the leachings then tested with blue litmus paper, no reaction occurs, for the solution is neutral, demonstrating the insoluble nature of the so-called soil acids. If acid soils are treated with a neutral salt solution the neutral salts may be decomposed, the base being taken by the surface of the soil particles, and the acid set free. It is because of this fact that the injudicious use of fertilizers often aids in the formation of acid soils as will be shown later under the discussion of absorption.

Two theories have been advanced to explain these properties of acid soils. The older, and perhaps still, the most generally accepted theory is the humic acid theory, which had its beginning in 1826 when Sprengel,[3] by treating a soil with ammonium hydroxide and afterward neutralizing the solution with sodium chloride, found that a brown precipitate separated out to which he gave the name of humic acid. This theory assumes that there are present in acid soils, as the result of decomposition of animal and vegetable matter, some very insoluble organic acids, which to-day are commonly called humic acids. These are supposed to be definite compounds which react with bases litmus salt when the test paper is brought in direct contact with the soil particles. A double decomposition with the salt of litmus takes place and leaves the red acid dye behind. The supporters of this theory believe that these

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organic acids will enter into a double decomposition with any neutral salt, liberating the acid radical.

In 1839[4] Berzelius obtained two substances by treating a soil with an acid, one being soluble and the other insoluble in an alkali. To the latter he gave the name humin. He later discovered two other acids, crenic and apocrenic acids, which were very similar to humic acid in both properties and composition.

Mülder[5] found a fourth acid which he called ulmic acid, differing in composition from humic acid by containing more water and less carbon, and which was also insoluble in alkalies.

Just at present there is some question as to the existence of these so-called complex humic acids, for although many claims have been made regarding their separation, no definite stable chemical compound of these humic substances has ever been separated. Nevertheless, it is a well-known fact that marshes and peaty soils are largely acid, and it is for this reason that soil acidity was claimed to be due to the organic acids present from decomposition and decay. That this held for all soils was doubted as far back as 1888, when Van Bemmlin[6] gave his theory on colloidal absorption to the public. Absorption was not a new thing at this time. Sand filters for the purification of sea water and impure drinking water were used as early as Aristotle's time. Dr. Steven Hale[7] announced to the Royal Society of England in 1793 that the first portions of sea water passed through stone cisterns were pure. Berzelius filtered salt solutions through sand and found that the salt concentration was more or less lowered. The clarification of

barnyard liquor by percolation through clay or loam soils was mentioned by Sir Humphrey Davy in 1813. In 1819 Gazzeri[22] held that clays and loams took up in their pores the soluble matters in solution and retained them for some time. And in 1836[22] Lambuschini suggested the name of corporation for the fixation of dung liquors by the soil. Liebig likewise found that aqueous ammonia lost its odor on filtration through clay. The absorption of salts by soils was studied by Way[8] who had no difficulty in proving that the active ingredients of soil in absorption of bases was its clay. Owing to the relatively small proportion of base taken up by the clay, he concluded that the action was due not to the clay as a whole but to some constituent present in small quantities. He obtained evidence to show that this exchange of basis was largely due to hydrated-alumino-silicates of alkali or alkaline earths. The author distinguished between these phenomena and that of capillarity, which would, he claims, be exerted on the salt and not individually on the acid or basic parts. He also found that clay had the power of absorbing potash from an aqueous solution, a phenomena which may have been due to the formation of aluminates, silicates, or both. Sodium, Calcium, and Magnesium acted likewise, not only from solutions of their hydrates, but of their salts also, with both strong and weak acids, the acid remaining in solution unabsorbed and combined with other bases leached from the soil. Phosphoric acid, however, was itself absorbed. These experiments furnished the basis for a great deal of the present work on selective absorption.

In 1856 Frank showed that the soil had a limit of ab-

sorption beyond which no more of the base could be absorbed. Experiments at this time explained the phenomena as absorption. The term absorption is used to designate the process by which a solid or liquid draws unto itself and retains within its structure, or on its surface another solid, liquid or gas. At the present time we often find the terms of absorption and adsorption used indiscriminately. Adsorption is a surface phenomena and refers to the concentration of dissolved substances surrounding the object. The selective absorption theory was not launched until 1872 when Knop[9] stated that the absorptive power of the soil was proportional to the "Aufgeschlossene Silicatbasen." He suggested that the absorptive power of a soil for phosphoric acid was due to a chemical combination and if it were merely of absorption of caustic potash or ammonium hydroxide he would class these also as chemical combinations.

The colloidal theory of absorption was given to the public in 1888 by Van Bemmelin.[6] He claimed that colloidal substances formed absorptive compounds with water, bases, acids, and salts when in contact with these solutions. He also suggested that colloids may often produce chemical decomposition of salts by their power of absorption. The soil contains colloids, colloid-silicates, iron oxides, silicic acid, and humus substances, all of which may bring about these actions. The important practical fact which he wished to bring out was that the absorptive power of colloids for entire salts was slight, and that colloid silicates as they occur in nature do not possess in any large measure the power of abstracting from solution and concentrating neutral salts. Water percolating through

such material will share its dissolved salts with the water of the colloid. As late as 1900 Van Bemmelin writes "As to a specific absorption, these complexes (colloid silicates) exert none or almost none; if salts are absorbed, the absorbed water is the chief cause thereof." Further contributions to the study of selective adsorption were made by Picton and Linder[10] in 1895. They precipitated arsenic trisulphide in a colloidal solution by the use of $BaCl_2$ and found that the precipitation was accompanied by the absorption of a small amount of Barium and the liberation of an almost equivalent amount of HCl.

The latest theories in regard to selective adsorption were given by Parker in 1913,[12] and Harris[11] in 1914. Parker firmly believes that the process of removing bases from a solution is purely "physical", depending on the concentration of the surface film surrounding the soil particles.

From the outline on the history of soil acidity it is clear that there are at the present time several conflicting theories as to the cause and determination of the acidity of soils. Recent works on this subject have shown conclusively that the acid reaction of upland soils is not due to the presence of organic matter and organic acids, butto the presence of acid clays and colloids. Pure clays behave like acids but because of the presence of alkalies all clays are not acid. The same applies to sandy areas. All sands contain more or less alumino-silicates and other colloidal substances which play an important part in soil acidity as will be shown later. Under alkaline conditions these colloidal substances exist in a flocculated condition. Now the question arises, why do these alkaline soils

turn acid? It is a well-known fact that where there is organic matter present there will be a considerable amount of carbon dioxide which is readily absorbed by the soil water, forming a dilute solution of carbonic acid which has a decomposing effect on the insoluble soil carbonates:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO)_2$$

The calcium acid carbonate resulting from this action is soluble in water and is lost through leaching. It is true that the amount of organic matter present in upland clays and sands is very small but nevertheless, large quantities of carbon dioxide are found in the atmosphere and in aeration is circulated through the soil. Hall[1] says that at a depth of 1.5 meters the percentage of carbonic acid in the soil gases varies from 3.84 per cent to 14.6 per cent at various periods of the year.

Another cause for the removal of carbonates from some soils is the injudicious use of fertilizers. Ammonium sulphate is a good illustration:

$$(NH_4)_2SO_4 + CaCO_3 = CaSO_4 + (NH_4)_2CO_3$$

The effect of the continued use of ammonium sulphate is shown in the accompanying table taken from Hall. (See next page.)

It is probable that the conditions for soil acidity are present in all soils, and when the excess of alkalies are removed, acid conditions result, due to the process of hydrolysis. Harris[11] and Parker[12] attributed this phenomenon, however, to the selective absorption properties of colloids for bases in the soil solution, leaving the acid radicle behind in combination with equivalent amounts of displaced bases. But Schreiner and Failyer[18] did not find this to be true. The bases in the

DEPLETION OF CALCIUM CARBONATE IN THE SOIL THROUGH CONTINUED USE OF AMMONIUM SALTS

Plot	Manuring Per acre per year	Rate of loss of Calcium Carbonate Lbs. per acre per year
3	Unmanured	800
5	Mineral manures only	880
6	Mineral manures plus 200 lbs. of ammonium salts	1170
7	Mineral manures plus 400 lbs. of ammonium salts	1010
8	Mineral manures plus 600 lbs. of ammonium salts	1170
9	Mineral manures plus 412 lbs. of $NaNO_3$	565
10	400 lbs. ammonium salts only	1045
2	Farm yard manure only	590

resulting solution, after leaching a soil with HCl solution, were not equivalent to the amount of potassium removed from the solution. There is a difference of opinion on this matter, but from the results of the numerous experiments along this line it does seem evident that there is an equivalent displacement of one base by another.

The theory in regard to the probable formation of acid conditions in the soil is not entirely modern, for in 1850 Way[8] wrote, "It will be evident as we proceed, that the absorption power of soils is entirely different from the surface attraction." Further, "The quantity of lime acquired by the solution corresponded exactly to that of the ammonia removed from it; the action was therefore a true chemical decomposition."

Peters[21] concluded from his experiments in 1862 that, "for the absorption of bases from salts a chemical exchange with the constituents of the soil is necessary, and this chemical exchange is made possible by the help of the great predisposing affinity exerted by the soil on the bases. The following table shows the removal of chemically equivalent amounts of the bases with the amounts of potassium absorbed.

COMPARISON OF BASES DISSOLVED WITH POTASSIUM ABSORBED FROM A CHLORIDE SOLUTION

Original Concentration	Bases dissolved equivalent to grams K_2O	Potassium absorbed equivalent to grams K_2O
N/80	0.0891	0.1012
N/40	0.1241	0.1381
N/20	0.2061	0.1990
N/10	0.3168	0.3124
N/5	0.4545	0.4513

Here the bases dissolved from the soil were replaced in nearly equivalent amounts by the absorbed base.

In 1870 Lemberg[19] found the exchange of bases to be equivalent between the silicates and the salt solutions. His work brings out over and over again the fact that sodium silicates and alumino-silicates are less stable in contact with water solutions than are the corresponding potassium compounds. The replacement of sodium in silicates by the potassium of the dissolved salt takes place far more rapidly than the reverse action.

The base carrying minerals are generally true salts and are not dissolved in water, but are decomposed through hydrolysis.

Lemberg[20] found later that by treating leucite ($KAlSi_2O_6$) with a ten per cent solution of sodium chloride, the corresponding sodium alumino-silicate, anachlite ($NaAlSi_2O_6H_2O$), was formed to some extent; potassium chloride also being formed. The reverse action, treating anachlite with a solution of potassium chloride and obtaining some leucite was also carried out; and the same investigator has also shown that the feldspars and other minerals undergo the same transformation when treated with solutions of ordinary soluble salts. These results were obtained under ordinary conditions of temperature and pressure.

Artificial orthoclase and zeolites have been prepared at lower temperatures. These results offer an attractive field for both phase rule and mass law studies.

The results which Lemberg obtained were chiefly due to hydrolysis and we can apply this same principle to the phenomena

going on in the soil.

METHODS FOR DETERMINATION OF SOIL ACIDITY

The remedy for acidity of soils is well known. If an acid soil be treated with some form of lime the acidity is neutralized and the "sick" or "exhausted" soil will recover its productivity if other conditions are favorable. Yet it has only been since 1895 that investigations for developing methods of determining acidity were started. To-day several methods have been worked out which will be briefly described.

The first practical quantitative method known was published by C. G. Hopkins, W. H. Knox, and J. H. Pettit.[13] They based their method on the assumption that when a mineral salt solution is added to the soil the acids apparently unite with mineral base, evidently liberating the mineral acid whose titration power furnishes a very satisfactory basis for the determination of the total acidity of the soil. Place 100 grams of the soil in a stout, medium wide-mouthed bottle of about 400 c.c. capacity; add a sufficient quantity of a 5 per cent NaCl solution to make 250 c.c. of liquid, including the moisture contained in the soil, but independent of the volume of the soil itself; close tightly with a rubber stopper; place in a shaking machine and shake for 3 hours. Place the bottle in a suitable centrifuge and whirl until the soil is thrown down sufficiently to allow at least 125 c.c. of clear liquid to be drawn off. Exactly 125 c.c. of the clear liquid is placed in an Erlenmeyer flask and heated to boiling to expel traces of CO_2 and to insure a sharp end reaction. Then titrate with standard fixed alkali, phenolphthalein being used as the indicator.

In shaking a soil sample with a neutral salt solution all of the acid set free will not be liberated with the first quantity used. So in order to shorten the process, it has been found that each succeeding portion differs from the other by two-thirds. Hence shake but once and multiply this result by three for a total acid determination.

A method which has been accepted by many as favorable was worked out by F. P. Vietch.[14] He proposes that 100 grams of the soil be allowed to stand over night with 100 c.c. of distilled water in a Jena flask. Fifty c.c. of the supernatant liquid are drawn off and boiled in a closed Jena beaker, after adding a few drops of phenolphthalein, until a pink color is developed or until the volume has been reduced to 5 c.c. without the appearance of a color. The pink color shows the soil to be alkaline, while no color shows it to be acid or neutral. The degree of acidity is determined by means of lime water as follows: To three portions of soil, each consisting of as many grams as the standard lime water contains milligrams of calcium oxide per c.c., are added 50 to 60 c.c. of distilled water, and different amounts oflime water, e.g. 10 c.c.; 20 c.c.; and 30 c.c. All three portions are at once evaporated to dryness on a steam bath; the residue transferred to stoppered Jena flasks with 100 c.c. of distilled water, and allowed to stand over night. Fifty c.c. are then drawn off from each portion and boiled, after adding a few drops of phenolphthalein until a pink color is produced, or until the volume is 5 c.c. The results will serve as a guide to the acidity of the soil. The test is then repeated on three more portions of the soil, the amounts

of lime water added in this case differing from each other by only 1 or 2 c.c. The quantity of lime water necessary to produce an alkaline reaction is taken as a measure of the acidity of the soil.

Another method worthy of attention here was worked out by H. Süchting.[15] From 10 to 30 grams of soil are placed in a flask together with some water. The flask is closed with a cork, through which pass inlet and outlet tubes and the stem of the tapered funnel. A weighed amount of calcium carbonate (about 0.40 grams) is now added to the flask and a current of hydrogen is passed through it for two hours. The outlet tube of the flask is then attached to an absorption tower containing a measured volume of standard sodium hydroxide solution, 50 c.c. of twenty per cent hydrochloric acid are added to the flask and the current of hydrogen is allowed to pass through the apparatus for one hour. The carbon dioxide liberated from the residue of calcium carbonate which has not been decomposed by the acidity of the soil is thus absorbed by the sodium hydroxide, and its quantity determined by titration in the usual way. The difference between the quantity so found and that added originally as calcium carbonate is a measure of the acids existing in the soils.

R. Albert[16] boils from 20 to 50 grams of soil with a known amount of lime and an excess of ammonium salt. From 20 to 50 grams of air-dried soil is mixed in a Jena flask of about 1 litre capacity with 200 c.c. of distilled water, a definite volume (from 50 to 100 c.c.) of standardized barium hydroxide solution is added from a burette, and 10 grams of solid ammonium

chloride are then introduced. The contents of the flask are then boiled, after the flask has been attached to a condenser, and the ammonia liberated is collected in a receiver containing a known quantity of standard acid. The distillation takes about twenty-five minutes, and after the excess of acid in the receiver has been titrated a simple calculation gives the quantity of barium hydroxide which has been used to neutralize the acid present in the soil; these acids may be expressed as grams of carbon dioxide per 100 grams of soil. Barium hydroxide was found preferable to calcium oxide or magnesium, as the calcium and magnesium compounds formed are partially dissociated by boiling.

The methods outlined above are all technical in nature and are designed for laboratory purposes. E. Truog[17] has perfected a method whereby the entire operation can be carried out in the field and the lime requirements for that particular piece of land determined by a mere comparison of results with a chart. Ten grams of soil are placed in a 300 c.c. Erlenmeyer flask and to this is added 1 gram of calcium chloride, 0.1 gram of zink sulphide, and 100 c.c. of distilled water. This is thoroughly shaken and then heated over a flame. After the contents have boiled one minute, a strip of moistened lead acetate paper is placed over the mouth of the flask and the boiling continued for two minutes more, when the paper is removed. If the soil is acid the paper will be darkened on the under side in porportion to the degree of acidity. If it is non-acid no darkening will occur.

EXPERIMENTAL WORK

Since the acid reaction of upland soils probably cannot be ascribed entirely to the presence of organic matter the experiments set forth in this paper were performed to determine, if possible, whether the cause be due to a physical process or to chemical combination brought about by hydrolysis.

Experiment I. To determine the effect of distilled water upon kaolin, a 25 gram sample of kaolin, slightly acid to litmus paper, was placed in a 300 c.c. Erlenmeyer flask with about 200 c.c. of distilled water and stoppered to exclude all air, and then set aside for three weeks with an occasional shaking once in two days. At the end of this time a 25 gram sample of the original kaolin was tested with blue litmus paper, and at the same time the kaolin which had been treated with distilled water was also tested for acidity. In a very short time the treated kaolin had turned the test paper a deep and uniform pink, indicating an acid reaction. The untreated kaolin gave negative results.

The possible explanation for the above results is that the kaolin is but an anhydride of an acid and on treatment with water hydrolysis has taken place. Some of the bases were also replaced by the hydrogen from the water, leaving the kaolin more acid. Equations:

$$2KAlSi_3O_8 + HOH = KOH + 2HAlSi_3O_8$$

$$HAlSi_3O_8 = HAlSiO_4 + 2Si\,O_2$$

$$2HAlSiO_4 + HOH = Al_2O_3.2SiO_2.2H_2O$$

Experiment II: To determine the action of acid on kaolin, two 25 gram samples were treated with 2 liters each of N/20 sulphuric acid and placed in a mechanical shaker for 24 hours. The sulphuric acid was then filtered off and the kaolin thoroughly washed until all the acid has been removed. The washings were added to the original filtrate and the whole was then tested with blue litmus paper, a test being made also on the original sample. The treated sample gave a very decided acid reaction in a very short time.

One hundred cubic centimeter portions of the N/20 sulphuric acid used in the experiment were then titrated with N/2 barium hydroxide. Two hundred cubic centimeter portions of the filtrate were likewise titrated to determine if possible the loss of the acid due to the treatment.

TABLE I. AMOUNT OF H_2SO_4 LOST IN TREATMENT OF THE KAOLIN.

Titration	Acid used c.c.	$Ba(OH)_2$ used cc.	Filtrate used c.c.	$Ba(OH)_2$ used c.c.	H_2SO_4 lost
1	100	9.90	100	4.95	0.00
2	100	9.90	200	9.90	0.00
3	100	9.95	200	9.90	0.10
4	500	49.20	1000	49.05	0.15

The litmus showed an increased acid reaction in the kaolin. The titrations show that this increased acid reaction was not due to any of the sulphuric acid being absorbed and held, in an insoluble condition, by the kaolin, for very little of the acid was lost in the treatment. The question that next suggests itself is, did the acid neutralize some of the base present in the kaolin and thus cause an increased acidity? But in order

to do this some of the acid would have been used in neutralizing and the results given above would not have been obtained. To further show the increase of acidity in the treatment of kaolin a 25 gram sample of the original kaolin, and the residue of the treated sample were then tested quantitavely for the amounts of acid present in each by Truog's method in which the samples were treated with 20 c.c. of N/25 barium hydroxide and carbonated water, and evaporated to dryness. Then the carbon dioxide fromthe barium carbonate was liberated by phosphoric acid and taken up again in 20 c.c. of barium hydroxide and titrated with N10/25 hydrochloric acid.

TABLE II. AMOUNT OF INCREASE IN ACIDITY DUE TO H_2SO_4

Treated Sample		$Ba(OH)_2$ Neutralized by soil acids	Untreated Sample		$Ba(OH)_2$ Neutralized by soil acid
$Ba(OH)_2$ used	Acid used		$Ba(OH)_2$ used	Acid used	
20 c.c.	32 c.c.	12	20 c.c.	24.8c.c.	4.8

It will be noticed from Table II that the treating of kaolin with carbonated water has rendered it considerably more acid than the original sample, which was undoubtedly due to the replacing of the aluminum in the silicate by hydrogen, causing hydrolysis as was previously shown.

Experiment III: This experiment was an attempt to prove that carbonated water extracts the bases from a soil, leaving it in an acid condition. If the removal of bases is due to the action of water the chemical action of hydrolysis must be taking place to cause the removal. Two 25 gram samples were placed in 8 liter bottles. To each bottle was added four liters of carbonated water. They were then placed in a mechanical shaker

for 24 hours and filtrated. The residue gave an acid reaction when treated with blue litmus paper, while the original sample was neutral. The filtrate from one of the samples was treated quantitatively for calcium and magnesium, an abundant precipitate being obtained in each case, showing the presence of considerable quantities of these bases in the filtrate.

Then to determine the amount of calcium and silica that had been extracted from the tremolite, one liter of the filtrate was evaporated to dryness and then taken up with hydrochloric acid and dehydrated. This was repeated several times to secure all the silica from the solution which was filtered off, ignited and weighed. The filtrate was then made alkaline with ammonium hydroxide and the calcium precipitated with ammonium oxalate. The calcium was weighed as calcium oxide. The results are shows in the following table:

TABLE III. AMOUNTS OF CALCIUM AND SILICON FOUND IN THE FILTRATE AFTER TREATMENT WITH CARBONATED WATER

No. of Sample	Amount of filtrate used	CaO	SiO_2
1	1000 c.c.	.0630	.0028
2	1000 c.c.	.0622	.0024

The facts brought out by the above experiments can be satisfactorily explained on the basis of hydrolysis. The calcium of the silicates is set free the same as the potassium in feldspar, previously given, and the removal of calcium from the tremolite causes a removal of an equivalent number of hydrogen atoms from the water and leaves an excess of hydroxyl ions in the solution to unite with the calcium. If this theory of replacement be true then the hydrogen takes the place of the

calcium and we have an acid reacting product.

In that this same principle holds true in regard to the colloidal silicates of the soil we have a probable theory for the formation of acid soils. As complex silicates decompose, silica separates out as quartz, due to the fact that the resulting compounds are unstable. The minerals in rocks are for the most part salts of strong bases combined with weak acids as alumino-silicic and ferro-silicic acids. Hence water not only dissolves but hydrolyses them.

Experiment IV. To further determine the effect of carbonated water on the removal of bases from a soil and the causing of acidity the previous experiment was repeated using ground basalt rock as the soil. Portions of the first filtrate were titrated with N 10/25 hydrochloric acid. The residue from the first filtration was treated again with four liters of carbonated water to note the further effect of carbonated water on the removal of bases. This residue was then used for the quantitative determination of the acidity.

TABLE IV-V

ACID NECESSARY TO NEUTRALIZE BASES IN FILTRATE AFTER TREATMENT OF BASALT WITH CARBONATED WATER

Sample I

First Filtration		Second Filtration	
Filtrate c.c.	HCl c.c.	Filtrate c.c.	HCl c.c.
250	0.55	1000	1.4
250	0.55	1000	1.4
Sample II			
500	1.10	500	0.3
500	1.10	500	0.3
500	1.10	500	0.3

It will be seen from Tables IV and V that the greatest amount of the base is set free in the first filtration. This slowing up of hydrolysis is due to the clogging effect of the insoluble silicates which precipitate on the surface of the particles and prevent the further action of the water on the soil particles.

On testing the residue with blue litmus paper an acid reaction was given. The original basalt was neutral. The treated basalt was likewise tested with Truog's zinc sulphide method and a positive reaction was obtained, showing the treated basalt to be acid.

Experiment V. To determine quantitatively the amount of acid present the residue was treated with 20 c.c. of N barium hydrate and evaporated to dryness. It was then taken up with carbonated water and again evaporated to dryness. A check sample was run on the original basalt also. The residue was then placed in a carbon dioxide machine for determining acidity and treated for 40 minutes, using 1-5 phosphoric acid to liberate the carbon dioxide which was taken up by barium hydroxide and then titrated with hydrochloric acid.

TABLE VI. INCREASE OF ACIDITY OF BASALT ON TREATMENT WITH CARBONATED WATER

	c.c. HCl N 10/25	c.c. of acid neutralized by bases removed
Treated basalt	23.60	3.60
Untreated basalt	21.10	1.10

Here again we have the same results brought out as were shown in Experiment IV.

Experiment VI. To determine whether soils made acid by the action of carbonated water would have the same results on plant growth as the acid soils found in the field, about 200 grams of basalt powder and 200 grams of a sandy soil were treated as described in Experiment V to make them acid. After treatment these soils reacted distinctly acid to litmus. The soils were then treated as follows:

The soil was placed in 50 c.c. beakers. In the case of the sand 90 grams were placed in a beaker, and in the case of the basalt but 30 grams were used together with 60 grams of quartz to give it the proper tilth. These beakers were prepared as follows:

#1. 90 grams of treated sand.

#2. 90 grams of treated sand and 0.15 grams Calcium carbonate.

#3. 90 grams of untreated sand.

#4. 90 grams of untreated sand and same amount of lime as in #2.

#5. 30 grams of treated basalt and 60 grams of quartz.

#6. 30 grams treated basalt; 60 grams quartz; and 0.15 grams of calcium carbonate.

#7. 30 grams of untreated basalt, and 60 grams of quartz.

#8. 30 grams of untreated basalt; 60 grams quartz; 0.15 grams of calcium carbonate.

To each beaker there was then added 20 c.c. of nutrient solution prepared as follows:

0.50 grams potassium chloride
0.30 grams calcium chloride
0.20 grams magnesium sulphate
1.00 liter of distilled water

THE EFFECT ON THE GROWTH OF ALFALFA

OF SOIL TREATED WITH CARBONATED WATER

(In Explanation of Photograph on Opposite Page)

I. Untreated Sand.

II. Untreated Sand and Calcium Carbonate.

III. Treated Sand.

IV. Treated Sand and Calcium Carbonate.

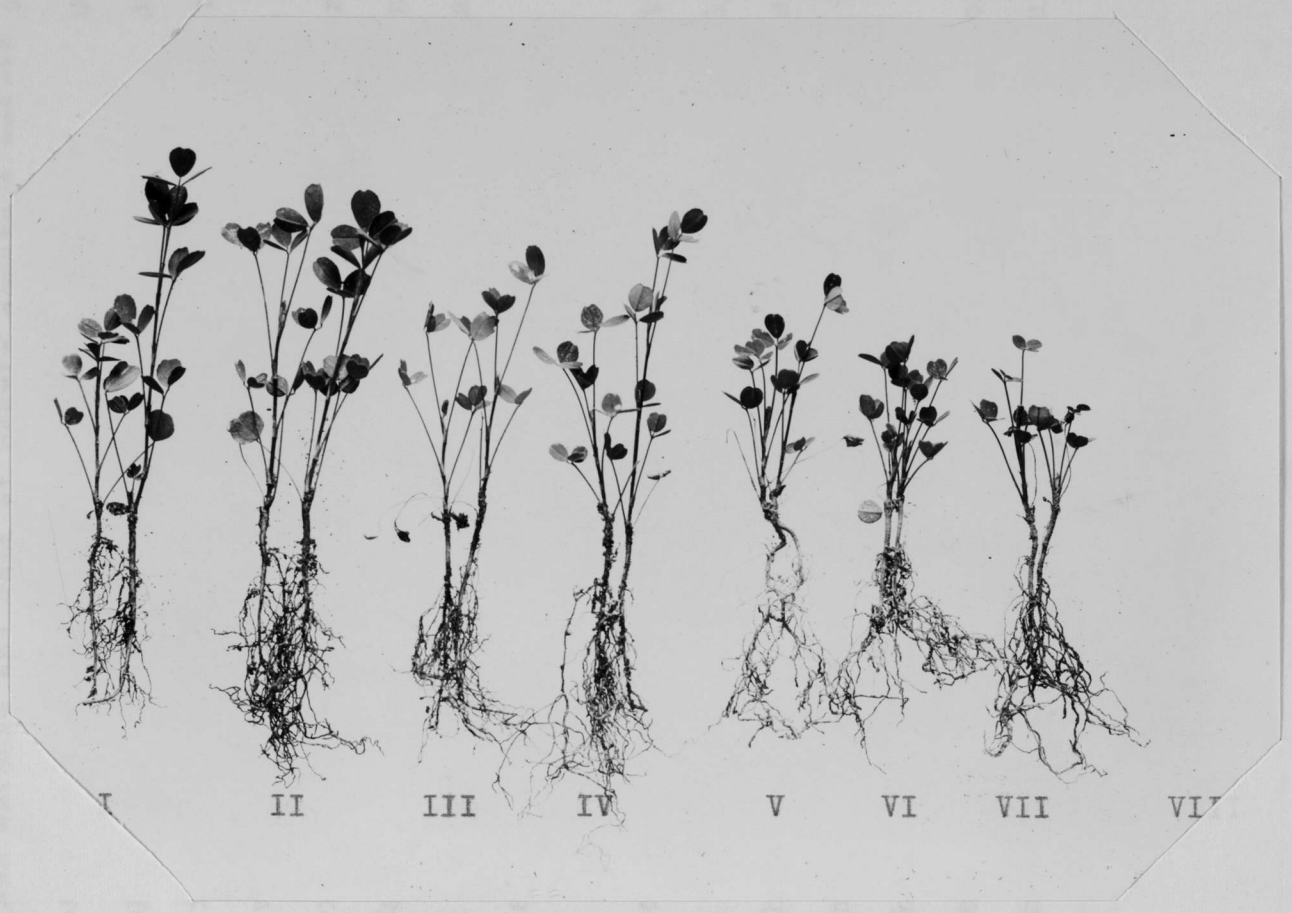
V. Untreated Basalt.

VI. Untreated Basalt and Calcium Carbonate.

VII. Treated Basalt and Calcium Carbonate.

VIII. Treated Basalt. (Plant killed by acidity.)

-oOo-


I
II
III
IV
V
VI
VII
VII

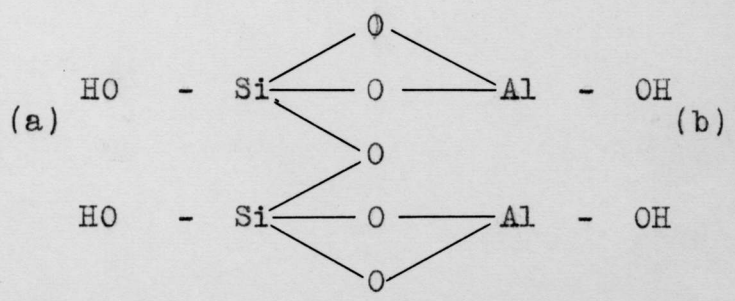
In addition to this 0.025 grams of ferric phosphate were added to each beaker.

Ten seeds of alfalfa were then sown in each beaker and the beakers weighed and kept at nearly constant weight all the time thereafter. At the end of two months the accompanying photograph was taken and from these results it is evident that the acidity formed through the treatment of the soil with carbonated water is similar to that formed in the field in so far as its effect on alfalfa is concerned, and helps to bear out the probability that our upland acid soils are formed in part at least through the action of carbonated water on the soil particles.

CONCLUSIONS

The experiments described in this paper indicate that the behavior of upland soils toward neutral salts is probably not due to the presence of organic acids or even to the presence of organic matter, but is most likely due to the colloidal silicates and to the soil particles themselves.

That clays may become acid when treated with carbonated water can be explained by the following structural formula for clay:[23]



By neutralization of the acid hydroxyls at (a) the clay would become neutral. For this reason we use lime to neutralize

acid clays. By prolonged treatment of a neutral clay with large quantities of carbonated water the base is set free and we have the acid hydroxyls forming an acid product again. In the treatment of the soil samples in the experiments given it can be assumed that the same chemical process forms acid soils.

The foregoing results seem to indicate that there is something more than a mere physical strength of surface tension of the soil particles causing the removal of the bases from a neutral salt solution. Soil acidity is probably due to the formation of soluble salts through the chemical action of the carbonated water on the soil particles, and the soluble bases that have been formed are leached away, leaving the acid formed behind.

In the removal of bases from a neutral salt solution the reactions are limited according to the laws of mass action and thus we have the limit of absorption, as this phenomenon is called at the present time.

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Just in Sails

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