THE RELATION BETWEEN THE GROWTH OF ALFALFA ON ACID SOILS AND THE LIME EXTRACTED BY CARBONATED WATER

BY

ELLSWORTH HAY

A Thesis Submitted for the Degree of
BACHELOR OF SCIENCE IN AGRICULTURE

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INTRODUCTION

It has long been known that some plants will make a good growth on acid soils, while others grow so poorly that they are entirely unprofitable for use as crops on such soils. Plants have been divided on this basis into two groups, the one, acid-tolerant, the other, acid-intolerant. There is no sharp dividing line between these groups since all degrees of acid toleration are found, from the most intolerant, like alfalfa, to sheep sorrel and similar plants which are commonly used as indicators of soil acidity. Certainly there must be some very marked differences in the structures or in the habits of growth of various plants to cause such wide variations in their behavior toward an acid condition of the soil.

A common opinion is that soil acids are harmful because of their corrosive or harmful action on the tissues of plant roots. If this were the case, it might well be expected that the roots of acid-intolerant plants, such as clover and alfalfa, would be more sensitive to an acid condition than those of acid-tolerant plants. However, some work which has been done by Dyer[1] on the acidity of the root sap of different plants, indicates that the acids in the sap of clover often reach a higher concentration than those in the

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[1] Jour. Chem. Soc. 65 (1894) 115-167.

sap of many acid-tolerant plants. Consequently, it seems improbable that soil acids cause harm because of their corrosive action.

There can be no doubt but that an acid reaction has a marked depressing effect on the bacterial life of the soil, and thus indirectly lessens the quantity and the rate at which plant food materials are made available. Such an action would of necessity affect all kinds of plants, excepting legumes, in much the same way, so that there would be no cause on this account for dividing non-legumes into two groups, depending on their ability to grow on acid soils.

Another possible explanation of the injurious effect of soil acids, which is brought out by Truog[2] in connection with a study of the feeding power of plants, is that they deprive the plant of a sufficient supply of calcium bicarbonate, which is necessary for neutralizing harmful organic acids formed in the plant, probably as by-products of protein synthesis. According to this theory it is to be expected that plants with a high protein content will also be high in lime, and Table I shows this to be the case.

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[2] Wis. Res. Bul. 41 (1916) 33-35.

Table I.--A Comparison of the Protein and the Lime Content of Plants.[3]

	Crude Protein %	Calcium Oxide %
Cowpea	19.3	2.54
Soybean	16.0	1.72
Alfalfa	14.9	1.95
Clover	12.8	1.60
Bluegrass	8.3	.43
Sorghum	7.4	.39
Timothy	6.2	.25
Mangel	1.4	.20

If calcium bicarbonate is necessary to keep down the acidity of plant juices, plants must be able to obtain it from all kinds of soils, or else they would make little growth beyond germination. There can be but little or no free, solid calcium carbonate in an acid soil, unless it has been freshly applied and has not had time to react with the soil acids, but plants certainly obtain calcium bicarbonate from such soils somehow. The way in which they do this is easily explained if the composition of the soil solution, so far as calcium bicarbonate is concerned, is considered to be the result of a balanced reaction between the dissolved carbon dioxide of the soil water and the calcium compounds

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[3] Henry and Morrison, "Feeds and Feeding" 640 and 672.

of the soil, as follows:

$$\text{Ca silicate} + 2H_2CO_3 \rightleftarrows Ca(HCO_3)_2 + \text{acid silicate}$$

From this reaction it can be seen that there must be in the soil solution a certain amount of calcium as the bicarbonate and consequently in a form available for plant use. As fast as any of this is removed, equilibrium is destroyed, and the law of mass action causes more calcium bicarbonate to be formed. Calcium bicarbonate may be made available to plants from other compounds than silicates by reactions similar to the following.

$$Ca_3(PO_4)_2 + 2H_2CO_3 \rightleftarrows Ca(HCO_3)_2 + Ca_2H_2(PO_4)_2$$

$$\text{Ca humates} + 2H_2CO_3 \rightleftarrows Ca(HCO_3)_2 + \text{humic acids}$$

The rate at which the bicarbonate is formed will depend on the active mass and the nature of the original calcium compounds, the concentration of the carbon dioxide in the soil water, and the amount and the strength of the soil acids. The active mass of the solid calcium compounds depends on the area of their surface exposure, which in turn depends on the amount and the degree of subdivision of these compounds. The same is true of the soil acids. The greater the active mass of the calcium compounds and the greater the concentration of carbon dioxide in comparison with the mass and the strength of the soil acids, the greater will be the amount of calcium bicarbonate which will be furnished for the use of plants in a given time. The strength of the acids in the calcium compounds will of course also have a marked influence.

With this explanation in mind, it is not difficult to understand how a plant with a low lime content may be able to get all of the soluble calcium bicarbonate it needs for normal growth, on an acid soil. However, with plants which require a considerable quantity of lime the case is different. Calcium bicarbonate may not be formed rapidly enough to meet their needs and consequently they may suffer. This theory also explains why it is often possible to grow good crops of clover on silt and clay soils that are decidedly acid, and only small crops on sandy soils that are but slightly acid. The silt and clay soils usually contain not only a greater quantity of calcium compounds, but also such compounds in a finer state of subdivision than the sandy soils, and thus calcium bicarbonate, in solution, is formed in larger amounts and replenished more rapidly in these silt and clay soils than in the sandy soils.

When a plant with a high lime content, such as alfalfa, is grown on acid soils, calcium bicarbonate is often probably the most important factor limiting its growth, and the growth which is made will depend to a large extent on the quantity of lime in the soil solution. If there is calcium bicarbonate in the soil solution of acid soils, due to the solvent action of carbonic acid, then extracts of such soils with carbonated water should contain calcium bicarbonate in amounts proportional to the amounts in the soil solution, and consequently proportional to the growth made by alfalfa.

In going over the literature in regard to this subject, no references were found in which a comparison was made between the calcium bicarbonate extracted from soils by carbonated water and the growth made by crops. A few references were found and are given, in which the calcium in soils was determined by extraction with various acids, in attempts to get at the lime needs of the soils.

Some work on the relation between soil acidity and the lime soluble in 10 per cent hydrochloric acid has been done by H. Kappen[4] in connection with a study of acid soils around Jena. He found that the amount of lime extracted from a soil upon heating it for three hours on a water bath with 10 per cent hydrochloric acid follows inversely the degree of acidity as expressed by the rapidity of the reddening of litmus paper.

Heinrich[5] has determined the relation between the lime content (not stated how determined) of soils and the growth of crops, and finds that a minimum content of from .2% to .5% of calcium oxide is necessary for the growth of peas and of clover.

Holleman[6] has investigated the relation between the lime that could be extracted with carbonated water and the physical

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[4] Land. Vers. Sta. 88 (1916) 13.

[5] Bied. Centr. 21 (1892) 311.

[6] Land. Vers. Sta. 41 (1892) 37.

condition of some heavy clay soils of Holland. Its relation to soil acidity is not discussed. His method of procedure consists in running carbon dioxide into one liter of distilled water containing 20 gm. of soil up to the point of saturation, and filtering after 24 hours. Five hundred cc. of the filtrate are evaporated down with acetic acid, and the calcium precipitated directly with a measured amount of N/10 ammonium oxalate, without the removal of the iron, aluminum, phosphorus, and manganese. The excess of ammonium oxalate is titrated with standard potassium permanganate, and by difference the amount of calcium is determined.

The object in mind when starting this thesis was to work out a suitable method for the extraction of calcium bicarbonate from acid soils, and to determine what relation the amounts, which could be extracted, had to soil acidity and to the growth of alfalfa.

EXPERIMENTAL METHODS

In the development of a method for determining the relation between the amounts of lime that are extracted with carbonated water from acid soils and the growths made by alfalfa on these soils, several problems arise as follows: the proportion of soil to carbonated water that should be used, the length of time of extraction, the method of filtration, and the method of determining the calcium in the filtrate. The first problem taken up was the determination of the calcium in the filtrate.

Determination of Calcium.--The final method which was adopted for determining the calcium in the extracts consists in precipitating it as the oxalate, after removing all iron, aluminum, manganese, and phosphorus and preventing the precipitation of magnesium. The precipitate is treated with sulphuric acid and the oxalic acid liberated is titrated with N/10 potassium permanganate. The complete procedure is as follows.

Pipette 500 cc. or other aliquot of filtrate into a 600 cc. beaker and evaporate dry on the steam bath. Take up with 2 cc. of concentrated hydrochloric acid and 100 cc. of distilled water. Boil 5 minutes. Add .5 cc. of a 10% solution of ferric chloride. Make alkaline with ammonia. Add 5 cc. of bromine water and boil 5 minutes. Add a few more cc. of bromine water and boil 10 minutes. Add 10 cc. of ammonium chloride solution. If acid, make just slightly alkaline with ammonia. Make very slightly acid with acetic acid. Heat to boiling and filter off the iron, aluminum, manganese, and phosphorus. Wash 10 times with hot water. Bring the acetic acid filtrate to a volume of about 100 cc. Heat to boiling. Add .5 gm. of oxalic acid, or 5 cc. of a 10% solution. Add dilute ammonia (3 cc. of concentrated ammonia in 90 cc. of distilled water) slowly with a pipette until the solution is alkaline. Digest until clear, let stand over night and filter. Wash and dissolve the precipitate on the filter with hot dilute sulphuric acid, 1 to 10 strength. Wash with hot water. Add about 5 cc. of half strength sulphuric acid, dilute to about 200 cc., warm to 70 degrees C. and titrate with standard potassium permanganate.

Discussion of Method.--By removing the iron, aluminum, phosphorus, and manganese all in one precipitation and filtration, an accurate determination of calcium is possible with a minimum amount of manipulation. The small amount of iron is added to insure complete precipitation of the phosphorus. Bromine is used to precipitate the manganese as manganese dioxide, and to destroy any organic matter which may be present. The method of separation of calcium from magnesium is one which was devised and which is recommended by W. C. Blasdale[7]. By precipitating calcium in an acetic acid solution, the possible occlusion of magnesium is prevented, since magnesium oxalate is much more soluble in acetic acid than calcium oxalate. A comparison was made between precipitating calcium in an acid solution by this method and precipitating it in alkaline solution by the addition of ammonium oxalate. The two methods gave exactly identical results, but since the former has the better theoretical basis, it was adopted.

The solutions used in the determination of calcium are as follows.

Ammonium Chloride: 200 gm. of NH Cl per liter of dis-

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[7] Treadwell and Hall, "Analytical Chemistry", Vol. II, 77.

tilled water.

Ferric Chloride: 10 gm. of $FeCl_3$ per 100 cc. of distilled water.

Acetic Acid: 50 cc. of 99.5% CH_3COOH per 800 cc. of distilled water.

Bromine Water: saturated solution of liquid Br in distilled water.

Oxalic Acid: 10% solution.

Potassium Permanganate: N/10 solution.

For the purpose of checking the method of analysis, a standard solution of calcium carbonate was made up by dissolving .6505 gm. of pure calcite in 500 cc. of distilled water, slightly acidified with hydrochloric acid. In order that this solution might be made analogous to the soil extracts, a second solution consisting of .3 gm. of each of the following salts was prepared.

$MgCl_2$
$MnSO_4$
Na_3PO_4-$12H_2O$

Ten cc. portions from each of these two solutions were mixed and analysed for calcium. As a check on the purity of the reagents in respect to calcium, analyses were also run on 10 cc. portions of the second solution alone. The results of these analyses, as given in Table II, demonstrate the purity of the reagents used and the accuracy of the method. It will be noted that the results of the analyses are a little too high, which is due to the fact that it is necessary to run beyond the end-point in the titration with potassium permanganate in order to get a perceptible color.

Table II.--Results of Analyses of Chemicals and Standard Solution for Calcium.

	cc. $KMnO_4$	$CaCO_3$ by analysis	$CaCO_3$ by calculation from standard solution
Blank--Mg, Mn, P, no Ca	1 drop	---	---
Blank--Mg, Mn, P, no Ca	1 drop	---	---
Check--Mg, Mn, P, Ca	2.65 cc.	.01325 gm.	.01301 gm.
Check--Mg, Mn, P, Ca	2.68 cc.	.01340 gm.	.01301 gm.

EXTRACTION AND FILTRATION

Preparation of Carbonated Water.--Carbon dioxide is run into distilled water from a pressure tank, impurities being removed by first passing it through a wash bottle containing sulphuric and chromic acid. The gas is passed into the distilled water until the solution is N/25. A solution of this normality is very nearly saturated and so is comparable to the strength of the solution in the soil. A saturated solution of carbon dioxide is not used because of the difficulty of reaching and maintaining it at the point of complete saturation. Ten to fifteen liters of N/25 solution can be prepared in this way in less than two hours. To determine the strength of the carbonated water, 50 cc. are measured into an

Erlenmeyer flask containing 50 cc. of distilled water, which dilutes the solution and helps prevent loss of carbon dioxide during titration. A drop of phenolphthalein is added, and 10 cc. of .4 N barium hydroxide run in at once. In this way all of the carbon dioxide is precipitated as barium carbonate, and the excess of barium hydroxide is titrated with .4 N hydrochloric acid before it has time to react with carbon dioxide from the air. When the carbonated water is exactly N/25, 5 cc. of .4 N hydrochloric acid are required to neutralize the excess of .4 N barium hydroxide. The strength of carbonated water decreases rapidly even when kept in a tightly stoppered container, and so it is necessary to make up a new solution every time a series of determinations is to be run.

Extraction Methods.--Extraction is accomplished by shaking 12 gm. of soil with 600 cc. of carbonated water in a one liter bottle for two hours in the end-over-end shaking machine.

In order to determine what effect the proportion of carbonated water to soil had on the amount of lime extracted, extractions were made on two soils, a Colby silt loam and a Sparta sand. The results of these extractions are given in Table III, and they are plotted in Figure 1.

Table III.--Effect of Dilution on the Amount of Calcium Extracted from Two Soils.

	Colby Silt Loam		Sparta Sand	
Dilution	cc. $KMnO_4$	Lbs. $CaCO_3$ per acre	cc. $KMnO_4$	Lbs. $CaCO_3$ per acre
1-100	1.59	3180	.76	1900
1-50	1.90	1900	.70	875
1-25	2.91	1455	1.07	668
1-1½	2.41	360	.59	109

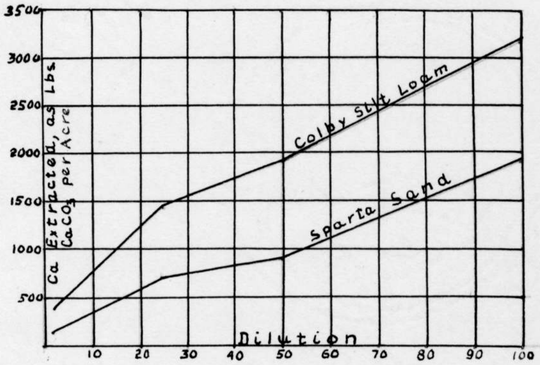

Figure 1.

Although a dilution of 1 to 1½ undoubtedly gives more nearly the amount of lime which the plant is able to obtain from a soil, than the other dilutions, there are some objections to its use. A very large supply of soil must be available for the determination, and the differences between the amounts of lime extracted from various soils are not so great as when larger dilutions are used. Of course, when greater dilutions than this are used, only comparative results between soils can be secured. According to the graphs it would seem that a dilution of 1 to 25 would be the proper one to use, because there seems to be a break in the curve at that point. However, if data were available for plotting more points between the 1 to 1½ and the 1 to 25 dilutions, the breaking point of the curve would probably be moved farther to the left. Since a dilution of 1 to 50 gives a convenient amount of soil to work with and shows fairly large differences between soils, this dilution was selected for use in the first series of extractions which were made.

It was learned by experiment that the amount of lime extracted increases very little after two hours of shaking. Twelve gram samples of two widely different soil types, Colby silt loam and Sparta sand, were extracted for 1, 2, 4, 8, and 18 hour periods, with the results as given on the following page in Table IV.

The decreased amount in the 18 hour extraction of Sparta sand was due to incomplete precipitation of the calcium as oxalate in the final steps of the procedure. Aside from this discrepancy the results show that practically all of the extractable calcium has been removed at the end of two hours of shaking.

Table IV.--Effect of the Period of Extraction on the Amount of Calcium Extracted. Calcium is Expressed in Terms of cc. $KMnO_4$.

Extraction time. Hours	Colby Silt Loam			Sparta Sand		
	A	B	Average	A	B	Average
1	1.73	1.67	1.70	.67	.73	.70
2	1.83	1.96	1.89	.67	.72	.70
4	1.85	1.85	1.85	.70	.72	.71
8	1.96	1.85	1.90	.72	.76	.74
18	2.00	2.02	2.01	.68	.64	.66

Filtration.--After two hours of shaking, the soil is allowed to settle for a few minutes and is then filtered with the apparatus shown in Figure 2.

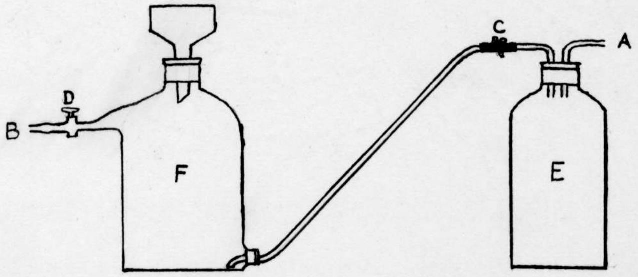

Figure 2.

The suction pump is first attached to A, the pinch-cock C is opened and the stop-cock D closed. A 9 cm. hardened filter paper is placed in the Büchner funnel, moistened and drawn down tight and smooth. A little over 500 cc. of the supernatant liquid is carefully decanted from the extraction bottle into a 600 cc. beaker. The sediment and liquid remaining in the extraction bottle is shaken up and dumped onto the filter paper and allowed to go just to dryness, forming a soil filter. A small watch glass is quickly placed on the filter and the contents of the beaker emptied on to it so as not to disturb the soil filter. The filtrate in making the soil filter and the first portions to come through after the contents of the beaker have been poured on to it, are drawn off by suction into the bottle E and discarded. As soon as filtration is well started and the filtration flask F has been rinsed by the first portions of the clear filtrate, the pinch-cock C is closed and the suction attached to B. The stop-cock D is opened and filtration continued.

Before this method of filtering was developed, difficulty in getting a clear filtrate was experienced. After the soil filter was made, the funnel was removed and the flask rinsed out with distilled water, the funnel was replaced and the contents of the beaker emptied on to it. Removing the suction frequently loosened the filter paper and allowed soil material to creep under the paper during subsequent filtration, giving a cloudy filtrate.

In order to check the accuracy of the filtration process, duplicate 14 gm. samples of a silt loam and of a clay were shaken for two hours with 700 cc. of N/25 carbonated water each, and filtered by pressure through Pasteur-Chamberlain porcelain filters. The two duplicates of each soil both went through the same filter, the first 150 cc. of each filtrate being discarded and 500 cc. of the remaining filtrate being analysed for calcium. Samples of the same soils were also extracted with N/25 carbonated water and filtered through soil filters as previously described, and the calcium in 500 cc. portions of the filtrate determined. Table V gives the results of these extractions and filtrations.

Table V.--Effect of the Kind of Filter on the Calcium in the Filtrate.

Soil	Order of filtrate	cc. $KMnO_4$ used in titration Kind of filter	
		Porcelain	Soil
Silt Loam	First sample filtered	2.00	1.65
	Second sample filtered	1.94	1.67
Clay	First sample filtered	1.52	1.37
	Second sample filtered	1.35	1.40

The results show that at first there is more calcium in the filtrate from the porcelain filter than from the soil filter, and that the first filtrate to come through the porcelain filter contains more calcium than the second. The explanation of the former phenomenon is to be found in the equilibrium reaction by which carbon dioxide extracts the calcium.

$$CaX + 2H_2CO_3 \rightleftarrows Ca(HCO_3)_2 + H_2X$$

The pressure employed in filtering with a porcelain filter keeps the carbon dioxide in solution and forces the reaction to the right, maintaining a maximum amount of soluble calcium in the filtrate. When a soil filter is used, filtration goes on under atmospheric pressure only, which allows some carbon dioxide to escape and hence allows the reaction to go slightly toward the left. If this were the only factor to be considered in the choice of a filter, either one could be used as long as the same one was adhered to throughout any series of determinations, since the determination does not give absolute but only comparative values when used with different soils.

However, the fact that the second filtrate through a porcelain filter contains less lime than the first, enters into the problem of selecting a suitable filter. Since porcelain filters are made of practically pure kaolin, which is an acidic substance, it was thought that perhaps it removed some of the lime from solution during filtration and experiments were carried on to test out this point.

One gram of precipitated calcium carbonate was dissolved in two liters of carbonated water, a small part which did not go into solution by the end of 24 hours being filtered off. One hundred cc. aliquots were titrated with approximately N/10 hydrochloric acid using methyl orange as an indicator. The two porcelain filters which had been used for filtering the soils previously referred to in Table V, were thoroughly cleaned and rinsed by running distilled water through them under pressure. Then 300 cc. portions of the calcium carbonate solution were run through the filters. The first portions to come through were discarded and the last 100 cc.

titrated with the approximately N/10 hydrochloric acid solution. The porcelain filters were then rinsed with distilled water and burned in an electric oven and 300 cc. portions of calcium carbonate solution run through them as before, the first of the filtrate always being discarded and the last 100 cc. titrated with hydrochloric acid. Table VI gives the results of this experiment.

Table VI.--Effect of Carbonated Water and Burning on Pasteur-Chamberlain Filters.

Treatment of calcium carbonate solution	cc. HCl used
None	7.00
None	7.05
Run through unburned porcelain filter	6.80
Run through unburned porcelain filter	6.80
Run through burned porcelain filter	7.00
Run through burned porcelain filter	7.00

These titrations indicate that carbonated water tends to bring out the acidic properties of clay causing it to react with and to retain bases. Drying and heating the kaolin causes it to become inactive, so that if porcelain filters were to be used in this determination, it would be necessary to burn them after each filtration; otherwise larger and larger amounts of lime up to a certain point would be retained by the filter from each successive filtrate. Since kaolin is thought to exist in two forms, one of which is more actively acidic than the other[8], it may be that treatment with carbonated water and heat causes changes from one form to the other to a greater or less extent.

Further experiments were carried on with these filters to determine how far this reaction would go and to see if distilled water would have the same effect as carbonated water. The two filters were rinsed with distilled water and burned in the electric oven. Then one of them was soaked for ten days in carbonated water and the other for the same length of time in distilled water. A new solution of calcium carbonate was prepared by running 500 cc. of N/25 calcium hydroxide into 1,500 cc. of carbonated water. Three hundred cc. portions of this solution were run through the filters as before and 100 cc. of the filtrate titrated with standard HCl. The results are given in Table VII.

Table VII.--Effect of Carbonated and Distilled Water on Pasteur-Chamberlain Filters.

Treatment of calcium carbonate solution	cc. HCl used
None	10.65
Run thru filter soaked 10 days in distilled water	10.35
Run thru filter soaked 10 days in carbonated water	10.45

The amount of lime removed from solution by the filters is probably not as large as it would be if fresh, new filters

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[8] Asch and Asch, "Silicates in Chemistry and Commerce", 114.

were used, because they had become loaded down with calcium more or less completely by the time these experiments were made. With the filters in the condition in which they were, N/25 carbonated water had less effect than ordinary distilled water which contains appreciable amounts of carbon dioxide. The bearing of this experiment on the retention of bases by soils is especially interesting. During wet periods when there is danger of excessive loss from leaching, the clay of the soil becomes more actively acidic and aids in retaining the bases. During dry seasons it becomes less actively acidic and releases the bases for the use of plants.

It was thought possible that traces of the sulphuric acid which is used in making hardened filters might still be in the paper and remove some calcium during filtration when a soil filter was used. In order to try this out, two portions of about 200 cc. each of the standard calcium carbonate solution were run slowly through a hardened filter paper and titrated with hydrochloric acid solution with the results given in Table VIII.

Table VIII.--Effect of Hardened Filter Paper on the Calcium Content of the Filtrate.

Treatment of calcium carbonate solution	cc. HCl used
None	7.00
None	7.05
First portion through hardened filter paper	7.00
Second portion through hardened filter paper	6.95

These results show that no lime is removed by the hardened filter. In order further to confirm this, each of two 14 gm. samples of a silt loam soil were extracted for two hours with 700 cc. of N/25 carbonated water and filtered with a porcelain filter, the first 200 cc. of the first filtrate being discarded. The two filtrates were then thoroughly mixed and one-half of the mixture slowly run through a hardened filter paper. Five hundred cc. portions were analysed for calcium and the results showed that the hardened filter paper had no effect on the lime content of the filtrate. The results are given in Table IX.

Table IX.--Effect of the Kind of Filter on the Amount of Calcium in the Filtrate.

Treatment of extract	cc. $KMnO_4$ used
Filtered thru porcelain filter only	1.75
Filtered thru porcelain and hardened filter	1.78

Calculation of Results.--The results of these extractions are calculated in terms of calcium carbonate extracted per acre eight inches of soil. An acre eight inches is taken to weigh 2,500,000 pounds for sands, 2,000,000 pounds for silt loams and clays, and 500,000 pounds for peats. Every cc. of N/10 potassium permanganate used in titration is equivalent to .005 gm. of calcium carbonate, and the .005 gm. is .05% of the 10 gm. of soil from which the filtrate was analysed for calcium. This, calculated to the acre basis, gives the following:

.05% of 2,500,000 lbs. is 1,250 lbs. for sands.

.05% of 2,000,000 lbs. is 1,000 lbs. for silts and clays.

.05% of 500,000 lbs. is 250 lbs. for peats.

In other words, every cc. of potassium permanganate is equivalent to-

1,250 lbs. of $CaCO_3$ per acre in the case of sands,
1,000 lbs. of $CaCO_3$ per acre in the case of silt loams and clay,
250 lbs. of $CaCO_3$ per acre in the case of peats.

RESULTS

In order to facilitate a comparison of results, the remaining experimental data is all given in condensed form at the end of the thesis, as tables and charts.

Twelve acid soils, collected from various parts of the state, were used in testing out the results of this extraction method. The response of alfalfa to liming, the amount of active acidity, the avidity of the soil acids, and the degree of acidity by the Truog Zinc Sulphide test had all been previously determined on these soils. This data is compared with the amounts of lime extracted by the method described in this thesis.

Table X gives the classes of the various soils extracted and the results of the extractions. All determinations were made in duplicate.

In Table XI are shown the results of pot tests on these soils, showing the increased growth of alfalfa resulting from the use of lime on each soil.

The active acidity, the avidity, the Zinc Sulphide test, and the lime extracted is tabulated for these soil in Table XII.

In Chart I, the twelve soils are divided into five groups according to the amount of lime which was extracted from them. Along with the quantity of lime extracted is expressed the growth made by alfalfa on fertilized but unlimed pots for each soil. If the average growth of alfalfa for each group is taken, the amount of lime extracted by carbonated water has a remarkably close relation to the growth made by alfalfa. The variations noted within the groups is undoubtedly due to uncontrolled factors in the pot tests or to individual peculiarities of the various soils.

As was earlier explained, the amount of calcium extracted depends to a large extent on the amount and strength of the soil acids. The most convenient way to measure these two factors is by the Zinc Sulphide test, and so in Chart II, the degree of acidity by the Zinc Sulphide test is plotted with the increase in the growth of alfalfa produced by liming on fertilized pots. Increase due to lime gives a direct comparison, whereas if the growth on the unlimed soil were used, it would be necessary to employ reciprocals to show the relation between the two, since the greater the acidity the smaller the growth. The actual increase in growth due to liming is used instead of the percentage increase in growth for two reasons. Small individual variations in pots growing small amounts of alfalfa cause abnormally large variations when expressed percentagely. Any given increase, such as one or two grams, would show up too low on a relatively good alfalfa soil and too high on a poor one, if expressed as the percent of the crop on the unlimed soil. Here, also, the chart shows that a distinct relationship exists between the two graphs, demonstrating that the degree of acidity gives an indication of the suitability of a soil for alfalfa, corresponding very closely to that given by the amount of lime in the carbonated water extract. Two of the most marked variations in this chart, soils F and L can be explained in part at least by the fact that they were the only soils of the twelve which had been manured the same year as collected.

Kossowitch and Althausen[9] have shown that lime does not give as large increases on fertilized soils as on unfertilized. The manure applied to these two soils has apparently lessened the response to liming for several reasons, as follows:

It greatly increases bacterial activity, which produces more carbon dioxide and causes a more rapid rate of formation of calcium bicarbonate in the soil solution, thereby lessening the need for adding lime.

Some calcium bicarbonate is produced in the decomposition of the manure itself.

By its fertilizing effect it produces a larger, more vigorous plant with a greater feeding machinery.

In Charts III and IV the increased growth of alfalfa from liming is plotted with the avidity of the active soil acids and with the total amounts of active soil acids, respectively, in order to determine which of these factors plays the more important part in the injurious effects of soil acidity.

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[9] Russ. Jour. Expt. Landw. 10 (1909) 693-695.

A glance at the two charts shows plainly that the avidity of the soil acids is much more important than their amount in determining the extent to which a soil will respond to liming. However, neither of these determinations give as accurate indications of the need of lime on a soil as do the Zinc Sulphide test or extraction with carbonated water, for the reason that the Zinc Sulphide test combines the factors of the first two determinations, and the extraction method combines the factors included in the Zinc Sulphide test with still another, namely, the amount and solubility of the calcium compounds of the soil.

The results of the foregoing extractions checked out so nicely with the results of pot tests, that it was thought that possibly by using the proper proportion of soil to water in the extraction, nearly the same amount of calcium might be extracted which the alfalfa plant is able to obtain in one growing season. Since alfalfa requires probably about 500 lbs. of water for every pound of dry matter produced, three million pounds of water must pass up from the soil through the alfalfa in the growth of three tons on one acre. Most of the feeding of crops is done in the upper eight inches of soil and thus this three million pounds of water has exerted its solvent action on two million pounds of soil in the case of silts, clays, and silt loams, and on two and one-half million pounds of soil in the case of sands, and on five hundred thousand pounds of soil in the case of peats. This makes a dilution of 1 to 1 1/2 in the case of silts, clays and silt loams, of 1 to 1 1/5 in the case of sands, and of 1 to 6 in the case of peats. By taking into account only the water which passes up through the plant, the quantity of lime lost from the soil in the field by leaching is eliminated from consideration. The drawing of water from below the eight inch layer by alfalfa unavoidably disturbs this basis of calculation somewhat, although this is at least partially compensated for in other ways.

Extractions of nine soils were made using these dilutions. Three hundred cc. of carbonated water were used with 200 gm. of silts, clays, and silt loams, with 250 gm. of sands, and with 50 gm. of peats. One hundred cc. portions of the extracts were analysed for calcium, which was calculated over to pounds of calcium carbonate per acre. In Table XIII, these results are compared with the growth made by alfalfa on the fertilized but unlimed pots and with the increase in growth produced by lime.

In most cases the growth of alfalfa on these nine soils is just about what would be expected from the amount of lime extracted by carbonated water, if the lime needs of an ordinary crop of alfalfa are considered. A three ton seasonal crop of alfalfa hay contains calcium equivalent to about 250 lbs. of calcium carbonate. Besides this amount there is some calcium needed for root growth, and some is taken up by the plants and washed off of the leaves, so that a three ton crop of alfalfa probably requires about 300 lbs. of calcium carbonate.

On the basis of this assumption, the four soils E, K, L, and O which give up less than 300 lbs. of calcium carbonate per acre upon extraction with carbonated water, should respond to applications of lime. Of these four, three do make a large response to lime and the fact that the other one, soil L, does not respond markedly is at least partially explained by the fact that it is one of the manured soils. Of the five remaining soils, the one with the most lime, soil M, produces a large crop and does not respond to liming. Soil N was limed in the field and so is in good condition so far as this factor is concerned, and does not respond to any additional applications. Soils F and G both contain over 300 lbs. of lime per acre as determined by this method, and both produce fairly good crops without the addition of lime. Soil D responds more to liming than would be expected from the amount of lime extracted, but it should be noted that alfalfa did not make a very good growth on this soil when both lime and fertilizer were added, indicating that some other factor was affecting the growth. Other lesser discrepancies can be found. For example, more lime is extracted from soil E than from soil O, but the growth on the former is less than on the latter. If calcium bicarbonate were the only thing limiting the growth of alfalfa on these two soils this would not be the case, and so it is evident that there are other important factors involved. The biological activity of the soil, which is dependent on its reaction, physical condition and chemical composition, is undoubtedly one of the chief of these other factors, in that it has a marked effect on the rate at which all of the plant food elements as well as calcium bicarbonate are made available. However, since there is considerable agreement between the lime content of the carbonated water extracts of the soils and the growth made by alfalfa, it would seem that a sufficient supply of calcium bicarbonate in the soil solution rather than a neutral or alkaline reaction of the soil itself is one of the chief requirements for the growth of alfalfa.

SUMMARY

The various theories concerning the harmful action of soil acidity are reviewed and discussed. Data showing the relation between the protein and the lime content of plants is given in support of the theory that soil acidity is injurious because it deprives the plant of sufficient calcium bicarbonate to neutralize the acids formed in plant growth. The possibility of extraction of acid soils with carbonated water indicating the growth which will be made by alfalfa on these soils is discussed and brought out experimentally. The literature bearing on this subject is reviewed briefly, which indicates that the subject has never been attacked from this angle. The solution of the problems of extraction, filtration, and analysis, which arise in the development of a suitable procedure for extracting the calcium of acid soils with carbonated water is discussed in considerable detail,

and a method is described which gives good results. Twelve acid soils upon which active acidity, avidity, Zinc Sulphide and pot tests had been made, were used in trying out the extraction method. The results of all of these tests are plotted and compared. There is found to be a close relationship between the response of alfalfa to liming and the degree of acidity as expressed by the Zinc Sulphide test. Practically the same relationship is also found between the response to liming and the avidity of the soil acids. There were two soils in which the response to liming and the indications by the above tests did not compare relatively as well as might be expected. However, this is explained by the fact that these soils were manured the same season that the samples were taken, and manure undoubtedly lessens the immediate effect of liming. There is no close relation between the response to liming and the total active acidity and reasons are given to show why this is so. With dilutions of 1 to 50 a rather close relationship between the lime extracted and the growth of alfalfa is found. This proportion of carbonated water to soil is undoubtedly large and much more calcium is extracted than alfalfa is able to secure in one growing season. In order to make an extraction as nearly comparable to the natural feeding of the alfalfa plant for calcium bicarbonate as possible, the following assumptions were made. It was assumed that 300 lbs. of calcium carbonate are needed for the growth of a 3 ton crop of alfalfa and the basis for this assumption is given. Assuming 500 lbs. of water to be necessary for the growth of 1 lb. of dry matter, and that 3 tons represents a seasons crop of alfalfa, it is found that 3,000,000 lbs. of water are used by the plant in the production of a season's crop. If the further assumption is made, that the feeding of the plant may be referred to an eight inch layer of soil, upon assuming the usual weights of soils, the following proportions of soil to water are obtained.

1 to 1½ for silts, clays and silt loams.

1 to 1 1/5 for sands.

1 to 6 for peats.

Extractions with these proportions of soil and water were made for nine acid soils. As the amount of calcium carbonate that is extracted becomes less than 300 lbs. per acre, a striking relationship is found in the response of alfalfa to liming. The results of this work seem to indicate quite strongly that it is not necessarily the total acidity of a soil, but the supply of calcium bicarbonate in the soil solution that determines the response of alfalfa to liming.

Table X.--Amounts of Calcium Extracted from Twelve Soils by N/25 Carbonated Water Using a Dilution of 1 to 50.

Soil	Class	Calcium in terms of pounds of $CaCO_3$ per acre eight inches.		
		I	II	Average
A	Light sandy loam	1170	1230	1200
B	Light sandy loam	1230	1280	1255
D	Black silt loam	1880	1820	1850
E	Dark sandy loam	900	875	890
F	Dark silt loam	1670	1700	1685
G	Dark silt loam	1940	1980	1960
J	Red clay	1370	1400	1385
K	Red clay	1180	1270	1225
L	Brown silt loam	2080	2020	2050
M	Dark mucky peat	3210	3310	3260
N	Medium coarse sand	1770	1750	1760
O	Medium coarse sand	850	900	875

Table XI.--Growth in Grams of the First Crop of Alfalfa on Pots Fertilized as Indicated.

Soil	Without Lime			With Lime			Average increase from lime
	K P	K P N	Average	K P	K P N	Average	
A	9.6	7.6	8.6	11.5	13.1	12.3	3.7
B	9.2	11.6	10.4	14.6	13.7	14.1	3.7
D	---	---	5.6*	---	---	*8.0	2.4
E	1.8	2.0	1.9	8.2	9.5	8.8	6.9
F	9.5	9.9	9.7	10.7	11.3	11.0	1.3
G	---	---	9.0*	---	---	*11.3	2.3
J	9.4	9.6	9.5	17.6	14.3	15.9	6.4
K	7.1	6.8	6.9	16.7	17.1	16.9	10.0
L	9.7	12.7	11.2	13.5	12.0	12.7	1.5
M	12.3	13.0	12.6	---	13.3	13.3	.7
N	14.0	13.7	13.8	15.2	13.5	14.4	.6
O	3.1	3.6	3.3	11.7	13.6	12.6	9.3

*P was the only fertilizer used on these pots.

Table XII.--A Comparison of the Calcium Extracted by Carbonated Water Using a Dilution of 1 to 50, with the Active Acidity, Avidity, and Zinc Sulphide Test of Twelve Soils.

Soil	Active Acidity	Avidity	ZnS Test	Lime Extracted Lbs. per acre.
A	3.00	72	Slight	1200
B	2.85	65	Very Slight	1255
D	9.26	96	Medium	1850
E	10.95	144	Very Strong	890
F	7.45	102	Medium	1685
G	6.00	71	Slight	1960
J	5.80	74	Medium	1385
K	6.55	152	Very Strong	1225
L	6.30	65	Medium	2050
M	5.60	15	Very Slight	3260
N	1.20	26	Very Slight	1760
O	3.40	113	Strong	875

Table XIII.--A Comparison of the Calcium Extracted by Carbonated Water Using a Dilution of 1 to 1½, with the Growth made by Alfalfa on the Fertilized but Unlimed Soils and with the Increase due to Lime.

Soil	Lbs. of $CaCO_3$ extracted per acre eight inches			Growth in gms. of alfalfa on unlimed fertilized pots	Increase due to lime
	I	II	Average		
D	664	641	652	5.6	2.4
E	213	207	210	1.9	6.9
F	330	319	325	9.7	1.3
G	432	420	426	9.0	2.3
K	131	139	135	6.9	10.0
L	270	270	270	11.2	1.5
M	1568	1542	1552	12.6	.7
N	355	361	358	13.8	.6
O	107	111	109	3.3	9.3

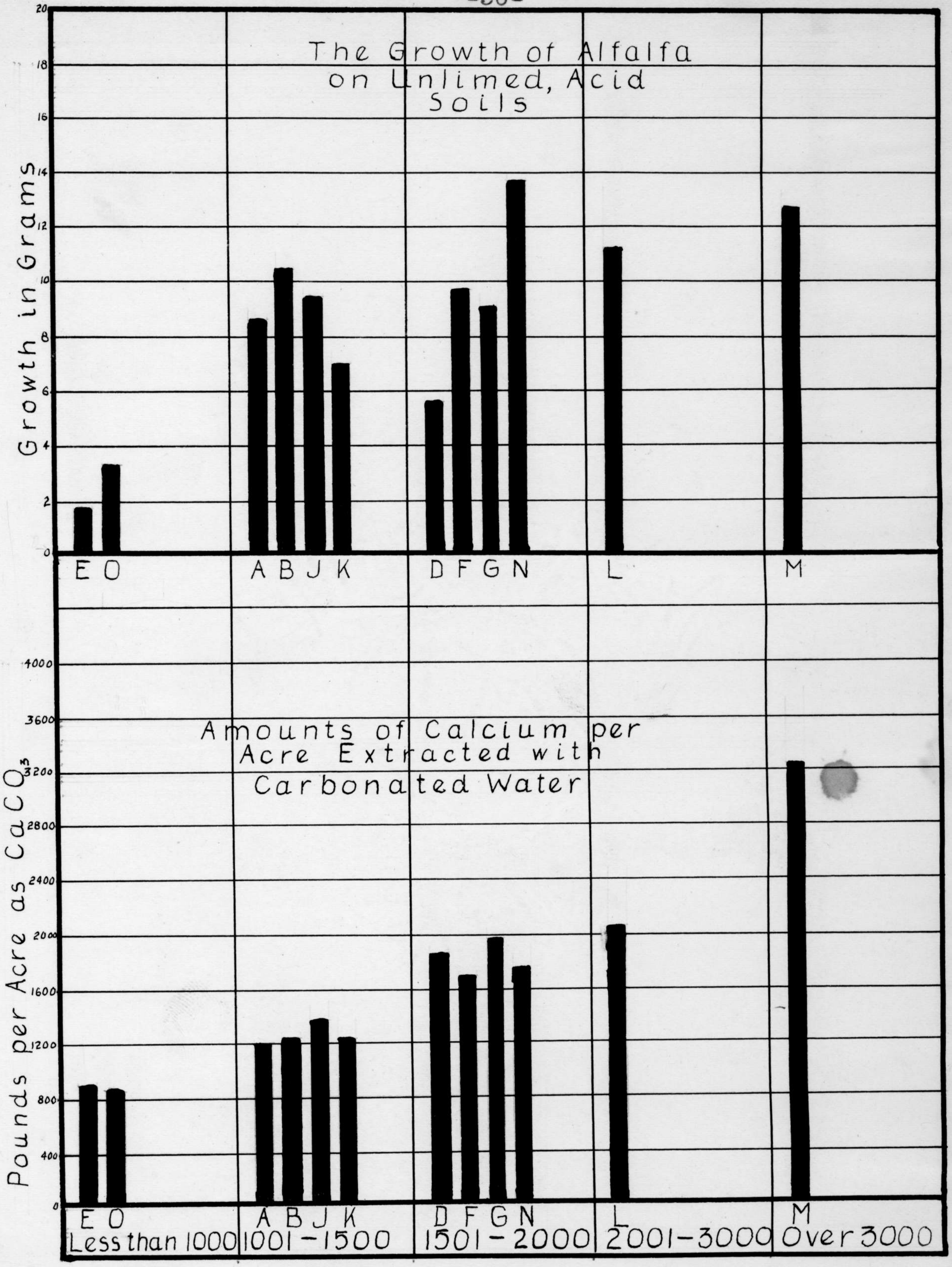

CHART I

The Relation of the Growth of Alfalfa on Unlimed, Acid Soils to the Amount of Calcium which is Extracted with Carbonated Water.

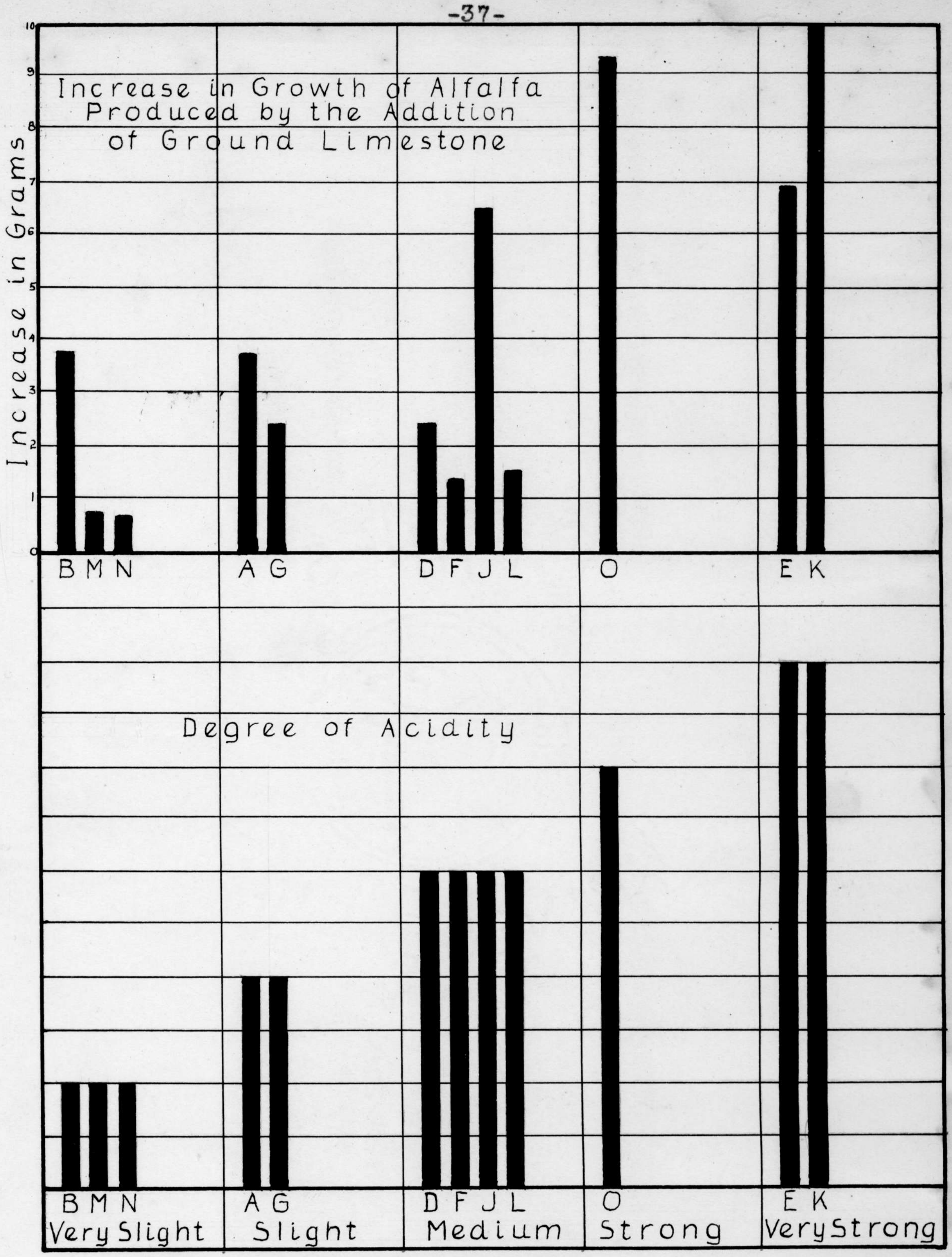

CHART II

The Relation of Degree of Acidity to the Increase in Growth of Alfalfa Produced by the Addition of Ground Limestone.

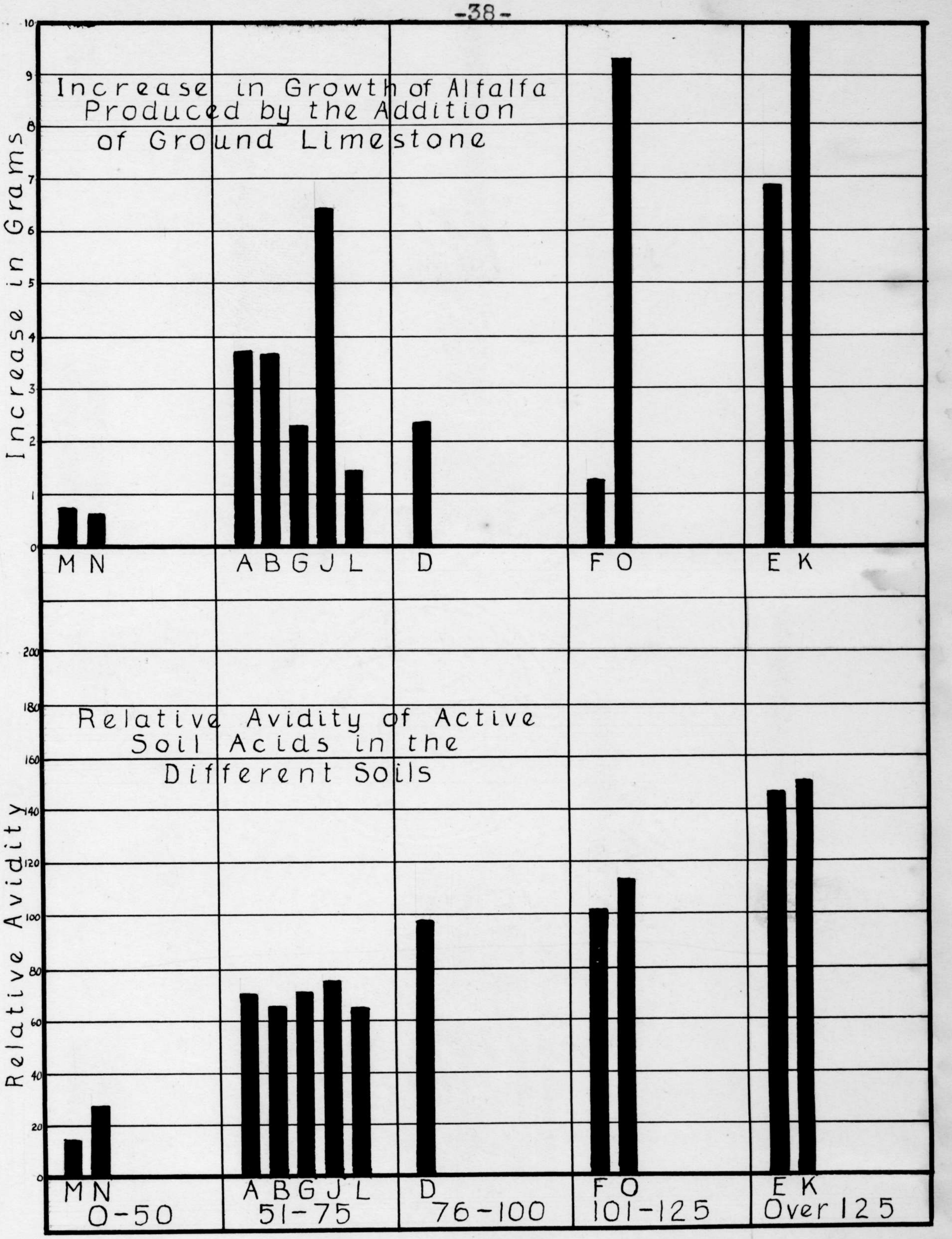

CHART III

The Relation of the Avidity of the Active Soil Acids to the Increase in Growth of Alfalfa Produced by the Addition of Ground Limestone.

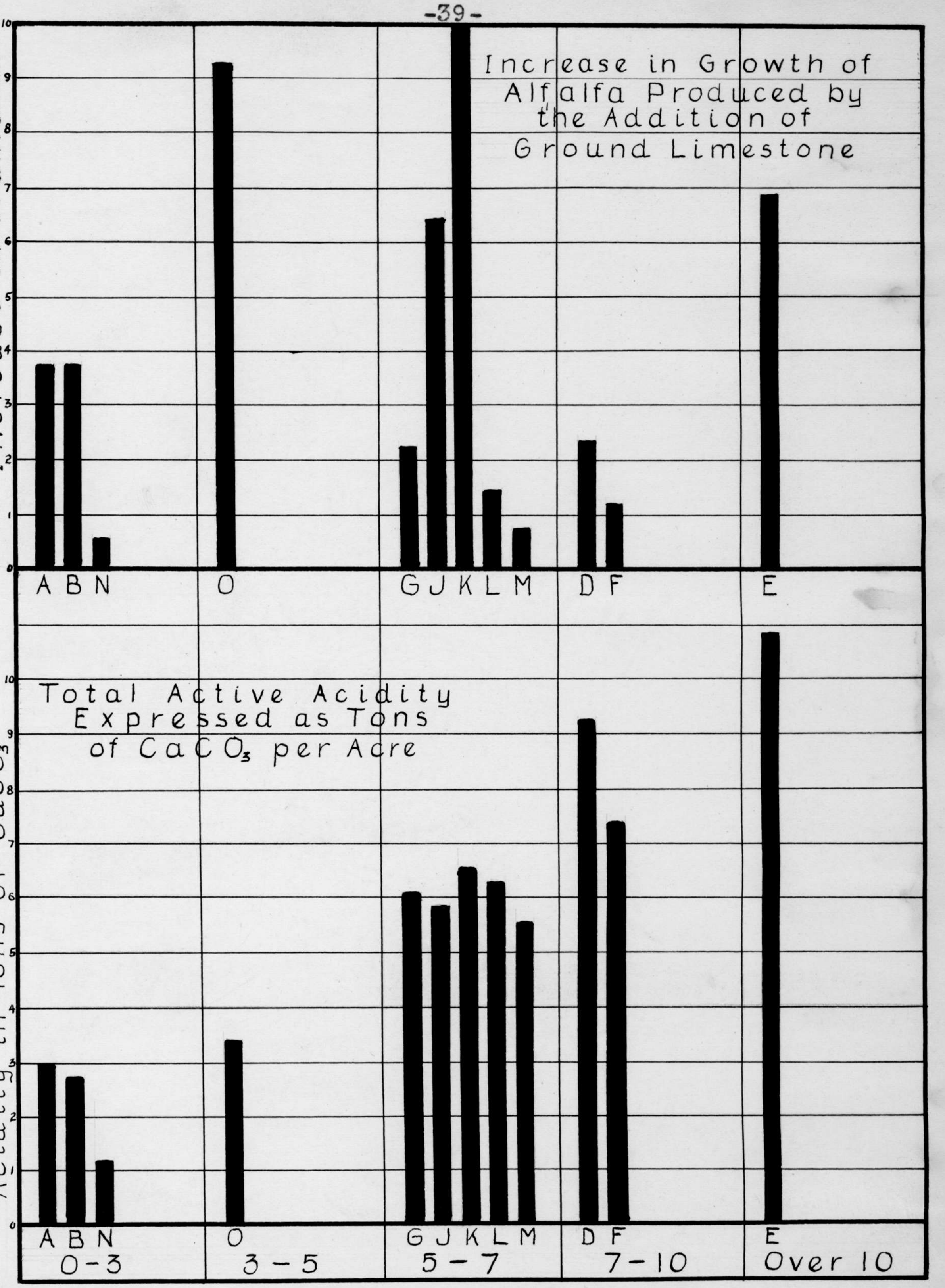

CHART IV

The Relation of Total Active Acidity to the Increase in Growth of Alfalfa Produced by the Addition of Ground Limestone.

Approved

E. Truog,

June 12, '17.