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COLLEGE STATION, BRAZOS COUNTY, TEXAS

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DIVISION OF CHEMISTRY

RELATIONS OF BUFFER CAPACITY FOR ACIDS TO BASICITY AND EXCHANGEABLE BASES OF THE SOIL

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The buffer capacity of a soil for acids is measured by the quantity of acids required to attain a given degree of acidity or to change the degree of acidity to a given extent. It is of both practical and scientific importance, in that it measures the resistance of the soil to acidifying agencies. Methods of measuring buffer capacity are studied in this Bulletin, together with the relation of the buffer capacity to the carbonates, to exchangeable bases, and to other properties of the soil. If unsuitable methods are used, the mixtures of soil may be acid even though undecomposed carbonates remain. The adequate expression of the buffer capacity of soil requires the construction of a curve, or statement of the total buffer capacity to a definite degree of acidity (pH) and of the specific buffer capacity between given pairs of pH values. The addition of soluble salts to an acid soil may increase its acidity; washing out soluble salts may decrease its acidity. The lime-requirement methods of Veitch and of Jones recovered approximately the net quantity of acid added to the soil, but the method of Hopkins recovered only a small proportion of it. The exchangeable hydrogen corresponds to the net acid on some soils treated with acid, but with other soils is decidedly lower than the net acid, which indicates removal of base from other compounds besides the exchange complex. The total exchange capacity of the soil was not changed by the treatments of acid to estimate buffer capacity or acid consumed.

Treatment with acid measures only approximately the exchangeable bases in the soil, since the net acid consumed by the acid-consumed process represents 86 per cent of the base in the exchange complex, and that by the Kappen method, 81 per cent. The percentage of exchangeable hydrogen varies with different soils at the same degree of acidity (pH) produced by treatment with acid. The base-exchange complex appears to consist of several compounds. The bases dissolved from the soil by dilute acids come from the carbonates, the base-exchange complex, and other compounds. The percentage taken from the base-exchange complex depends upon the degree of acidity (pH) and the nature and amount of the exchange compounds present.

The basicity of liming materials containing silicates or phosphates can be estimated by the method for buffer capacity. Direct solution in acid is likely to give excessively high results on such materials.

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RELATIONS OF BUFFER CAPACITY FOR ACIDS TO BASICITY AND EXCHANGEABLE BASES OF THE SOIL

G. S. FRAPS AND J. F. FUDGE

Soil acidity is an important problem in the eastern and southern parts of the United States. Large areas of soil are either sufficiently acid to require treatment with lime, or liable to become acid under the usual conditions of agriculture. In the southwestern and western parts of the United States, soils are more basic in character than those just mentioned. Texas has some acid soils and some which may become acid, but large areas of Texas are covered by basic soils, some highly so.

In a previous bulletin (Bulletin 400) the term basicity was arbitrarily used to designate the quantity of acid neutralized by a soil, when applied in excess, under definite conditions, expressed in terms of calcium carbonate. The buffer capacity of a soil for acids is measured by the quantity of acid required to secure a definite degree of acidity, or to bring about a definite change in the degree of acidity. The basicity of a soil may also be used to designate its total buffer capacity up to a selected degree of acidity. A number of questions arise in connection with the establishment of this end point to be used in measuring the basicity of the soil. The degree of acidity is expressed in terms of the hydrogen ion concentration expressed as pH. A pH of 7 is neutral. Below 7, it is acid; above 7, it is basic. The pH is a logarithmic expression, so that a medium having a pH of 5 has ten times the hydrogen ion concentration of one with a pH of 6.

A knowledge of the basicity of soils or the buffer capacity for acids is needed in connection with a number of practical questions. A soil of low basicity may become acid through ordinary natural weathering processes, or by applications of fertilizer such as ammonium sulphate, which tends to produce acids. Such a soil would also require small amounts of sulphur or other acidifying materials to render it acid, if it should be desirable to do so for experimental purposes, or to render it suitable for plants (such as certain flowers) which prefer an acid medium, or to aid in controlling plant diseases. The measurement of the degree of basicity of a soil would thus show the extent to which it would be susceptible to the influences mentioned above, and would indicate the quantity of acidifying material which could safely be used without danger of injurious acidity, or which should be used to secure a desired degree of acidity.

The buffer capacity measures the ease with which the reaction of the soil may be changed by treatment. The treatment may be artificial as in the case of the decrease in acidity following the application of one of the various forms of lime or of basic slag to an acid soil, or in the acidification of the soil with acid-forming fertilizers, such as ammonium sulfate or the addition of sulphur. The change in acidity may be natural, as in the removal of basic material by weathering and the leaching action of water. The change may be either beneficial or detrimental to plant growth, either directly or indirectly. Legumes require a neutral or alkaline soil for best growth. Certain plant diseases, such as potato scab and cotton root rot, apparently are most easily controlled in acid soils. The buffer capacity of the soil and its determination have consequently received considerable attention by soil chemists.

A large amount of work has been done on methods for the determination of the amount of lime required to neutralize acid soils. Other work has been done on the buffer capacity of soils for acids. The present study on the buffer capacity of soils originated in connection with the study of the possibility of making certain soils sufficiently acid by treatment with sulfur to inhibit the growth of the organism causing the cotton root-rot disease.

PREVIOUS WORK

Several methods have been proposed for the determination of the buffer capacity of soils for acids. Pierre (19-21) proposed that to 20 grams of soil in collodion bags in extraction flasks, various amounts of acid or base be added, the volume made up to 100 cc., and after three days, the hydrogen ion concentration (pH) of the clear solution outside of the bag be determined colorimetrically. This method is satisfactory for soils of low buffer capacity but is subject to a number of objections when the soil has a high buffer capacity. No allowance is made for a stirring of the soil sufficiently to insure complete reaction between carbonates and acid. The collodion is attacked and the sack destroyed by acid strong enough to neutralize carbonates or to acidify soils of high buffer capacity. The method is, therefore, not applicable to a large group of soils of great agricultural importance.

Lemmermann and Fresenius (15) treat 100 grams of soil in 100 cc. of water with 10 cc. of 0.1N nitric or hydrochloric acid or 0.1N sodium hydroxide and determine the hydrogen ion concentration (pH) of the mixture. The amount of hydrogen or hydroxyl ions which have disappeared is calculated in the percentage of the amount added. This method merely gives the acid or base consumed by the soil under the conditions of the treatment.

Hissink (26, p. 26) calls the buffer value the amount of lime (CaO) in grams which must be taken up by or removed from 100 kg. of soil in order that the pH may rise or fall by 0.1. He regards the total buffer capacity of the soil for acids as the total exchangeable bases in the soil.

The method previously followed in this laboratory (3) has been to add acid and water to separate portions of the soil and test the supernatant liquid for hydrogen ion concentration. The tests are continued on separate portions of the soil until a pH between pH 4.7 and 4.3 is reached. The method is satisfactory, but slow. It was also desired to secure a method which would give the buffer capacity at any desired degree of acidity (pH).

PRELIMINARY TESTS WITH CALCIUM CARBONATE

Any method for basicity or buffer capacity for acids must involve the complete solution of calcium or magnesium carbonates present in the sample of the soil. It is true there are acid soils which contain nodules of hard limestone rock, but these are exceptional cases and require special treatment. A method for buffer capacity which gives an acid end-point, and yet permits undecomposed carbonates to remain in the sample, is clearly faulty. Dissolved carbon dioxide and calcium bicarbonate in solution affect the degree of acidity.

A study was made of the acidity of mixtures of calcium carbonate and 0.1 N nitric acid treated in different ways. Varying amounts of acid were added to 0.5 gram of precipitated calcium carbonate, the mixtures well stirred in different ways, and the hydrogen ion concentration determined in the supernatant liquid. The stirring varied from light stirring or shaking by hand to a prolonged, vigorous stirring with a stirring apparatus operated by a motor. The 0.5-gram sample of calcium carbonate was found to neutralize 96.2 cc. of 0.1N acid. The methods tested were as follows:-

(1) The acid was added with hand shaking in such a way that a good suspension was secured during the addition, and the suspension was then allowed to stand 24 hours in a stoppered flask. The pH was then determined colorimetrically.

(2) The mixture was stirred with a motor-operated stirring machine provided with a stirring rod supplied with the apparatus, in which a simple bend of about 30 degrees was made. This stirrer left a quiet space in the center of the beaker.

(3) The mixture was stirred with the machine mentioned above, provided with a special stirring rod so designed that no quiet space existed at the center of the beaker.

The results of these tests with calcium carbonate are presented in Table 1. The table shows that in the presence of calcium carbonate the buffer capacity would depend upon the details of the procedure used in the treatment of the soil with acid. With moderate hand stirring, the mixture had a reaction of pH 4.95 when over 20 per cent of the calcium carbonate was still undissolved, even after the mixture had stood overnight. With vigorous stirring by the machine, the mixture has practically the same reaction (pH 5.00) when the acid was just about sufficient to neutralize all the calcium carbonate, while with vigorous stirring with the modified stirring rod on the machine, the same mixture had a pH of 6.20. Under the most favorable conditions, the calcium carbonate was completely neutralized at pH 6.20; under less favorable conditions, the amount of acid to neutralize the calcium carbonate gave a pH of 5.0; and under still less favorable conditions the pH was 3.4.

Table 1—Acidity of mixtures of calcium carbonate and 0.1N nitric acid.

Nitric acid added to 0.5 gram calcium carbonate (Equals 96.2 cc)	Excess acid 0.1 N	With shaking and standing pH	Purchased stirrer pH	Modified stirrer pH
98.0	+ 1.8 cc	2.35	3.90	3.50
97.5	+ 1.3 cc	3.60	4.40	3.60
97.0	+ 0.8 cc	3.00	4.70	3.90
96.0	— 0.2 cc	3.40	5.00	6.20
95.0	— 1.2 cc	3.35	5.05	7.05
94.0	— 2.2 cc	3.30	5.25	7.25
93.0	— 3.2 cc	4.55	5.25	7.05
91.0	— 5.2 cc	4.90	5.35	7.25
85.0	—11.2 cc	4.90	5.75	7.45
80.0	—16.2 cc	5.25	5.75	7.70
75.0	—21.2 cc	4.95	5.75	7.70

Some of this effect is, no doubt, due to dissolved carbon dioxide and to the presence of calcium bicarbonate in solution. The vigorous stirring with exposure to air eliminates the carbon dioxide and decomposes the bicarbonate. The vigorous stirring also enables the calcium carbonate to go into solution, as shown by the pH of 7 or over, when an excess of calcium carbonate was present.

According to this work, a mixture of soil and acid with a pH of 6.2 may retain undecomposed calcium carbonate, under some conditions, while under less favorable conditions for an equilibrium the mixture may have a pH of 5.0 or even 3.4 and still retain undecomposed calcium carbonate. This would, of course, enter into reaction later on and decrease the acidity. In measuring the basicity of a soil, it would be necessary to adopt an end point of pH 6, if the procedure is to be effective. It would be well for one to make preliminary tests of procedure and apparatus with the use of carbonate of lime and acid, to see what acidity (pH) was secured with the apparatus and procedure to be used.

METHOD USED FOR THE BUFFER CAPACITY

In the work previously reported (3), 8 grams of soil was treated with varying amounts of sulfuric acid, the volume made up to 100 cc., and allowed to stand overnight. The pH was determined colorimetrically on the supernatant liquid the following morning. The process was repeated with other portions of soil, and quantities of acid added based upon the results previously secured until the desired degree of acidity was secured. The buffer capacity of the soil was expressed as the parts of sulfur per million of soil necessary to give a reaction between pH 4.7 and pH 4.3, 1 cc. of 0.01N acid being equivalent to 20 p.p.m. of sulfur. A number of modifications of this method were tested in the present study for the purpose of shortening the procedure and making it more accurate.

The amount of soil to be used depends upon the form in which the results are expressed; 8 grams for sulfur because of the ease of calculation of results to sulfur equivalent used in connection with the work on the acidification of soil for the control of cotton root rot. If the results are desired in terms of calcium carbonate or hydrogen, 10 grams of soil should be used. The acid used was hydrochloric acid of three strengths, 0.01 N, 0.1 N, and 1.0 N. The use of sulfuric acid was discontinued because it was thought possible that sulfuric acid on soils high in calcium carbonate might produce an insoluble layer of calcium sulfate around the carbonate particles, thus preventing their complete neutralization, and giving low results for buffer capacity.

Table 2. Estimation of buffer capacity, for acid, with acid-consuming power as the basis, on 10 grams soil.

If acid consumed 15 Min. is	Acid added		Calcium carbonate corresponding to acid used, in parts per million	Acid added		Calcium carbonate corresponding to acid used, in parts per million
	Normal	cc		Normal	cc	
%						
0- 3	0.01	5	100	0.01	10	200
3- 6	0.01	10	200	0.01	20	400
6- 9	0.01	15	300	0.01	30	600
9-12	0.01	20	400	0.01	40	800
12-15	0.01	25	500	0.01	50	1000
15-18	0.01	30	600	0.01	60	1200
18-21	0.01	35	700	0.01	70	1400
21-25	0.01	40	800	0.01	80	1600
25-30	0.01	60	1200	0.1	12.0	2400
30-40	0.1	12.5	2500	0.1	17.5	3500
40-50	0.1	17.5	3500	0.1	20.0	4000
50-60	0.1	35.0	7000	0.1	40.0	8000
60-70	0.1	50.0	10000	0.1	60.0	12000
70-80	0.1	75.0	15000	0.1	85.0	17000

Tests were made of the effect of various periods of stirring, from 5 minutes to 3 hours, with the determination of the degree of acidity (pH) the following morning. This work showed that a 15-minute stirring of the mixture of soil and acid at a speed of 300-400 r.p.m. was sufficient to give a pH reading identical with that secured after prolonged stirring. Consequently the 15-minute period was adopted.

The number of mixtures of soil and acid required was reduced by basing the first addition of acid to be made on the quantity of acid consumed by the soil. First, 5 grams of soil was treated with 50 cc. of 0.2 N hydrochloric acid, stirred on the stirring apparatus for 15 minutes, and filtered; 20 cc. of the filtrate was then heated to boiling and titrated with 0.2 N sodium hydroxide, phenol phthalein being used as the indicator. If the acid consumed exceeded 8 per cent, the procedure was repeated, except that 10 grams of soil, 100 cc. of 1.0 N acid, and 0.5 N sodium hydroxide were used. The second method was also used if the soil was known to contain more than 8 per cent of calcium carbonate. The first additions of acid in the procedure for buffer capacity were based upon the acid-consuming power, according to Table 2. The amounts of acid and the buffer values are based upon 10 grams of soil and expressed as parts per million of calcium carbonate. Subsequent additions to new portions of the soil depend upon the acidity resulting from the first additions, as shown in Table 2. Individual soils of similar acid-consuming power may vary considerably in the quantity of acid required to reach a definite reaction, but this procedure gives a very convenient starting point and shortens the work required.

Determinations of pH were in almost all cases made by means of the potentiometer using quinhydrone and Veibel's electrode, and with the observance of the various precautions necessary for accurate work with that method, as outlined by the International Society of Soil Science (26). When the colorimetric procedure was followed, Clark and Lubs indicator solutions and LaMotte's Roulette comparator were used.

The method as finally adopted, based upon the results of the experiments mentioned above, was as follows:

To 10 grams of soil, add the desired amount of hydrochloric acid, (Table 2) dilute to a total volume of 100 cc., stir for 15 minutes on the motor-operated stirring apparatus, and let stand overnight. Pour off 60 cc. of the supernatant liquid, transfer the remaining soil suspension after thorough mixing to a 50-cc. beaker, add quinhydrone and determine the pH by the regular potentiometric procedure.

After securing a number of determinations covering the range of acidity between about pH 6.5 and pH 3.5, the data are plotted on regular graph paper, the pH being plotted on the Y axis and the amounts of acid on the X axis. A curve termed the buffer curve is constructed by joining these points as shown in Figure 1. This method of recording the data has a number of advantages over the method in which a definite degree of acidity (pH) is finally reached as the end point. It allows easy estimation of the buffer capacity (d pH/d acid) over a considerable range of values of either the acid added or the pH secured. By interpolation on the curve, depending upon the axis to which the interpolation is referred, the buffer capacity may be expressed as the total amount of acid required to reach a given degree of acidity (pH) considerably more closely than in the method previously used where the end point varies between pH 4.7 and pH 4.3. The buffer capacity may also be expressed as the amount of acid required to give a change of acidity (pH) between two values of pH, or as the change in acidity (pH) caused by a definite amount of acid between any two pH values.

In this laboratory, the data and curves secured by this procedure are called the "pH acid" data and curves. This is a convenient expression for either form of buffer capacity. For example, "pH 400 acid" would call for the pH which was reached when the amount of acid equivalent to 400 p.p.m. of calcium carbonate was added to the soil. On the other hand "pH acid 6.0" would call for the amount of acid required to change the soil to a pH of 6.0, "pH acid 6.0-5.0" would call for the amount of acid required to cause the indicated increase in acidity. The data secured from the buffer curves are calculated to the parts of calcium carbonate per million parts of soil which are equivalent to the various amounts of acid used.

ESTIMATION OF CARBONATES

The carbonates were determined by decomposing them with acetic acid as recommended by Lunt (16), collecting the carbon dioxide in barium hydroxide, and titrating the residual barium hydroxide. The reaction chamber is a 150-cc. extraction flask, closed by a No. 8 rubber stopper supporting an 8-inch condenser and a dropping funnel. A source of air free of carbon dioxide is connected to the top of the dropping funnel. The top of the condenser is provided with a 1-hole rubber stopper from which a rubber tube leads to a Fisher absorption tower containing 200 cc. of standard barium hydroxide solution. The tower is in turn connected to suction. The system, without the tower, is first swept out with air free of carbon dioxide. Then, proper precautions being taken against entry of ordinary air into the system, the absorption tower is connected in place and 50 cc. of a mixture of one part of acetic acid to 2 parts of water is placed in the dropping funnel, which has the stop cock closed. Lunt (16) has shown that this strength of acetic acid will not decompose the organic matter of the soil, with consequent evolution of carbon dioxide. The dropping funnel is stoppered with a rubber stopper through which purified air is led. In decomposing the sample, slight suction is applied, and the stop cock cautiously opened. After the vigorous evolution of carbon dioxide has ceased, the acid is slowly brought to a boil, boiled 2 minutes, and allowed to cool. Care must be taken that there is no back pressure at any time. An aliquot of the barium hydroxide solution is titrated with standard hydrochloric acid. By varying the weight of the sample and the normality of the barium hydroxide, accurate results are obtained over a wide range of carbonate content. The results secured, calculated to parts per million of calcium carbonate, are used in various tables in this Bulletin.

EFFECT OF TIME ON THE ACTION OF ACID ON THE SOIL

The data secured in the procedure for buffer capacity are of little practical value unless they can be utilized for experimental purposes with a reasonable degree of accuracy. In such work, the element of time plays an important part. The questions thus arise as to whether or not there is with time a recovery from the acid treatment, that is, a decrease in acidity, and if so, how great it is and how long a time is required for the attainment of final equilibrium.

A large number of data which bear directly upon this point are presented by Fraps and Carlyle (3, Tables 4 and 5), who used the original method from which the present method for buffer capacity here described has been developed. They used soils low in carbonates which required acid in amounts up to an equivalent of 2800 p.p.m. of calcium carbonate to produce, with the regular method then used, a pH value of approximately 4.3. The soil may be expected to decrease slightly in acidity. The average pH of 24 soils after standing over night, 30 days, 60 days, 5.5 months, and one year were 4.4, 4.9, 4.9, 4.7, and 4.7 respectively. These data show that the soils decrease slightly in acidity but that the results secured with the method for buffer capacity indicate the pH value of the soils after they have been treated with the required amount of acid. The procedure may therefore be used with assurance that the results secured may be used where acidification of the soil is for any reason desired. Moreover, the data secured represent, with a satisfactory degree of accuracy, the reaction of the soil after treatment.

INFLUENCE OF TIME OF CONTACT ON AMOUNT OF ACID CONSUMED BY SOILS HIGH IN CARBONATES

A comparison of the data secured in the regular acid-consumed procedure with the data from the determination of carbonates indicated that even with vigorous stirring and an excess of normal hydrochloric acid, there was a possibility that in a few highly calcareous soils all of the carbonates present might not be neutralized. It was thought that possibly with an increase in the amount of time allowed for the operation a more nearly complete neutralization of the carbonates might be assured. In order to determine whether or not the period of contact of acid on the soil had any influence on the results secured, the following experiment was conducted. Two portions of each of 12 soils high in carbonates were weighed out, after a very careful mixing of the samples. One portion was subjected to the regular treatment for estimating acid consumed, that is, stirring for 15 minutes, then filtering and titrating an aliquot of the filtrate with standard sodium hydroxide. The other portion was stirred for 15 minutes and allowed to stand over night before filtering. A comparison of the results obtained by the two methods is presented in Table 3.

Table 3. Effect of period of contact on acid consumed.

Laboratory Number	Calcium carbonate content, %	Acid consumed expressed as % calcium carbonate	
		15 Minutes	Overnight
25869	4.56	4.00	4.00
31329	5.46	5.78	5.74
26089	5.90	6.88	7.02
29331	8.59	8.82	8.68
31800	9.03	9.42	9.34
28011	9.91	10.40	10.18
31884	12.74	13.14	12.96
30963	14.30	14.48	13.92
25905	15.88	15.38	15.18
26817	17.77	18.00	17.92
31330	25.43	26.50	26.20
31882	40.40	40.08	40.04
Average (12)	14.16	14.41	14.27

An examination of Table 3 shows that the increase in the length of the period of contact of the soil and acid did not increase the amount of acid consumed, and consequently is not to be recommended, since the procedure with the shorter time is the simpler and equally accurate.

In only two of the soils, Nos. 25869 and 25905, was the amount of acid consumed significantly lower than the total carbonates present, and in these two soils, the difference was quite small. The difference can be explained as due to the presence of difficultly soluble carbonates which were decomposed by the boiling strong acetic acid but were resistant to the normal hydrochloric acid. In all other soils, the amount of acid consumed slightly exceeded the amount of carbonates present.

The conclusions are that the 15-minute period of contact gives as good results as standing overnight and this shorter procedure is therefore to be recommended and that the acid-consumed procedure neutralizes practically all of the carbonates in the soil, even when the carbonate content exceeds forty per cent.

INFLUENCE OF TIME OF CONTACT ON ACIDITY OF SOILS HIGH IN CARBONATES

In the determination of both the acid-consuming power and the total carbonate content of the soil, a considerable excess of acid is added to the soil. In estimating the buffer capacity, excess of acid is carefully avoided. Carbonates which would be neutralized quickly where an excess of acid is present, might go into solution only very slowly where the system has a pH value of, say, 5.0. In the latter case, the period of standing after the addition of the acid would have an important bearing upon the pH value secured. The question thus arises as to how long a period should be allowed between the addition of the acid to the soil and the determination of the pH value of the system. The following work was done in order to secure data which might answer that question.

Three portions of each of 12 calcareous soils were treated with the same amounts of acid. The regular pH acid determination was run on one portion. After standing over night, the other two portions were stirred for 15 minutes, and set aside for 24 hours. The pH of the second portion was then determined in the usual way. The third portion was stirred for 15 minutes and set aside for a second 24-hour period. The pH of the third portion was then determined. The experiment thus gave pH acid data after the soil had stood in contact with the acid for 16, 40, and 64 hours. The results are presented in Table 4.

Table 4. Influence of period of contact on acidity of soils.

Laboratory Number	pH after standing			Difference in pH due to change in time of standing		
	16 hours	40 hours	64 hours	16 to 64 hours	16 to 40 hours	40 to 64 hours
25869	3.69	4.17	4.59	.48	.90	.42
31329	3.48	4.01	4.26	.53	.78	.25
26089	3.95	3.97	4.10	.02	.15	.13
31800	2.87	2.97	2.97	.10	.10	.00
29331	4.36	5.67	5.73	1.31	1.36	.05
28011	4.28	4.53	4.65	.25	.37	.12
31884	5.18	5.55	5.68	.37	.50	.13
30963	4.72	4.87	5.01	.15	.29	.14
25905	4.43	4.35	4.47	.08	.03	.11
26817	3.69	4.29	4.33	.60	.64	.04
31330	3.76	5.07	5.03	1.31	1.27	.04
31882	4.25	4.95	4.93	.70	.68	.02
Average (12)	4.06	4.53	4.65	.49	.59	.12

Table 5. Buffer capacity of soils, expressed as parts per million of calcium carbonate.

Laboratory Number	Soil type	Carbonates as Calcium Carbonate p.p.m.	Total buffer capacity			Buffer capacity for 1 unit change in pH		Depth
			For pH 6.0	For pH 5.0	For pH 4.0	pH 6.0 to 5.0	pH 5.0 to 4.0	
25871	Dune sand	0	....	150	300	....	150	0- 7
31888	Webb fine sandy loam	60	150	400	900	....	500	0- 7
31890	Miguel fine sandy loam	150	150	700	1400	....	700	0- 7
25873	Lomalto fine sandy loam	0	175	375	845	300	370	0- 7
26103	Crockett fine sandy loam	130	280	600	1100	320	500	0- 7
31880	Duval fine sandy loam	450	330	700	1300	370	600	0- 7
31914	Orelia fine sandy loam	180	470	1200	2250	730	1050	0- 7
31896	Moore fine sandy loam	180	500	780	1300	280	520	0- 7
31820	Amarillo fine sandy loam	490	700	1125	2000	425	875	0- 7
31332	Amarillo fine sandy loam	460	700	1000	1700	300	700	7-19
31804	Fitch fine sandy loam	170	825	1450	2600	625	1150	0- 7
29315	Amarillo fine sandy loam	650	1250	1550	2100	300	550	0- 7
26075	Irving clay	620	1250	2300	4400	1050	2100	0- 7
31331	Amarillo fine sandy loam	700	1470	1650	1900	180	250	0- 7
31321	Amarillo silty clay loam	1440	1700	2950	4400	1250	1450	0- 7
25883	Willacy fine sandy loam	3960	3000	4150	5700	1150	1550	0- 7
26823	Lake Charles clay	5670	5500	6900	8750	1400	1850	0- 7
31905	Victoria clay loam	5500	5700	7200	8700	1500	1500	0- 7
31883	Spur fine sandy loam	10730	6550	9000	12500	2450	3500	0- 7
25865	Lomalto clay loam	10070	8000	9300	12000	1300	2700	0- 7
25966	Trinity clay	12330	9200	12000	15700	2800	3700	7-19
25891	Donna fine sandy clay loam	13400	10600	13500	15500	2400	2500	0- 7
23094		29600	21000	23200	28600	2200	5400	Surface
31802	Yahola fine sandy loam	30550	23500	32000	36000	6500	4000	0- 7

Table 5. Buffer capacity of soils, expressed as parts per million calcium carbonate—(continued).

Laboratory Number	Soil type	Carbonates as Calcium Carbonate p.p.m.	Total buffer capacity			Buffer capacity for 1 unit change in pH		Depth
			Por pH 6.0	Por pH 5.0	4.0 Por pH	pH 6.0 to 5.0	pH 5.0 to 4.0	
25869	Point Isabel fine sandy loam	45600	37000	44500	48000	7500	3500	0- 7
31329	Potter clay loam	54600	48500	54000	59000	5500	5000	0- 7
26089	Catalpa clay	59000	49000	58000	63500	9000	5500	0- 7
31800	Miller clay loam	90300	71500	77000	94000	5500	17000	0- 7
29331	Frio silt loam	85900	74000	79000	85000	5000	6000	0- 7
31844	Hidalgo clay loam	143000	133000	140000	145000	7000	6000	0- 7
30963		127400	108000	115000	121000	7000	5000	Surface
25905	Laredo silt loam	158800	136000	147000	152000	11000	5000	0- 7
26817	Guadaloupe silty clay loam	177700	157000	174000	181000	17000	7000	0- 7
31330	Potter clay loam	254300	240000	250000	257000	10000	7000	7-19
31882	Frio clay	404000	337000	370000	390000	33000	20000	0- 7

There is a significant decrease in the acidity of some soils with an increase in the time of contact. Eight of the twelve soils decreased in acidity when the period was extended from 16 hours to 40 hours, and two made still further decreases when the time was extended to 64 hours. In the consideration of these data, however, two points must be emphasized. First, the amount of acid added was sufficient to bring the soil to a relatively low pH value. There is undoubtedly a greater shift if the reaction is 4.0 after the 16-hour period than if it had been 6.0. Second, with a soil as calcareous as these, and using an acid as strong as must be used for them, there is considerable opportunity for variations in pH acid values secured, even on identical treatments. Since there is in some cases such a large decrease in acidity due to increasing the period from 16 hours to 40 hours and the difference in cost of time and labor is small, the 40-hour period should be used with soils of high carbonate content.

TYPES OF BUFFER CURVES OF SOILS

Texas soils studied in this work varied from a light dune sand to heavy calcareous soils. The acid consumed expressed as parts per million of calcium carbonate varied from 0 to 400,800. As will be shown later, these soils varied widely in content of total exchangeable bases. This selection of soils provided a wide range with respect to almost all of those soil characteristics ordinarily associated with buffer capacity. Only the section of the curve on the acid side of neutrality was studied. It was found that as long as there was any considerable amount of calcium carbonate left in the soil there was practically no change in reaction with increasing amounts of acid. Buffer curves for 60 soils were constructed. The data for 36 soils as interpolated on the curves are presented in Table 5. In this table all results are calculated to parts of calcium carbonate per million of soil.

Table 5 contains the laboratory number of the soil, which is presented here in order to facilitate comparison with other tables to be presented later. The soil type and the total carbonates, expressed as calcium carbonate, are given. The next three columns give the number of parts of calcium carbonate per million of soil which are equivalent to the acid required to bring the soil to a reaction of pH 6.0, pH 5.0, and pH 4.0, respectively. The next two columns give the amount of calcium carbonate equivalent to the acid required to cause a change of one unit in the pH value of the soil.

Three types of buffer curves occur, as plotted in Fig. 1. The differences between the types are almost entirely due to the presence or absence of carbonates. The three types may be briefly described as follows:

Type I. These curves are concave toward the X, or acid, axis. In the soils having this type of buffer curve, a greater amount of acid is required to cause the change from pH 5.0 to pH 4.0 than the change from pH 6.0 to pH 5.0. This group includes all of the soils relatively low in buffer capacity. The soils belong to Type 1 which are listed above soil No. 31331, in Table 3. This soil requires acid equivalent to 1470 p.p.m. of calcium carbonate to reach a pH of 6.0. Some of the soils more basic than Soil No. 31331 also have buffer curves of Type 1.

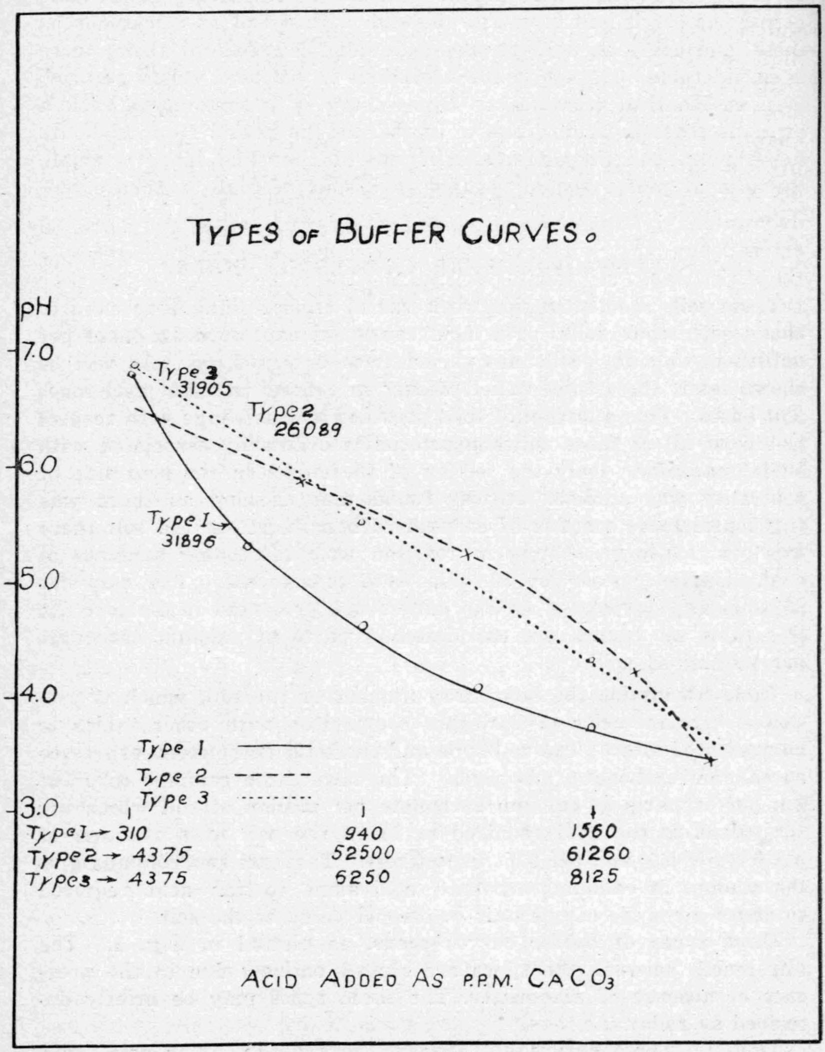

Figure 1—Three types of buffer curves. Note also the wide differences in the quantities of acid added.

Since there are practically no carbonates present, the buffer action in these soils is due to the difficultly soluble silicates for the most part, with perhaps the organic matter playing a small part in some of the soils.

Type II. The buffer curves of this type (Fig. 1) are convex toward the X, or acid, axis. In the soils having this type of buffer curve a much smaller amount of acid is required to change the reaction from pH 5.0 to pH 4.0 than to change from pH 6.0 to pH 5.0. The soils in this group are comparatively high in carbonates and have a high basicity. This shape of the curve is probably due to the fact that all of the carbonate has not been destroyed at pH 6.0, and most of this is destroyed in the change from pH 6.0 to pH 5.0. Small quantities of carbonate remain to be decomposed from pH 5.0 to pH 4.0 while practically all of the carbonate is destroyed before pH 4.0 is reached. In these soils, then, the carbonates are the determining factor in the development of buffer action, to a greater extent than the silicates, which determined the buffer curve in the first group of soils. Attention should be called to the fact that not all of the soils high in carbonates have buffer curves of this type. Soils 23094 and 31800 have buffer curves falling very definitely with Type 1, altho the carbonate content is appreciable, as is shown by the amount of acid required to bring the soil to pH 6.0. This difference is probably due to the difference in the nature of the carbonates. For example, a much higher percentage of the total carbonates would be destroyed by mild acid treatment of a soil in which the carbonates were present as finely divided calcium carbonate than would be the case if the carbonates were in coarse granules. In general, however, the curves conform well to the type.

Type III. Curves of this type approach a straight line. The soils having curves of this type are comparatively few, and are slightly calcareous in nature. In these few cases, the factors which determine a buffer curve of Type I are apparently approximately at equilibrium with those determining the curve of Type II.

In no case, regardless of the nature of the soil or the buffer curve, was there anything like a definite end point or break in the curve. The data presented show conclusively the futility of adopting any procedure in which the buffer capacity is expressed by the pH value resulting from adding an arbitrary amount of acid to a given quantity of soil, as is suggested in the method of Lemmermann and Fresenius. They also show that a method similar to that proposed by Pierre or Hissink in which the buffer capacity is expressed as the amount of acid required to cause a change between any two given pH values, while giving valuable information, by no means presents all the data pertinent to the buffer capacity of a particular soil. For example, for soils Nos. 25873 and 31331 the "specific buffer capacities" between pH 6.0 and pH 5.0 are 300 and 180 p.p.m of calcium carbonate, while the buffer capacities to pH 6.0 are 75 and 1470 p.p.m., and to pH 5.0 are 375 and 1650. The quantities of acid necessary to give soils Nos. 29315, an Amarillo fine sandy loam, and 26075, and Irving clay, a reaction of pH 6.0 are identical, equivalent to 1250 p.p.m. of calcium carbonate, but for pH 5.0 the quantities are 1550 and 2300, and for pH 4.0, 2100 and 4400. Thus, if pH 6.0 had been accepted as the single value desired, the two soils would have been practically identical. If, however, pH 4.0 had been the desired end point, soil No. 26075 would have had over twice the buffer capacity of soil No. 29315. Soil No. 29315 has an acid-comsuming power of 4000, while for soil No. 26075, the value is 15,500, or nearly four times as great.

Obviously in order to express adequately the buffer action of these soils, two sets of data are required: (1) the "total buffer capacity" to a definite pH value; (2) the "specific buffer capacity" between a given pair of pH values, usually, for convenience, differing by one pH unit.

EFFECT OF WASHING OUT THE ELECTROLYTE UPON THE BUFFER CAPACITY

In connection with the study of the effect of acid upon the soil, it is desirable to know whether the degree of acidity secured by adding acid would be affected by washing out the products of the reaction, chiefly calcium chloride. It is known that the reaction is more acid when a soil is treated with a solution of an electrolyte such as potassium chloride than if it is treated with water. Some of the potassium chloride reacts with the insoluble exchange complex to produce potash salt of the exchange complex and hydrocloric acid. The reaction is reversible and is indicated as follows:

$$HX + KCl = KX + HCl$$

If the acidity of a soil is less when the electrolyte is washed out in the laboratory, the acidity will likewise decrease if the electrolytes are washed out of the soil by rain.

This matter was tested on a number of soils. Acid was added as previously described, and the degree of acidity (pH) estimated as usual. The soil was [illegible] transferred quantitatively to Gooch crucibles provided with filter paper discs and washed three times with distilled water. The acidity (pH) of the residue was then determined as usual. The data, together with others to be discussed later, are presented in Table 6. The figures in the column are to be compared with the original pH in the heading, namely, 6.0, 5.0, and 4.0. It is evident from these results that the washed soil has a lower degree of acidity than is secured by the regular procedure, or the pH is higher in every case. The average difference in pH is 0.7 at 6.0, 0.9 at 5.0, and 1.0 at 4.0. With some soils the difference is large, with others it is small; but in all cases the difference is in the same direction—a shift toward the alkaline side. The

Table 6. Acidity of washed-soil residue compared with acidity of mixture of soil and acid.

Washed Residue from soil number	Type	Acid for pH 6.0		Acid for pH 5.0		Acid for pH 4.0	
		Residue with water	Residue with KCl	Residue with water	Residue with KCl	Residue with water	Residue with KCl
25871	Dune sand	----	----	5.9	5.0	5.4	4.7
25873	Lomalto fine sandy loam	6.3	6.7	5.5	5.1	5.3	3.9
31880	Duval fine sandy loam	6.2	5.8	5.6	4.7	4.8	3.8
26103	Crockett fine sandy loam	6.2	5.6	5.2	5.0	4.1	3.8
31888	Webb fine sandy loam	----	----	5.6	4.4	4.8	3.6
31896	Moore fine sandy loam	6.2	5.1	5.5	4.6	4.5	3.7
31890	Miguel fine sandy loam	----	----	5.5	4.5	4.7	4.0
31804	Fitch fine sandy loam	6.5	5.5	5.5	4.6	4.7	3.9
31905	Victorian clay loam	7.0	6.0	5.9	5.0	5.0	4.2
25865	Lomalto clay loam	6.5	6.1	5.8	5.1	4.8	4.0
31833	Spur fine sandy loam	7.3	6.1	6.3	5.4	5.1	4.3
25891	Donna fine sandy clay loam	6.9	6.0	6.0	5.0	5.0	4.2
26089	Catalpa clay	6.8	6.7	6.3	5.1	5.2	4.1
31800	Miller clay loam	6.8	6.6	6.7	6.1	6.1	4.9
31884	Hidalgo clay loam	7.3	6.4	6.6	5.7	5.9	5.2
	Average (15)	6.7	6.1	5.9	5.0	5.0	4.2

curves drawn from the data parallel each other. If a soil is treated with the amount of acid to give a certain degree of acidity by the method previously described, and afterwards washed with distilled water or exposed to rain, it will become less acid. This was found to take place in boxes of soil prepared with different degrees of acidity for experimental work, and was especially noticeable in the surface layer of the soil. The total buffer capacity is greater when the electrolyte is washed out. This must be allowed for in experimental or field work, the conditions under which the work is conducted being kept in mind.

EFFECT OF POTASSIUM CHLORIDE ON THE BUFFER CAPACITY

In both of the preceeding methods, there is some question as to whether or not the system is sufficiently buffered to prevent large differences in acidity (pH) resulting from small amounts of impurities or special materials in the system.

This subject was also studied in another way. After the electrolyte had been washed out, as described above, the soil residue was suspended in a solution of normal potassium chloride, and the acidity estimated. The results also are given in Table 6.

As is seen by comparing the parallel columns, the acidity of the residue is usually higher when the electrolyte is added, the maximum difference from the residue washed with water being 1.4 pH and the average 0.6 to 0.9 pH. It is noted, however, that the average acidity of the soil residue with the potassium chloride is practically the same as that of the original soil with acid. That is to say, the addition of the potassium chloride brings back the acidity to where it was before the electrolyte was washed out with water.

The acidity of a soil will vary to some extent according to the quantity of soluble neutral salts added to it. The acidity would decrease when the salts are washed down by rain or irrigation water, unless the irrigation water contained the same quantity of salt as the original soil or a larger quantity. When the salts come to the surface in dry weather, the acidity would increase. However, the soils of dry sections are usually slightly alkaline or neutral, so that this effect on acidity would seldom occur.

The addition of soluble fertilizer salts, such as potassium salts, nitrates, or sulphate of ammonia, would increase the acidity of the soil, at least temporarily. The equation is:-

$$2HX+(NH_4)_2SO_4=2NH_4X+H_2SO_4$$

Gypsum or sulphate of lime would have the same effect, increasing the degree of acidity of the soil. This was observed in box tests, in which the acidity of the soil to which gypsum was added was higher than at first expected; it was also observed in laboratory tests, in which sulphate of lime was added to the soil.

EFFECT OF THE POTASSIUM CHLORIDE WITH THE ACID UPON THE BUFFER CAPACITY

It is well known that the acidity of samples of soil taken from the same field is found to be somewhat variable if the measurement is made with the soil suspended in water, but the variation is less if the measurement of pH is made with the soil suspended in a solution of potassium chloride. However, the acidity is usually greater in the presence of the potassium chloride than it is really in the field.

Lemmermann and Fresenius (26) and others have recommended that, in order to avoid the possible variations due to absence of buffer material, the pH of the soil be taken with the soil in suspension in a normal solution of the potassium chloride. They state that although this procedure does not give the true acidity of the soil, it gives a valuable characteristic constant of the soil. In order to determine whether this procedure would be of value in the determination of buffer capacity, pH determinations were made similar to those just described, but with the soil suspended in a normal potassium chloride solution instead of in water.

By using the potassium chloride and water in different combinations, data were secured for the following three treatments of the soil, the amounts of acid added remaining the same. These were:

(1) The acidity of the soil (pH) in the presence of potassium chloride.

(2) The residue from (1), suspended in a solution of potassium chloride.

(3) The residue from (1), suspended in water.

The data thus secured were plotted and the curves constructed. Points on this curve are given in Table 7. The amounts of acid added were sufficient to produce the pH of 6.0-5.0-4.0 in the regular procedure, shown in the head of the column.

In soils of low buffer capacity, the degree of acidity is greater, or the pH lower, when potassium chloride is present than when water only is used. The average difference was 0.3 pH, although the maximum difference was 1.0. In soils of higher buffer capacity, the results differ very little. The explanation is simple. In soils of low buffer capacity there is very little salt formed as the result of the addition of the small amount of acid added. In all of the soils of low buffer capacity exchangeable hydrogen is present. The exchange reaction between the soil and acid is a reversible reaction. With a low concentration of salt in the solution, there is little exchange of the base of the salt for the hydrogen of the soil complex. When, however, the salt content of the solution is comparatively greatly increased by the use of the potassium chloride solution, the solution becomes more acid. In soils of high buffer capacity, salt is produced by the action of the acid on the bases of the soil to such

Table 7. Effect of addition of potassium chloride upon the degree of acidity of the soil and acid mixture and of the residue.

Soil Number	Type	Acid for pH 6.0			Acid for pH 5.0			Acid for pH 4.0		
		Filtrate with KCl	Residue with KCl	Residue with water	Filtrate with KCl	Residue with KCl	Residue with water	Filtrate with KCl	Residue with KCl	Residue with water
25871	Dune sand	----	----	----	4.1	5.3	7.5	3.7	5.1	7.3
25873	Lomalto fine sandy loam	5.4	5.8	8.3	4.5	4.9	7.0	3.6	4.0	6.3
31880	Duval fine sandy loam	5.2	5.5	6.6	4.5	4.7	6.9	3.5	4.0	6.5
26103	Crockett fine sandy loam	5.2	5.2	6.8	4.9	4.8	7.1	3.4	3.8	6.3
31888	Webb fine sandy loam	----	----	----	4.2	4.5	6.6	3.5	3.7	6.2
31896	Moore fine sandy loam	5.0	5.5	6.8	4.4	5.0	6.5	3.5	4.2	6.4
31890	Migurel fine sandy loam	----	----	----	4.7	4.7	7.3	3.8	3.8	6.4
31804	Fitch fine sandy loam	5.4	5.5	6.5	4.7	4.7	7.4	3.7	4.0	6.0
31905	Victoria clay loam	6.0	6.5	7.9	4.8	5.9	6.7	3.8	4.0	5.8
25865	Lomalto clay loam	5.5	6.5	8.0	5.0	5.5	7.5	4.1	4.4	6.2
31833	Spur fine sandy loam	6.4	6.8	8.2	5.4	5.9	7.3	4.2	4.7	6.1
25891	Donna fine sandy clay loam	6.0	6.6	7.9	4.8	5.6	6.9	4.0	4.4	6.5
26089	Catalpa clay	5.9	6.8	8.3	5.0	6.0	6.7	3.8	4.8	5.7
31800	Miller clay loam	6.0	6.6	8.0	5.1	6.4	7.7	4.1	5.6	7.0
31884	Hidalgo clay loam	6.1	6.9	8.3	5.1	6.6	7.5	4.0	5.5	6.4
	Average (15)	5.7	6.2	7.6	4.7	5.4	7.1	3.8	4.4	6.3

an extent that the addition of the potassium chloride has no effect on the acidity of the system.

The soil treated with acid was filtered off and washed with water. The acidities (pH) of the residue treated with potassium chloride, and with water, are given in Table 7. The residue treated with potassium chloride differs in acidity (pH) only slightly from the original acidity of the soil and acid mixture, averaging 0.2 to 0.4 pH higher. The residue treated with water is much more alkaline, averaging 1.6-2.1-2.3 pH higher. These results are somewhat similar to those secured by Joffe and McLean (6), and the explanation of the results secured in the two investigations is similar. The potash compound of the base-exchange complex dissociates, thus:

$$KX+H_2O=HX+KOH$$

Working with soils from plats at the New Jersey Experiment Station they found a considerable difference in acidity, depending upon whether the extractant was water or normal barium chloride. In every case, the barium chloride gave lower pH values than did the water. The pH by water was mostly between 5.0 and 5.5. They found also that even after 10 days' treatment of the soil with barium chloride, only about 40 per cent of the acid in the soil had been extracted. These results show that a portion of the soil hydrogen was replaced by barium, but that the reaction by no means goes to completion, even when the extractant is finally removed and the soil residue subjected to long washing with the original extractant.

In a majority of cases, the acidity of the residue treated with potassium chloride was, within a very small range, identical with the acidity of the mixture of the soil and acid. This means simply that the tendency toward alkalinity due to the residue was counteracted by the tendency due to acidification resulting from the use of potassium chloride in the final determination of reaction. It should be noted, however, that when there is any considerable difference between the two, the residue treated with potassium chloride is always the more alkaline.

Irregular results were secured when the residue from the treatment with acid and potassium chloride was suspended in water for the determination of pH. The erratic results may be easily explained. After the treatment with acid and potassium chloride, all of the soluble buffering materials are washed out. The exchange complex of the soil contains potassium in place of most of the calcium. A very slight hydrolysis of this complex results in the formation of a small amount of potassium hydroxide. Due to the fact that all of the buffering materials of the solution have been removed, this small amount of potassium hydroxide has an enormous effect upon the reaction (pH) of the remaining material. Any slight trace of impurity would also have a marked influence on the reaction. The consequence is that this residue is less acid than the other residues and the results are erratic.

QUANTITATIVE RELATIONS OF THE ACIDITY OF THE RESIDUE TO THE QUANTITY OF ACID USED

It is of significance to know the relation of the quantity of acid in the residue after the soil has been treated with the acid to quantity of acid used. This relation might throw some light on the chemistry of the process. It also aids in judging whether or not the measurement of soil acidity is related to the quantity of acid-forming fertilizers added to the soil, or to the production of nitrates, or to other acidifying influence.

The quantity of acidity of the soil residue was estimated by several methods proposed for ascertaining the lime requirements of the soil, namely, the Veitch, the Jones, and the Hopkins method, and also by barium hydroxide and by barium acetate.

LIME REQUIREMENT OF SOIL RESIDUE

Eleven soils of low buffer capacity were used. One hundred grams of each soil was treated with sufficient acid to bring the soil to a pH of 4.0. as calculated from the pH acid curve. After standing overnight. the soil was transferred to a filter, the supernatant liquid filtered off, and the residue washed twice with water. The soil, after drying, was passed through a 20-mesh sieve. Determinations of the lime requirement were then made on the soil residue by the Veitch, the Hopkins, and the Jones methods. In the Veitch method (29) the soil is treated with increasing amounts of lime water until the filtrate upon boiling turns pink with phenolphthalein. In the other two methods the soil is treated with neutral salt solution and the filtrate titrated with sodium hydroxide with phenolphthalein as the indicator. The Hopkins method (5) uses sodium chloride, while the Jones method (7) uses calcium acetate. The results of this work are presented in Table 8.

Table 8. Relation of acid added to the soil to the acidity measured by various methods expressed as parts per million of calcium carbonate.

Laboratory Number	Total acid added	Carbonates in original soil	Net acid added equivalent to calcium carbonate	Acidity of residue equivalent to calcium carbonate		
				Veitch method	Hopkins method	Jones method
25871	312	0	312	410	36	320
25873	812	0	812	1250	48	976
31880	1562	450	1112	1607	348	1584
26103	1000	130	870	1250	81	1008
31888	781	60	721	821	186	1334
31896	1250	180	1070	1607	216	1584
31890	1310	150	1160	1607	78	1680
31804	2615	170	2445	2680	213	2128
31914	2190	180	2010	2320	33	2400
31820	1815	490	1325	1960	62	1696
31321	3750	1440	2310	3035	27	2368
Average (11)			1286	1686	121	1553

The first column of Table 8 gives the laboratory number of the soil. The next three columns present data relative to the amount of acid added. The third column of the table shows that a small part of acid added would be used in the neutralization of carbonates; the total amount of acid added has been corrected to allow for the amount of carbonate present, the results being termed the net acid added, and presented in the fourth column. The last three columns give the lime requirements of the various soils, as determined by the Veitch, the Hopkins, and the Jones method.

The Veitch method indicated a recovery of acid greater in every case than the net acid added. The average excess was about 30 per cent. It should be remembered, however, that the method is not adapted to measuring small differences, because the lime water is added in cubic centimeters and 1 cc. of lime water is equivalent to 410 parts per million of calcium carbonate. However, the order of the soils is the same, and there is no outstanding difference between acid added and acid recovered.

The results by the Hopkins method are erratic and low. The average is only 10 per cent of the acid added. This and similar methods are evidently not suitable for work of this kind.

With the Jones method, the agreement between the amounts of acid added and the amounts recovered is fairly close, although the lime requirements are uniformly greater than the amounts of acid added. The average excess is 20 per cent. Results by the Jones method average a little lower than by the Veitch method, although the results in some cases are higher, and in other cases lower. Both the Jones method and the Veitch method give an approximate measure of the quantity of acid added to the soil.

ACIDITY OF THE SOIL RESIDUE BY BARIUM HYDROXIDE

The effect of the treatment with acid upon acidity of the soil was studied by means of barium hydroxide. The soils used in this experiment were low in calcium carbonate and high in total exchange capacity. Portions of the soil were treated in the regular way with amounts of acid sufficient to cause a pH of 4.0, filtered, washed twice with distilled water, placed in Erlenmeyer flasks, and treated with amounts of 0.01 N barium hydroxide equivalent to the difference in amounts of acid required to develop a pH value of 4.0 and those of 4.5, 5.0, 5.5, and 6.0 by the method previously described. For example, the soil No. 29435 required 43 cc. of 0.01 N hydrochloric acid to produce a pH of 4.0, 29 cc. for pH 4.5, 18 cc. for pH 5.0, 13 cc. for pH 5.5, and 9 cc. for pH 6.0. Five 8-gram portions were treated with 43 cc. of 0.01 N acid. The resulting pH was determined in one portion, and varying amounts of 0.01 N barium hydroxide added to the other four portions. These amounts were 14 cc. (43-29) to each pH of 4.5, 25 cc. (43-18) for pH 5.0, 30 cc.

(43-13) for pH 5.5, and 34 cc. (43-9) for pH 6.0. After the addition of the barium hydroxide, the flasks were tightly stoppered and allowed to stand with occasional shaking, for 48 hours. At the end of that time, the pH of the system was determined. The results secured are presented in Table 9.

Table 9. Recovery with barium hydroxide of acid added, by buffer curve of soil residue.

Laboratory Number	$CaCO_3$ content p.p.m.	Acid added to original soil as p.p.m. CaCO3	pH secured	pH of $Ba(OH)_2$ treated soil residue when net acid would give a pH value on untreated soil of			
				4.5	5.0	5.5	6.0
29365	55	1125	4.16	5.49	6.10	6.57	7.02
29425	348	1720	4.22	5.46	5.87	6.16	6.64
29434	672	2438	4.16	5.53	5.85	6.45	7.02
29427	492	2438	4.15	4.99	5.41	6.07	6.49
25972	80	2500	4.02	5.37	5.76	6.23	6.64
29435	440	2685	4.00	5.35	5.88	6.37	6.45
29441	200	2750	4.06	5.20	5.84	6.24	6.86
25959	1000	3950	4.18	5.75	6.85	7.50	8.10
31327	256	4063	4.11	5.51	5.91	6.30	6.60
26075	610	4375	4.11	5.66	6.67	7.25	7.74
31321	3132	4688	4.84	7.01	7.54	8.05	8.51
25967	1052	5155	3.97	5.33	6.15	6.50	7.34
Average (12)				5.55	6.15	6.64	7.11

The pH values secured by the various additions of barium hydroxide are considerably higher than those which would have been secured by adding to the untreated soil the net amount of acid, that is, the total acid added minus the amount of barium hydroxide added. The average excess is 1.05 to 1.14 pH. The acidity as measured by this method is less than that measured by the methods discussed in the preceding sections. This is explained by the fact that almost all of the soluble salts which would act as buffering materials were removed in the preliminary treatment; consequently, when the barium soil-complex hydrolyzes slightly, the resulting pH is considerably increased. This same tendency toward increases in pH after removal of the soluble salts was noted in connection with the work discussed above. A fairly strong base has been added to the system, and the increase in pH is still more pronounced. When an allowance is made for this increase, the curves secured by plotting the results of the experiment closely parallel the curves secured by plotting the pH acid data. That is, if 10 cc. of 0.01 N acid causes a difference in pH of 1 unit, the same amount of 0.01 N barium hydroxide will cause a difference of 1 unit in pH toward the alkaline side. In other words, the slopes of the two curves are nearly identical, but the intercepts are different.

It must be remembered that the pH of the residue of the soil washed with water (Table 6) is on an average 0.7 to 1.0 higher than the residue in the presence of potassium chloride (Table 7) or the reaction products (Table 6). These differences alone are almost sufficient to account for the excess pH secured by means of the back titration with barium hydroxide.

ACIDITY OF THE SOIL RESIDUE IN TERMS OF EXCHANGEABLE HYDROGEN

In addition to the quantitative estimations of acidity just discussed, determinations were made of the amount of exchangeable hydrogen in soils after treatment with various amounts of acid. The treatments included the additions of the quantity of acid necessary to bring the soil to pH values of 6.0, 5.0, and 4.0, in the presence of the reaction products on the regular pH acid buffer curve and after the regular treatment for acid consumed. A determination was subsequently made of the total exchange capacity, in order to determine whether or not the acid additions had caused any alterations of the exchange complex, other than the substitution of hydrogen for the various bases, which will be discussed later.

The procedure used was as follows: Eight grams of soil was treated with the required amount of acid, the volume made up to 100 cc., and the suspension set aside overnight. The following morning the suspension was transferred to 35-cc. Gooch crucibles, and the residue washed twice with water. The suction flask was washed out and replaced. The soil was then leached with 250 cc. of neutral normal barium acetate solution contained in the leaching apparatus described elsewhere (4). After the 250 cc. had leached through the soil, the filtrate was titrated electrometrically, using quinhydrone and 0.1 N barium hydroxide. Instead of using the regular Veibel electrolyte, a portion of the original barium acetate solution was used and changed after each determination. Two circuits were provided for the titration, one leading through a potentiometer, and a second circuit leading directly to the galvanometer through a tap key. The major part of the titration was done with the use of the resistance provided in the potentiometer. The final end point was reached by using the second circuit. By means of this arrangement, the end point was easily determined, one drop of the 0.1 N barium hydroxide used in the titration causing a very distinct deflection of the galvanometer. The results were calculated as parts per million of calcium carbonate. The procedure for the determination of exchangeable hydrogen after acid consumed was similar with the exception that the regular acid-consumed procedure was carried through prior to leaching with barium acetate. The results secured in this study are presented in Table 10.

After the determination of exchangeable hydrogen, the soil was

Table 10. Exchangeable hydrogen in soils after various acid treatments (Results as p.p.m. $CaCO_3$).

Laboratory Number	Soil type	CaCO3	Acid added to reach a pH of				Exchangeable hydrogen equivalent to calcium carbonate					Depth
		p.p.m.	6.0	5.0	4.0	Acid consumed	Untreated soil	pH acid 6.0	pH acid 5.0	pH acid 4.0	Acid consumed	inches
25871	Dune sand	0	0	-------	300	0	-------	-------	-------	350	-------	0. 7
31888	Webb fine sandy loam	60	150	-------	900	1500	1150	1210	-------	1755	2450	0- 7
31890	Miguel fine sand loam	150	150	-------	1400	3400	1260	1330	-------	1650	3600	0- 7
25873	Lomalto fine sandy loam	0	175	-------	845	1400	550	720	-------	1095	1215	0- 7
26103	Crockett fine sandy loam	130	280	-------	1100	1500	735	960	-------	1540	2100	0- 7
31880	Duval fine sandy loam	450	330	-------	1300	1400	825	1135	-------	1720	1800	0- 7
31914	Orelia fine sandy loam	180	470	-------	2250	6240	985	1285	-------	1930	5050	0- 7
31896	Moore fine sandy loam	180	500	-------	1300	2750	785	1235	-------	1650	2500	0- 7
31820	Amarillo fine sandy loam	490	700	-------	2000	2900	815	1220	-------	1590	3050	0- 7
31804	Fitch fine sandy loam	170	825	-------	2600	4000	620	1060	-------	2235	4435	0- 7
26075	Irving Clay	620	1250	-------	4400	15500	705	1395	-------	2330	4000	0- 7
31321	Amarillo silty clay loam	1440	1700	-------	4400	8750	0	1590	-------	2480	6900	0- 7
25883	Willacy fine sandy loam	3960	3000	-------	5700	9100	0	1105	-------	2000	4760	0- 7
31905	Victoria clay loam	5500	5700	7200	8700	15000	0	0	0	2690	7500	0- 7
31833	Spur fine sandy loam	10730	6550	9000	12500	17000	0	765	530	1690	4550	0- 7
25865	Lomalto clay loam	10070	8000	9300	12000	15500	0	0	0	1690	5550	0- 7
25891	Donna fine sandy clay loam	13400	10600	13500	15500	20750	0	440	1280	3470	6950	0- 7
31802	Yohola fine sandy loam	30550	23500	32000	36000	36600	0	450	655	560	2100	0- 7
25869	Point Isabel fine sandy loam	45600	37000	44500	48000	48400	0	0	190	3000	3235	0- 7
26089	Catalpa clay	59000	49000	58000	63500	69100	0	0	1565	4470	8450	0- 7
31800	Miller clay loam	90300	71500	77000	94000	96000	0	0	3440	6010	6600	0- 7
31884	Hidalgo clay loam	127400	108000	115000	121000	123000	0	0	0	2750	6500	0- 7
25905	Laredo silt loam	158800	136000	147000	152000	153000	0	0	1380	1755	3275	0- 7
31882	Frio clay	404000	337000	370000	390000	398000	0	0	0	1940	7550	0- 7

leached with 250 cc. of neutral normal ammonium chloride, washed free of excess ammonia, and the determination of total exchange capacity completed in the usual way. This work is discussed on a subsequent page.

The net acid and the net exchangeable hydrogen, expressed in terms of calcium carbonate in parts per million of soil, are given in Table 11. The net acid is secured by subtracting from the total acid used for each treatment, as shown in Table 10, the carbonate of lime in the soil. The net exchangeable hydrogen is secured by subtracting from the total exchangeable hydrogen, shown in Table 10, the exchangeable hydrogen in the untreated soil. It is to be noted, in Table 10, that a soil may contain both exchangeable hydrogen and calcium carbonate.

The net acid and the net exchangeable hydrogen is, in some cases, the same within the limits of error, at pH 6, pH 4, and with the treatment for acid consumed. With soils 31888 and 26103 the two agree for all three treatments. With some other soils, however, the exchangeable hydrogen is appreciably lower than the net acid used. With soil 31890, the exchangeable hydrogen is only two-thirds of the net hydrogen added; with soil 26075, it is less than 50 per cent at 4.0 acid and less than 25 per cent on the residue from the acid consumed estimation. Other differences are evident in the table. The differences are usually greater with the residues from the treatment for pH 4 and for acid consumed. This would seem to indicate that either the acid destroys the base-exchange complex, or that base is removed from other compounds than the exchange complex. As it is shown elsewhere in this Bulletin that acid has little effect on the exchange complex, it follows that the acid has acted upon bases in other compounds. It appears probable that while in some soils the only compounds which give up bases to acids are carbonates and base-exchange complex, other soils contain, in addition, compounds which give up bases to acids without the base being replaced by hydrogen. This is in accordance with the work of Pierre (19), who found that in some soils part of the acid resulting from the application of acid-forming fertilizers was neutralized by soil materials other than those of the base exchange complex.

Table 11. Comparison between net amounts of acid added to soils and the amount of exchangeable hydrogen in the soils after treatment (as parts per million of calcium carbonate).

Laboratory Number	Soil type	pH 6.0		pH 5.0		pH 4.0		Acid consumed	
		Net acid	Net exch. H	Net acid	Net exch. H	Net acid	Net exch. H	Net acid	Net exch. H
25871	Dune sand	-------	-------	-------	-------	300	350	-------	-------
31888	Webb fine sandy loam	90	60	-------	-------	840	605	1440	1300
31890	Miguel fine sandy loam	0	70	-------	-------	1250	390	3250	2340
25873	Lomalto fine sandy loam	175	170	-------	-------	845	545	1400	665
26103	Crockett fine sandy loam	150	225	-------	-------	970	805	1370	1365
31880	Duval fine sandy loam	–120	310	-------	-------	850	895	950	975
31914	Orelia fine sandy loam	290	300	-------	-------	2070	945	6060	4065
31896	Moore fine sandy loam	320	450	-------	-------	1120	865	2570	1715
31820	Amarillo fine sandy loam	210	405	-------	-------	1510	765	2410	2235
31804	Fitch fine sandy loam	655	440	-------	-------	2430	1615	3830	3815
26075	Irving clay	630	690	-------	-------	3780	1625	14880	3295
31321	Amarillo silty clay loam	260	1590	-------	-------	2960	2480	7310	6900
25883	Willacy fine sandy loam	–960	1105	-------	-------	1740	2000	5140	4760
31905	Victoria clay loam	200	0	1700	0	3200	2690	9500	7500
31833	Spur fine sandy loam	–4180	765	1730	530	1770	1690	6270	4550
25865	Lomalto clay loam	–2070	0	770	0	1930	1690	5430	5550
25891	Donna fine sandy clay loam	–2800	440	100	1280	2100	3470	7350	6950
31802	Yohola fine sandy loam	–7050	450	1450	655	5450	560	6050	2100
25869	Point Isabel fine sandy loam	–11400	0	–1100	190	2400	3000	2800	3235
26089	Catalpa clay	–20100	0	–1000	1565	4500	4470	10100	8450
31800	Miller clay loam	–18800	0	–13300	3440	3700	6010	5700	6600
31884	Hidalgo clay loam	–19400	0	–12400	0	–6400	2750	–4400	6500
25905	Laredo silt loam	–22800	0	–11800	1380	–6800	1755	–5800	3275
31882	Frio clay	–67000	0	–30400	0	–6400	1940	–6000	7550

RELATION OF CARBONATES TO THE BUFFER CAPACITY

The carbonate content and buffer capacity are given in Table 5. The soils are arranged according to the amount of acid required to reach a pH of 6.0. Since the carbonate is practically in the same order, it is apparent that the buffer capacity increases approximately as the carbonates increase.

After the carbonate content of the soil reaches about 4000 parts per million, or 0.4 per cent of calcium carbonate, there is some carbonate still present in the soil when the pH of the soil as determined by the method is at 6.0. This is more clearly brought out in Table 11. The amount still present varies, undoubtedly due to the fact that in some soils the carbonates are more easily dissolved by acids than in others. The last six soils in the list still contain small amounts of carbonate at pH 5.0 (see Table 11), altho in three of these the amount is nearly within the range of experimental error. At a pH of 4.0, some calcium carbonate is still present in two soils (Table 11), but in these the difference is within the range of experimental error (Table 5). It should be remembered that there is a great difference in the procedures for buffer capacity and total carbonates. At pH 6.0, there is only a very small amount of acid present, while in the carbonate determination there is a large excess of very strong acid. It is to be expected that there would be considerable differences in the amount of carbonates soluble in the two procedures. The degree to which the carbonates are neutralized at pH 6.0 is, in fact, remarkable, and affords a strong indication of the accuracy of the procedure for buffer capacity.

The data on the total carbonate content of the soil corroborate the conclusions already stated in connection with the discussion of the types of buffer curves.

RELATION OF THE BASE-EXCHANGE COMPLEX TO THE BUFFER CAPACITY

Various workers have shown that the base-exchange complex plays an important role in the buffer capacity of the soil. The pH of an acid soil is closely associated with the degree of saturation of the exchange complex with bases, altho Pierre and Scarseth (22) have recently shown that the relationship is not as close as had been assumed by some of the earlier workers. Consequently, the greater the exchange capacity, the more bases must be exchanged for hydrogen before the soil reaction changes materially. Parker (17, 18) has shown that the same proportion of bases exchanged for hydrogen at a low degree of acidity will cause a much larger change in pH than if the exchange were made in a soil already acid. For these and similar reasons, a study was made of the exchange capacity of the soils for which buffer data had been secured, and the degree of relationship between the exchange capacity and the buffer capacity was determined.

The total exchange capacity was determined essentially as outlined by Kelley and others (2, 9, 11, 23, 24). Ten grams of soil was placed in a 35-cc. Gooch crucible provided with a disk filter paper. The soil was then leached with neutral, normal ammonium acetate until the leachate gave no further test for calcium. The ammonium acetate was then washed out with 95 per cent ethyl alcohol until the leachate gave no test with Nessler's solution. The apparatus described by Fudge (4) was of great assistance in this work. The soil was immediately placed in an 800-cc. Kjeldahl flask, light magnesium oxide added, and the ammonia distilled into 0.2 N hydrochoric acid. The excess acid was titrated with 0.1 N ammonium hydroxide. Results in this study were expressed as parts of cacium carbonate per million of soil. This was done in order to facilitate comparison with the data in other tables. One milligram equivalent, the usual unit used in exchange-capacity studies, is equal to 500 p.p.m. of calcium carbonate, and the conversion can be readily made if desired.

The total base-exchange capacity was compared with the buffer capacity of a number of soils. The quantities of acid necessary to increase the acidity from pH 6.0 to pH 5.0 and from pH 5.0 to pH 4.0 were taken as measurements of the buffer capacity. As previously noted, there are in many soils significant differences between the buffer capacities at these two points, especially in the case of soils low in carbonates, which were used for this comparison.

The total quantity of acid required to reach a pH of 6.0 and also the net quantity, are given in the table. The net quantity of acid used for pH 6 was the total less the carbonates. The results of the work are given in Table 12.

The relationship between the specific buffer capacity, that is, the amount of acid required to cause a change of 1 unit pH, and the total exchange capacity is given in the last two columns of the table. The specific buffer capacity was divided by the total exchange capacity and multiplied by 100. The figures given may be considered as the percentage of the total bases in the exchange complex neutralized by the acids in changing the pH to the extent given. There is fair uniformity in the results, when the wide variation in the soils is taken into consideration. However, the degree of relation between the two properties of the soils seems to depend upon two factors: the size of the total exchange capacity, and the pH values between which the specific buffer capacity is taken. The percentage of bases taken by the acid tends to decrease as the buffer capacity increases for the specific buffer capacity for pH 6.0 to pH 5.0. The average for the 18 soils with exchange capacities smaller than the equivalent of 14,000 parts per million of calcium carbonate is 9.8 per cent of the bases used, while the average is 6.4 for the 12 soils of greater exchange capacity. With the specific buffer capacity for pH 5.0 to pH 4.0, the average per cent of the sixteen soils with the exchange capacities smaller than 10,000 parts per million is 17.0, while the average is 11.1 for

Table 12. Relation between exchange capacity and buffer capacity (results expressed as parts per million $CaCO_3$).

Laboratory Number	Soil type	Carbonate content	Total exchange capacity	Net acid to pH 6	Specific buffer capacity		Percentage of bases used in neutralizing acids	
					From 6.0 to 5.0	From 5.0 to 4.0	From 6.0 to 5.0	From 5.0 to 4.0
25871	Dune sand	0	345	-------	-------	150	-------	43.5
25873	Lomalto fine sandy loam	0	1770	175	300	370	17.0	20.9
29315	Amarillo fine sandy loam	650	2375	600	300	550	12.6	23.2
26103	Crockett fine sandy loam	130	2465	150	320	500	13.0	20.3
31896	Moore fine sandy loam	180	3160	320	280	520	8.9	16.5
29450	Amarillo fine sandy loam	1200	3400	–300	310	800	9.1	23.5
31880	Duval fine sandy loam	450	3655	–120	370	600	10.0	16.4
31890	Miguel fine sandy loam	150	4140	0	-------	700	-------	16.9
31331	Amarillo fine sandy loam	770	4230	700	180	250	4.3	5.9
31888	Webb fine sandy loam	60	4290	90	-------	500	-------	11.7
31820	Amarillo fine sandy loam	490	4575	210	425	875	9.3	19.2
31332	Amarillo fine sandy loam	460	4845	240	300	700	6.2	14.5
31804	Fitch fine sandy loam	170	5780	655	625	1150	10.8	19.9
31914	Orelia fine sandy loam	180	6170	290	1730	1050	11.8	17.0
29436	Wilson clay	520	10200	355	1065	1410	10.4	13.8
31321	Amarillo silty clay loam	1440	10310	260	1250	1450	12.1	14.1
31323	Amarillo silty clay loam	-------	10330	-------	1530	1810	14.8	17.5
29426	Crockett clay loam	496	11680	0	-------	1100	-------	9.4
29438	Lufkin fine sandy loam	24	11950	2375	1180	1180	9.9	9.9
29425	Crockett clay loam	480	12950	–300	625	780	4.8	6.5
31326	Amarillo silty clay loam	780	13385	1200	1410	1780	10.5	13.3
31327	Randall clay	256	13800	750	1065	1690	7.7	12.3
29434	Wilson clay	672	14205	–350	910	1190	6.4	8.4

Table 12. Relation between exchange capacity and buffer capacity (results expressed as parts per million $CaCO_3$)—(Continued).

Number Laboratory	Soil type	Carbonate content	Total exchange capacity	Net acid to pH 6	Specific buffer capacity		Percentage of bases used in neutralizing acids	
					From 6.0 to 5.0	From 5.0 to 4.0	From 6.0 to 5.0	From 5.0 to 4.0
31328	Randall clay	240	14315	1100	970	2060	6.8	14.4
29427	Crockett clay loam	492	14425	-450	970	1440	6.7	10.0
29435	Wilson clay	440	14515	60	610	1580	4.2	10.9
25972	Wilson clay loam	80	14850	------	970	1535	6.6	10.3
29365	Amarillo fine sandy loam	55	15050	350	310	470	2.0	3.1
29441	Lufkin fine sandy loam	200	15725	200	785	1615	5.0	10.3
25968	Houston clay	384	16050	620	980	2360	6.1	14.7
25967	Houston clay	1052	17890	1400	1250	2320	7.0	13.0
26075	Irving clay	610	18430	630	1050	2100	5.7	11.4
25959	Irving clay	1000	19110	-400	1150	2380	6.0	12.4
26823	Lake Charles clay	4400	22550	600	1400	1850	6.2	8.2
	Average (34)				821	1200	8.4	14.5

sixteen soils above that amount. Variations from the average of the percentages of bases used are much smaller at the specific buffer capacity of pH 5.0 to pH 4.0 than at the specific buffer capacity of pH 6.0 to pH 5.0. Results on soils 25871 and 29365 were not included in the averages mentioned above, because they were much different from any of the other soils.

Attention should be called to the fact that lighter soils have lower total exchange capacity and lower buffer capacity than heavy soils. In heavy soils a smaller percentage of the exchange complex must be taken up by hydrogen in order to produce a given change in reaction than is the case with lighter soils.

Several conclusions with reference to soils containing low amounts of carbonates may be drawn from this work.

As the total exchange capacity of the soil increases, the relative amount of acid required to cause a change in reaction of 1 unit pH (the specific buffer capacity) tends to decrease.

The specific buffer capacity between pH 5.0 and pH 4.0 represents nearly twice as much of the total exchange capacity as does the specific buffer capacity between pH 6.0 and pH 5.0. Assuming that most of the acid is used in the exchange of hydrogen for exchangeable bases, this means that nearly twice as much exchangeable base is removed in changing from pH 5.0 to pH 4.0 as when the change is from pH 6.0 to pH 5.0. However, it requires ten times as many hydrogen ions to change the pH from pH 5.0 to 4.0 as from pH 6.0 to 5.0.

The fact that equal amounts of acid changes so much less of the exchange complex in soils of high exchange capacity than in soils of low exchange capacity, probably explains in large measure why, in applying laboratory results to field studies, a larger conversion factor is necessary for the soils of high exchange capacity.

When the buffer curve is of Type I, indicating an absence of appreciable quantities of carbonates, a fair indication of the size of the total exchange capacity may be secured from the specific buffer capacity.

EFFECT OF ACID ON THE EXCHANGE COMPLEX

Treatment of the soil with acid is necessary in the determination of buffer capacity. Since the amount of acid used depends upon the character of the soil, and a soil containing a considerable quantity of carbonates requires a large amount of acid, it is of some importance to know whether or not there is a breakdown of the exchange complex with the addition of this acid.

This question is also of considerable importance in connection with the determination of the exchange capacity of a soil. The method requires leaching the soil with a normal neutral solution of ammonium acetate until the leachate gives no test for calcium. Many of the soils used in the present study were highly calcareous, and much time was

Table 13. Effect of treatment with acid on the exchange capacity of soils (expressed as parts per million calcium carbonate).

Laboratory Number	Soil tpye	Acid consumed by original soil	Exchange capacity		Net effect of treatment with acid
			Original soil	Soil treated with acid	
29450	Amarillo fine sandy loam	12500	3400	3540	
29336	Richland fine sandy loam	22200	5210	5500	+ 140
29333	Midland fine sandy loam	28600	5290	4970	+ 290
31802	Yohola fine sandy loam	36600	5450	5470	— 310
25883	Willacy fine sandy loam	9100	5805	5770	+ 20
25865	Lomalta fine sandy loam	15500	6700	6610	— 35
31833	Spur fine sandy loam	17000	7100	7140	— 90
25871	Victoria fine sandy loam	14200	7940	7840	+ 40
25968	Houston clay loam	15900	8075	8000	— 100
31329	Potter clay loam	62100	9320	9420	— 75
31325	Amarillo silty clay loam	9700	9375	9080	+ 100
25891	Donna fine sandy loam	20750	9560	9480	— 295
31905	Victoria clay loam	15000	9610	9710	— 80
29436	Wilson clay	12600	10200	10080	+ 100
31323	Amarillo silty clay loam	9600	10330	11480	— 120
26824	Lake Charles clay	22750	11230	11400	+1150
29426	Crockett clay loam	18100	11680	12320	+ 170
29438	Lufkin finesandy loam	12250	11950	11740	+ 650
29366	(Unknown	9100	12405	12660	— 210
29425	Crockett clay loam	8750	12950	12940	+ 255
31326	Amarillo silty clay loam	14600	13385	13360	— 10
31327	Randall clay	11300	13800	14040	— 25
29434	Wilson clay	10500	14205	14720	+ 240
31828	Randall clay	12100	14315	14460	+ 515
29427	Crockett clay loam	11300	14425	14940	+ 145
29435	Wilson clay	15100	14515	14620	+ 515
25972	Wilson clay loam	11500	14850	15260	+ 105
29365	Amarillo fine sandy loam	12500	15050	14660	+ 410
29441	Lufkin fine sandy loam	12000	15725	16120	— 410
26089	Catalpa clay	69100	17540	17170	+ 395
25967	Houston clay	17200	17890	18220	— 370
26075	Irving clay	15500	18430	18280	+ 330
25959	Irving clay	11900	19110	19520	— 150
25869	Point Isabel fine sandy loam	48400	19300	18180	+ 410
26823	Lake Charles clay	23500	22550	21980	—1120
25966	Trinity clay	31000	26420	26230	— 570
					— 190

Differences total	5930
Differences net	—1770
Average difference	— 50

required to leach them free from calcium. If it were possible to add acid to the soil in order to destroy a part of the carbonates without causing a significant alteration in the exchange complex, the determination could be greatly expedited. In a private communication, Doctor Homer Chapman stated that he had added acid to a few calcareous soils without any apparent injury to the exchange complex, but added that the work had been done on only a few soils. In order to test this matter, 36 soils were treated with hydrochloric acid equivalent to 35 cium carbonate and the total exchange capacity from 3400 to 26,420 p.p. city was determined in the residue and in the original soils.. The acid-consuming power of these soils varied from 8750 to 69,100 p.p.m of calcium carbonate and the total exchange capacity from 3400 to 26,420 p. p. m. Soils high in carbonates were not used because it was thought that the soils low or medium in carbonates might be more easily affected by the acid than would those high in carbonates. The results of the work are presented in Table 13, with the soils arranged in order of increasing exchange capacity. In most cases, the exchange capacity is practically the same before and after treatment with the acid.

Table 14. Total exchange capacity, in parts per million of calcium carbonate, in original soils compared with soils treated with acid.

Laboratory Number	Soil type	Untreated soil	After pH acid 4.0	After acid consumed
25871	Dune sand	350	350	350
31888	Webb fine sandy loam	4240	4250	4190
31890	Miguel fine sandy loam	4080	4190	4000
25873	Lomalto fine sandy loam	1770	1640	1650
26103	Crockett fine sandy loam	2420	2450	2450
31880	Duval fine sandy loam	3710	3550	3510
31914	Orelia fine sandy loam	6160	6125	5890
31896	Moore fine sandy loam	3130	3065	3090
31820	Amarillo fine sandy loam	4610	4640	4540
31804	Fitch fine sandy loam	5750	5775	5560
26075	Irving clay	18430	18810	17100
31321	Amarillo silty clay loam	10500	10100	9790
25883	Willacy fine sandy loam	5805	5775	5880
31905	Victoria clay loam	9610	9850	9680
31833	Spur fine sandy loam	7100	7065	7000
25865	Lomalto clay loam	6700	6765	6580
25891	Donna fine sandy loam	9560	8850	9480
31802	Yahola fine sandy loam	5450	5390	5800
25869	Point Isabel fine sandy loam	17300	17175	17420
26089	Catalpa clay	17540	17375	17720
31800	Miller clay loam	11860	11925	10410
31884	Hidalgo clay loam	8795	8815	7250
25905	Laredo silt loam	7490	7625	7550
31882	Frio clay	13190	13075	12975
	Average (24)	7731	7693	7494

In only 5 of the 36 cases is the difference between the results secured by the regular method and that secured after treatment with acid larger than could be accounted for by experimental error. Three of these differences are increases and two decreases, with the use of the acid, so that the differences cannot be due to the acid treatment. These differences are but a small fraction of the total exchange capacity, so that even in these cases they are scarcely significant. The average net differences for the 36 samples is only 50 p.p.m. of calcium carbonate, an amount within the experimental error.

The exchange capacity was also determined upon residues left after treatment with acid to secure a pH of 4.0, and after treatment with acid to measure the acid consumed. The results, compared with results on the untreated soil, are given in Table 14. The exchange capacity is practically the same in the residue after treatment with acid to secure pH 4.0, as in the original soil. It is a little less in the residue from the estimation of acid consumed, but the differences are small.

The treatment with acid has little or no effect upon the exchange capacity of the soil. The bases are replaced partly by hydrogen, but the exchange complex is not decomposed. Consequently, the time and work required for making the determination of exchange capacity may be considerably lessened by adding the acid before leaching commences.

RELATION BETWEEN THE ACID-CONSUMING POWER AND THE BASE-EXCHANGE CAPACITY OF THE SOIL

The determination of the acid-consuming power of a soil is much more simple and rapid than the determination of the exchange capacity. It is a necessary preliminary step in the determination of buffer capacity for acids by the method previously described. The relationship between the acid-consuming power and the exchange capacity is therefore of considerable importance.

Kappen (8) states that the determination of the acid-consuming power of a soil which does not contain carbonates will give approximately the amount of exchangeable bases in the soil, and in the case of soils very nearly neutral, the total exchange capacity. If this be true, it is possible to get valuable information concerning a number of factors associated with the exchange capacity without the comparatively slow and laborious procedure of leaching with ammonium acetate. The following work was undertaken in order to determine the relation between the acid-consuming power and the total exchange capacity of a number of soils.

Methods. Two methods for the determination of the acid-consuming power were used. The first is the regular method which has been described above. The procedure is as follows: Five grams of soil is treated with 50 cc. of 0.2 N hydrochloric acid, stirred with a stirring machine for 15 minutes, and filtered; then 10 cc. of the filtrate is titrated with 0.2 N sodium hydroxide, phenolphthalein being used as the indicator. The amount of acid consumed may be calculated to per cent of calcium carbonate, to milligram equivalents of hydrogen consumed per 100 grams of soil, or to parts per million of calcium carbonate. The latter calculation has been used here in order to give the same units which are used in other experiments reported in this Bulletin. The second method is one which has been proposed by Kappen. Fifty grams of soil is stirred or shaken with 250 cc. of 0.1 N hydrochloric acid for one hour. The suspension is then allowed to stand overnight. The clear, supernatant liquid is decanted the next morning, and 125 cc. is titrated with standard sodium hydroxide, phenolphthalein being used as the indicator. The results are calculated to milligram equivalents of hydrogen consumed per 100 grams of soil by Kappen's method, but for the sake of comparison here, to parts per million of calcium carbonate.

In neither of these methods is the amount of acid used in bringing iron and aluminum into solution of any significance, since in the titration with sodium hydroxide and phenolphthalein, their hydroxides are precipitated and the acid neutralized. Obviously, however, the soils must be practically free from carbonates if the acid consumed is to give an accurate indication of the exchange capacity, since the bulk of the carbonates are destroyed before the exchange complex is attacked, and the acid consumed by the carbonates is not freed by later titration, as in the case of iron and aluminum.

Results. The acid-consuming power of 36 soils was determined by both methods, and the results compared with the total exchange capacity of the soils. Table 15 gives the results of this study.

The total acid-consuming power of the soil, as determined by the two methods, is given in the fourth and fifth columns of Table 15. It has been shown in the preceding work that most of the carbonates are neutralized before the exchange complex begins to exert its full influence upon the added acid. Consequently, the amount of carbonates in the soils has been subtracted from the total acid consumed, giving what is termed the "net acid consumed." These data are given in the sixth and seventh columns, and are to be compared with the data for total exchange capacity, given in the last column of the table. The net acid-consuming power is practically always lower than the exchange capacity. The difference in some cases is small but sufficiently wide to prevent the acid-consumed procedure from being used as an exact measure of the base-exchange capacity. It could, however, be used as an approximate measure for total base-exchange capacity. The hydrogen in the acid does not replace all the bases in the complex. The reaction does not go to completion. It is evident from the comparatively close agreement of the results that the bases which neutralize acid come chiefly from the bases in carbonates and in the base exchange complex.

In an average of all the soils, the net acid consumed, by the regular method, represents 86.4 per cent of the bases in the exchange

Table 15. Relation between basicity and total exchange capacity (Results as parts per million calcium carbonate).

Laboratory Number	Soil type	Carbonate content	Acid-consuming power		Net acid consumed		Total exchange capacity
			Regular	Kappen	Regular	Kappen	
25873	Lomalto fine sandy loam	0	1400	1070	1400	1070	1770
26103	Crockett fine sandy loam	130	1500	1775	1370	1645	2460
31896	Moore fine sandy loam	180	2750	2475	2570	2385	3160
29450	Amarillo fine sandy loam	1200	4600	3310	3400	2110	3400
31880	Duval fine sandy loam	450	1400	2750	950	2350	3655
31890	Miguel fine sandy loam	150	3400	3010	3250	2860	4140
31888	Webb fine sandy loam	60	1500	2680	1440	2620	4290
31820	Amarillo fine sandy loam	490	2900	4115	2410	3625	4575
29336	Richland fine sandy loam	16380	22200	21150	5820	4770	5210
25883	Willacy fine sandy loam	3960	9100	10095	5140	6135	5805
31914	Orelia fine sandy loam	180	6240	5750	6060	5570	6170
25865	Lomalto clay loam	10070	15500	17290	5430	7220	6700
31833	Spur fine sandy loam	10730	17000	17655	6270	6925	7100
25781	Victoria fine sandy loam	3428	14190	12690	10762	9172	7940
25891	Donna fine sandy loam	13400	20750	22110	7350	8710	9560
31905	Victoria clay loam	5500	15000	14650	9500	9150	9610
29436	Wilson clay	520	12600	9260	12080	8740	10200
26824	Lake Charles clay	4400	22750	19025	18350	14625	11230
29438	Lufkin fine sandy loam	24	12250	10160	12226	10136	11950
31326	Amarillo silty clay loam	780	14600	12695	13820	11915	13385
31327	Randall clay	256	11300	11675	11044	11419	13800
29434	Wilson clay	672	10500	9990	9828	9318	14205
31328	Randall clay	240	12100	12830	11860	11590	14315
29427	Crockett clay loam	492	11300	10400	10908	9908	14425

Table 15. Relation between basicity and total exchange capacity (Results as parts per million calcium carbonate).—Continued.

Laboratory Number	Soil type	Carbonate content	Acid-consuming power		Net acid consumed		Total exchange capacity
			Kappen	Regular	Regular	Kappen	
29435	Wilson clay loam	440	12550	9825	12110	9385	14515
25972	Wilson clay loam	80	11500	10470	11420	11390	14850
29365	Amarillo fine sandy loam	55	12500	12260	12445	12205	15050
29441	Lufkin fine sandy loam	200	12000	9740	11800	9540	15725
25968	Houston clay	384	15900	17210	14516	16826	16150
25967	Houston clay	1052	17200	13515	16148	12463	17890
26075	Irving clay	610	15500	14720	14890	14110	18430
25959	Irving clay	1000	11900	13910	10900	12910	19110
26823	Lake Charles clay	4400	23500	19750	19100	15350	22550

complex, while by Kappen's method, the figure is 81.0 per cent.

The total exchange capacity in almost every case is larger than the amount of net acid consumed. This difference is small in many cases, but since it occurs in practically all of the soils, and in some cases is fairly large, it is certainly significant. Moreover, in all of these soils, the titration of the acid solution in the determination of the acid-consuming power of the soil resulted in the participation of some iron and aluminum hydroxides, indicating that a portion of the acid consumed was taken up by solution of minerals. This would indicate that not all of the acid consumed was taken up by carbonates and the exchange complex, and the difference referred to above would be somewhat increased.

The difference in the procedures must be remembered in this connection. In the total exchange capacity, the soil is leached with a large excess of a neutral salt solution. The products of the reaction are constantly being removed, and the reaction can thus go to completion. In the acid-consumed procedure, the soil is treated only once with an excess of acid. The products of the reaction are not removed. The final product is the result of a state of equilibrium between soil material, acid, and reaction products.

These results indicate that not all of the bases in the exchange complex are replaced by the hydrogen of the acid. Since, however, there is in general a good agreement between the two procedures, a fairly definite proportion of the bases of all the soil exchange complexes must be replaced by hydrogen, regardless of the nature of the soil. This whole question is taken up in detail later in this work.

REPLACEMENT OF EXCHANGEABLE BASES BY HYDROGEN

It has been shown (Tables 13, 14) that the addition of the acid in the estimation of buffer capacity or of acid consumed does not decompose the base-exchange complex in the soil. The exchangeable hydrogen was determined (Table 11) in various residues left after treatment of the soil with acid. From these results, the percentage of base unsaturation of the exchange complex was calculated, and these results are given in Table 15.

For purposes of the present discussion, the soils studied may be placed into two groups, based upon their carbonate content. The first 12 soils are relatively low in carbonates, the soil with the highest amount of carbonate being soil No. 31321 with 1440 p.p.m. of calcium carbonate. The last 12 vary in carbonate contents from soil No. 25883 with 3960 p.p.m. to soil No. 31882 with 404,000 p.p.m.

With the soils low in carbonates perhaps the most outstanding point is the comparatively wide variation in the percentage of base unsaturation of the exchange complex at a definite pH value. This value as pH 6.0 runs from 8 per cent for soil 26075 to 41 per cent for soil 25873. At pH 4.0, the variation is between 13 per cent for soil 26075 to 64 per cent for soil 26103. A comparison of the data presented in Table 15 will show that this variation is not closely related to the size of the exchange capacity. Pierre and Scarseth (22) obtained similar results, and conclude from their study that, in general, old soils are lower in percentage of base saturation at a given pH value than are younger soils.

In the group of soils which contained large amounts of carbonates, there is little relation at pH 6.0 and pH 5.0 between the acid added and the percentage of base unsaturation. In only three of these soils at pH 6.0, is there any exchangeable hydrogen. Indeed, in most of these soils, there is sufficient solubility of bases in the determination of exchangeable hydrogen to make the barium acetate solution definitely alkaline. In seven of these soils at pH 5.0 there is some exchangeable hydrogen, but only in small quantities.

In both groups, there is a considerable percentage of the exchange capacity taken by hydrogen at pH acid 4.0, altho there is still a great deal of variation between the individual soils. In general, the base unsaturation in the first group of soils low in carbonates amounts to about 50 per cent, while in the second group high in carbonates this value is about 25 per cent.

Table 16. Percentage base unsaturation of exchange complex of soils after various acid treatments.

Laboratory Number	Soil type	Percentage base unsaturation after acid treatment of			
		pH Acid 6.0	pH Acid 5.0	pH Acid 4.0	Acid consumed
25871	Dune sand	----	----	100	----
31888	Webb fine sandy loam	28	----	42	58
31890	Miguel fine sandy loam	35	----	52	89
25873	Lomalto fine sandy loam	41	----	61	69
26103	Crockett fine sandy loam	40	----	64	87
31880	Duval fine sandy loam	31	----	47	49
31914	Orelia fine sandy loam	21	----	42	82
31896	Moore fine sandy loam	40	----	53	80
31820	Amarillo fine sandy loam	27	----	37	80
31804	Fitch fine sandy loam	19	----	38	72
26075	Irving clay	8	----	13	76
31321	Amarillo silty clay loam	15	----	24	65
25883	Willacy fine sandy loam	19	----	34	82
31905	Victoria clay loam	0	0	28	78
31883	Spur fine sandy loam	11	8	24	64
25865	Lomalto clay loam	0	0	25	83
25891	Donna fine sandy clay loam	5	13	36	73
31802	Yahola fine sandy loam	9	12	11	37
25869	Point Isabel fine sandy loam	0	1	15	17
26089	Catalpa clay	0	6	25	48
31800	Miller clay loam	0	29	50	56
31884	Hidalgo clay loam	0	0	31	74
25905	Laredo silt loam	0	19	18	44
31882	Frio clay	0	0	15	57

The greatest degree of uniformity with respect to exchangeable hydrogen in the soils is secured after the "acid consumed" treatment (Table 16), in which the soil is treated with an excess of acid. As a rule, the base unsaturation is close to 80 per cent; that is, 80 per cent of the exchange complex is taken up by hydrogen. Soil 25869 is a decided exception to this statement, the base unsaturation for this soil being only 17 per cent. The reason for this exception is not known.

The variation in the percentage of base unsaturation after the various acid treatments and the difference in this respect between different soils offer a partial explanation of the fact that different soils vary widely in the quantity of acid which is necessary ao give a definite pH value. This is particularly true with respect to the first group of soils, in which exchange and acidity relationships are not obscured by the presence of large amounts of carbonates. The explanation is found in the fact that while the percentage of the base unsaturation at "acid consumed" tends to be fairly constant, there is a great deal of variation in the percentage at any of the "pH acid" values.

The conditions of the experiment must be remembered in studying these data. In the buffer-capacity procedure, a quantity of acid is added which will leave only a very small amount of acid after the reaction with the soil has reached equilibrium. In soils originally containing considerable amounts of carbonates, such as those soils lower than No. 31905 in Table 11, there is at the time of determining pH and exchangeable hydrogen, a considerable quantity of calcium chloride and very little hydrochloric acid. As the result of mass action, the tendency is very strong towards the exchange of calcium for small amounts of hydrogen which might have been taken up by the exchange complex. Such an exchange would leave the exchange complex completely taken up by calcium while there would still be enough hydrochloric acid in the solution to cause a pH of 6.0, or even 5.0. This explains why there is such a small amount of exchangeable hydrogen in the calcareous soils at these pH values. The same reasoning applies to the other soils and pH values, but not to such a degree.

The determination of the total exchange capacity after the acid treatments (Table 10) shows that there is no destruction of the exchange complex in these soils with the addition of the acid. This fact is of considerable importance for two reasons. The first and most important point from the standpoint of the present work is that since there is no destruction of the base exchange complex with the addition of acid, the method proposed is satisfactory from this important point of view. The second is that, in the determination of the total exchange capacity with ammonium acetate solution, the carbonates can be destroyed by treatment with acid and the time required for the determination is thereby greatly reduced.

NATURE OF THE BASE-EXCHANGE COMPLEX

It is generally believed that the inorganic base-exchange complex is made up of one or more alumina-silicates. Truog and his students (13, 14, 28) have separated colloidal material from soils, which they claim is a single compound and alone responsible for base-exchange phenomena. This compound was found in a number of samples of bentonite. It is perhaps significant to note that the material separated by Kerr (13, 14) had an alumina-silica ratio of 1:6, while that separated by Chuka (28) had an alumina-silica ratio of 1:4. Kelley and his coworkers (9, 10, 12), on the other hand, claim that a number of different compounds are involved, and there may be wide differences in the base-exchange activity of the several compounds. Baver and Scarseth (1) state that soil material capable of base exchange may originate in a number of ways, and that the properties of the material will vary with the factors conditioning their development. According to Britton (1 A, page 474), the soil colloids are simply mixtures of hydrated alumina and silica.

The data presented in this paper appear to show that there may be two or more compounds in the inorganic base-exchange complex. The exchangeable hydrogen introduced into the soil by acid in estimating acid consumed is not always a definite percentage of the total exchange capacity. Thus in Table 16, with soils low in carbonates, the percentage of base unsaturation of the exchange complex after acid consumed varied from 49 for soil 31880 to 89 for soil 31890. With soils high in carbonates, there was a wider variation. The percentage of base unsaturation after acid treatment to produce definite pH values was subject to still greater variations. As previously noted, these results are in accord with those of Pierre and Scarseth (22). The light, noncalcareous soils listed in the first part of Table 16 are similar in most of the properties which influence the relation between the pH value and the percentage of base saturation. The only way in which they could vary sufficiently to account for the differences in percentage of base saturation at similar pH values is in the nature of soil acids. The only way in which the same pH can be secured under identical experimental conditions by two different quantities of acid is to have different acids having different dissociation constants. These facts all indicate that the base-exchange complex is made up of several different acid compounds.

RELATION BETWEEN CERTAIN OTHER SOIL FACTORS AND TOTAL EXCHANGE CAPACITY

There appears to be no regular relation between the carbonate content of the soil and the total exchange capacity, though soils containing carbonates have higher exchange capacity than others. This is to be expected, since the exchange capacity is associated almost entirely with the colloidal siliceous and humate materials of the soil.

There is a very close relationship between the physical character of the soil and the total exchange capacity. As the soil class becomes heavier the total exchange capacity becomes greater. This was to be expected, since in the heavier soils there is generally a greater amount of colloidal material, and a portion of this is the source of the base-exchange constituents of the soil.

INFLUENCE OF SOIL MATERIAL OTHER THAN CARBONATES AND BASE-EXCHANGE COMPLEX ON BUFFER CAPACITY

The work reported above has indicated that heavy, noncalcareous soils have a greater buffer capacity than light noncalcareous soils, after due allowance has been made for the influence of the exchange complex. This indicates that the finely divided materials of the soil, other than those associated directly with the exchange complex, play a significant role in the buffering of the soil. Pierre (19) has shown that in the application of the buffer-curve data to field work a factor of more than 1.0 must be used and suggests that this is because of the reaction of the acid added with non-exchangeable material in the soil. Joffe and McLean (6) maintain that when a soil has a reaction of or below pH 5.6 or 5.4, it contains free acids from inorganic sources, which may react with silicates other than those of the exchange complex and bring iron and aluminum into solution. This material is probably for the most part complex alumino-silicates in which the hydrogen of the acid replaces bases in a manner analogous to the weathering of feldspar with the formation of kaolin. The reaction of the acid with this material is rather slow and indefinite and at present no method is known by means of which a quantitative measurement of the extent to which this material influences the buffer capacity may be made. It is possible and even probable that considerable acid may be absorbed by this material, without bringing into solution any significant amount of substance. An analysis of the solution would therefore be of no value. Extraction of the soil with 0.2 N nitric acid in the determination of active phosphoric acid and potash removes appreciable amounts of iron, aluminum, and silica. This material is undoubtedly brought into solution by the breaking-down of the non-exchange material. It has already been shown that treatment with an excess of 0.2 N acid is not sufficient to remove all of the bases in the exchange complex. From these two facts must follow the conclusion that the non-exchange complex is consuming some acid while there is still an appreciable amount of bases in the exchange complex.

The fact that non-calcareous soils of similar acid-consuming power and exchange capacity vary widely in the percentage of the acid consumed required to give a definite pH value in the buffer-curve determination indicates quite strongly that the amount and activity of this portion of the soil material varies over a wide range. While, under the conditions of the determination of buffer capacity in the laboratory, this portion plays a minor part in the results obtained, it is probable that in the field over a longer period of time, it bears a significant relationship to the change in reaction following any treatment. Because of the uncertain composition and reaction of this material, however, no attempt was made in this work to evaluate it.

No attempt was made to determine the influence of organic matter on buffer capacity. All of the soils reported in this study are relatively low in organic matter and hence this portion of the soil material played a very minor part. Undoubtedly, in soils high in organic matter, this factor plays an important part in the buffer capacity. Even though a detailed study of the influence of organic matter was not made, the "pH acid" procedure itself is adaptable to this type of soil, as well as to all others.

METHOD FOR BASICITY OF LIMING MATERIALS AND FERTILIZERS

The estimation of basicity of carbonates of lime or magnesium is merely the estimation of carbonates. There are other materials, such as mixtures of limestone and superphosphate, basic slag, and calcium silicates, in which the estimation of basicity is not so easy. The work here presented gives the basis for a method for such materials. The buffer capacity of such materials depends upon the degree of acidity (pH) secured. In order to estimate basicity, it is necessary to decide on a degree of acidity (pH) at which to stop. The total buffer capacity at this point would be the basicity. The pH decided upon must be low enough to ensure the decomposition of carbonates, but high enough to exclude buffer capacity which is not useful in decreasing soil acidity.

If the basicity of liming materials is defined as the power to neutralize acidity which is harmful to plants, then the pH should be between 4.5 and 5.5. A pH of 4.5 is harmful to most plants, while a pH of 5.5 is harmful to only a few plants. The use of 5.0 is suggested. If plants to be grown are very sensitive to acidity, a pH of 6.0 could be adopted were it not for the fact that pH 6 is too high to ensure decomposition of all the carbonates. A pH of 5.0 is suggested as a tentative stopping point for this determination.

The pH acid procedure is applicable not only to soils but to any other solid material possessing buffer capacity. As examples of possible applications, the buffer capacities of two samples of rock phosphate and one of colloidal phosphate were determined. The buffer curves plotted from the data secured were very smooth; in no instance was a pH acid determination as much as 0.1 pH off the regular curve.

The rock phosphates required acid equivalent to 310 and 220 p.p.m. of calcium carbonate for pH acid 6.0, and 620 and 540 for pH acid 5.0. The corresponding figures for the colloidal phosphate were 1125 and 1875. On the other hand, the acid consumed by one sample of rock phosphate was 14.5 per cent, and by the colloidal phosphate, 28.0 per cent, both as carbonate of lime. Thus entirely misleading results regarding the basicity of these materials may be obtained from the acid consumed by them. These data are sufficient to illustrate the usefulness of the method for materials other than soils.

SUMMARY

The total buffer capacity of the soil for acids is measured by the quantity of acid required to secure the desired degree of acidity.

The specific buffer capacity is measured by the quantity of acid required to cause a definite change in degree of acidity.

The buffer capacity for acids measures the reserve bases of the soil and the resistance of the soil to acidifying agencies, such as weathering, acidifying fertilizers, or other additions.

A mixture of calcium carbonate and acid may be slightly acid (pH 6.2) when vigorously stirred while the same mixture may have a pH of 5.0, or even 3.4, when only moderately stirred.

A mixture of acid with an excess of calcium carbonate may be acid (pH 4.25, or even 3.3) unless the conditions are such as to promote the escape of carbon dioxide, the decomposition of calcium bicarbonate, and the completion of the reaction. Manipulation for basicity may be tested by ascertaining the acidity (pH) of mixtures of calcium carbonate and definite amounts of acid.

A modified method for buffer capacity of soils for acids is described, the buffer capacity at a desired acidity (pH) being read from buffer curves. The method used for estimating carbonates is described.

A mixture of soil and acid may decrease slightly in acidity (pH) during 60 days.

Stirring vigorously for 15 minutes gave as good results for acid consumed for soils high in carbonates as stirring and standing overnight.

In the estimation of buffer capacity of soils high in carbonates, stirring for 15 minutes followed by standing for 40 hours was found slightly better than stirring and standing overnight.

Three types of buffer curves of soil are discussed.

The adequate expression of the buffer capacity of soils requires the construction of a curve, or statements of the total buffer capacity to a definite degree of acidity (pH) and of the specific buffer capacity between given pairs of pH values.

If the salts are washed out after the reaction between the soil and acid, the residue becomes less acid in an amount varying in different soils but averaging about .9 pH.

The addition of potassium chloride to the acid decreases the buffer capacity; that is, it increases the acidity (pH) of soils with low buffer capacity, but may have little effect upon soils with high buffer capacity. The increase varies, but averages about .6 pH.

Addition of potassium chloride to a residue of a soil treated with acid and washed with water increases the acidity (pH) of the mixture to approximately the acidity of the original mixture of soil and acid.

The acidity of a natural soil would vary according to the quantity of salts present, increasing to a certain extent when the quantity of soluble salts is increased and decreasing when the soluble salts are washed out or otherwise removed. Additions of nitrate of soda, sulphate of ammonia, gypsum, and similar salts may temporarily increase the acidity of acid field soils.

The lime requirement was estimated on washed residues from soils treated with acid to secure a pH of 4. When the amount of acid was corrected for the carbonates in the soil, the Veitch method for lime requirement gave approximately 30 per cent more than the net acid added, and the Jones method 20 per cent more. The Hopkins method gave erratic and low results, only about 10 per cent of the net acid added.

Titration of the soil residue with barium hydroxide also gave results in excess of the acid used.

Exchangeable hydrogen was determined on some soil residues after treatment with various amounts of acid. A soil may contain both exchangeable hydrogen and calcium carbonate. With some soils, the net exchangeable hydrogen agrees with the net acid used, within the limits of error. The net acid is the total acid added less that used by carbonates in the soil. With other soils, the exchangeable hydrogen is appreciably lower than the net acid used, which seems to indicate that bases are removed from other compounds in addition to the exchange complex.

Some calcium carbonate was still present in some soils when acid had been added to secure a pH of 6.0, and some soils still contained small amounts of carbonates at pH 5.0.

For soils low in buffer capacity 9.8 per cent of the bases in the exchange complex was removed in changing the pH from 6.0 to 5.0, while with soils of greater exchange capacity only 6.4 per cent was removed. To change the pH from 5.0 to 4.0, 17 per cent of the bases of the complex was removed with soils low in exchange capacity and 11 per cent with those with high base-exchange capacity. This indicates differences in the base-exchange complex in different soils.

The total base-exchange capacity of the soil was not changed by treatment with acids to secure various degrees of acidity or in the estimation of acid consumed.

The net acid consumed by the regular method represented 86.4 per cent of the base in the exchange complex while by the Kappen method it represented 81.0 per cent.

The percentage of exchangeable hydrogen varied with different soils at the same degree of acidity produced by treatment with acid. At pH 6.0 it varied from 8 to 41 per cent and at pH 4.0 from 13 to 64 per cent.

In the residue left after treatment for acid consumed approximately 80 per cent of the exchange bases was replaced by hydrogen.

The base-exchange complex appears to consist of several different compounds.

The percentage of base extracted by the acid from the exchange complex depends upon the degree of acidity of the mixture (pH) and on the nature and quantity of the base-exchange compounds in the particular soil used. The bases of the soil neutralized by acid came from the carbonates, from the base-exchange complex, and from other compounds.

The basicity of lime materials containing silicates or of fertilizers can be determined by the procedure here described, if a definite degree of basicity is used as the end point. The use of pH 5.0 is suggested. Acid consumed is not a correct measure of the basicity of some of these materials, for it exceeds the real capacity of the material to neutralize soil acidity by a very large amount.

REFERENCES

1. Baver, L. D. and Scarseth, G. D., 1931. The nature of the soil acidity as affected by the S:O2-sequioxide ratio. Soil Sci. 31:159.

1a. Britton, H. T. S., 1929. Hydrogen Ions, their determination and importance in pure and industrial chemistry. D. Van Nostrand Co., Inc., New York.

2. Chapman, H. D. and Kelly, W. P., 1930. The determination of the replaceable bases and the base exchange capacity of soils. Soil Sci. 30:391.

3. Fraps, G. S. and Carlyle, E. C., 1929. The basicity of Texas soils. Texas Agr. Exp. Sta. Bul. 400.

4. Fudge, J. F., 1931. Apparatus for continuous leaching with suction. Ind. Eng. Chem. (Anal. Ed.) 3:114.

5. Hopkins, C. G., 1910. Soil fertility and permanent agriculture, p. 267.

6. Joffe, J. S. and McLean, H. C., 1926. Colloidal behavior of soils and soil fertility: II The soil complex capable of base exchange and soil acidity. Soil Sci. 21:181.

7. Jones, C. H., 1913. Method of determining the lime requirement of soils. Am. Fertilizer 39:28.

8. Kappen, H., 1929. Die Bodenaziditat, Julius Springer, Berlin.

9. Kelley, W. P., 1929. The determination of the base exchange capacity of soils and a brief discussion of the underlying principles. Jour. Amer. Soc. Agron. 21:1021.

10. Kelley, W. P., 1930. The agronomic significance of base exchange. Jour. Amer. Soc. Agron. 22:977.

11. Kelley, W. P., and Brown, S. M., 1928. Base saturation in soils. Proc. First Internatl. Cong. Soil Sci. 2:491.

12. Kelley, W. P., Dore, W. H., and Brown, S. M., 1931. The nature of the base exchange material of bentonite, soils, and zeolites, as revealed by chemical investigation and X-Ray analysis. Soil Sci. 31:25.

13 Kerr, H. W., 1928. The identification and composition of the soil alumino-silicate active in the base exchange and soil acidity. Soil Sci. 26:385.

14. Kerr, H. W., 1928. The nature of base exchange and soil acidity. Jour. Amer. Soc. Agron. 20:309.

15. Lemmerman, O, and Fresenius, L., 1929. Bodenaziditat und Bodenadsorption. Tran. Second Comm. Internatl. Soc. of Soil Sci. A:36.

16. Lunt, H. A., 1930. The determination of carbonates in soils. Science. n. s., 72:295.

17. Parker, F. W., 1928. Method for the determination of the amount and acidity of exchangeable hydrogen in soils. Proc. Internatl. Soc. Soil Sci. 2:164.

18. Parker, F. W., 1928. The determination of exchangeable hydrogen in soils. Jour. Amer. Soc. Agron. 21:1030.

19. Pierre, W. H., 1928. Nitrogenous fertilizers and soil acidity. Jour. Amer. Soc. Agron. 20:254.

20. Pierre, W. H., 1931. Hydrogen ion concentration, aluminum concentration in the soil solution and percentage base saturation as factors affecting plant growth on acid soils. Soil Sci. 31:183.

21. Pierre, H. W. and Parker, F. W., 1927. The use of collodion sacks in obtaining clear soil extracts for the determination of the water soluble constituents. Soil Sci. 23:13.

22 Pierre, W. H. and Scarseth, G. D., 1931. Determination of the percentage base saturation of soils and its value in different soils at definite pH values. Soil Sci. 31:99.

23. Schollenberger, C. J., 1927. Exchange hydrogen and soil reaction Science 65:552.

24. Schollenberger, C. J., and Dreibelbis, 1930. Analytical methods in base exchange investigations on soils. Soil Sci. 30:165.

25. Tidmore, J. W. and Parker, F. W., 1924. Methods of studying the strength of soil acids. Soil Sci. 18:331.

26. 1930. Transactions of the Second Commission of the International Society of Soil Science.

27. Truog, E., 1916. A new apparatus for the determination of soil carbonates and the new methods for the determination of soil acidity. Jour. Indus. Eng. Chem. 8:341.

28. Truog, E. and Chucka, J. A., 1930. The origin, nature, and isolation of the inorganic base exchange compound of soils. Jour. Amer. Soc. Agron. 22:553 .

29. Veitch, F. P., 1920. Lime water method for determining the lime requirements of soils. Jour. A. O. A. C. 3:372.