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**THE EFFECT OF LIMING ON THE CATION STATUS OF SEVERAL SOILS,
SOIL COLLOIDS AND CLAY MINERALS**

by

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**A Thesis Submitted to the Graduate Faculty
for the Degree of**

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INTRODUCTION

Liming has long been recognized as a starting point in programs directed toward the improvement and maintenance of the productivity of acid soils. Wide variability in the acidity of soils early created a need for methods of determining the amount of lime that should be added to effect the desired changes. The concept of the reaction between lime and soil as a neutralization reaction early turned the attention of investigators to the development of methods for determining the capacity factor of soil acidity. Numerous methods have been developed for this purpose. The outcome of liming soils according to these determinations, however, has been quite variable. Discrepancies between liming results and soil acidity measurements have indicated that the reaction between soil and lime is somewhat more complex than the neutralization concept would suggest.

The variability of soils with respect to the mineralogical nature of their clay fractions has provided an additional frame of reference within which to organize the data of soils, and has been helpful in explaining properties of soils.

2.

In this investigation an attempt has been made to obtain more information with respect to the reactions that take place when soil is limed.

To this end, the reaction between lime and several soils, soil colloids, clay minerals, and variously treated materials prepared therefrom was evaluated in terms of the rate of evolution of carbon dioxide, the distribution of bases, and the neutralization of soil acidity.

REVIEW OF LITERATURE

Methods for Determining the Lime Requirement of Soil

In 1895 Tacke (43) reported what appears to be the first attempt to measure the capacity factor of soil acidity. By measuring the CO_2 evolved from a moistened mixture of CaCO_3 and soil, he obtained an estimate of the capacity factor of the acidity of the moor soils with which he worked. At about the same time Wheeler, Hartwell, and Tucker (48) applied the method to mineral soils.

Various modifications of this method were tried during the first twenty years of this century. In general, the objections to these methods were that they were slow and gave an indefinite end point.

Another class of methods was developed in which the reaction between soil and a neutral salt solution formed the basis for a measure of the capacity factor. The Hopkins (17) and Jones (20) methods are examples of this class. The objection to these methods was that the final equilibrium was an equilibrium between soil and acidified salt solution and estimates of the capacity factor were thus consistently low. This was in large measure overcome in the barium acetate procedure of Parker (35). Barium acetate is much more highly buffered in the vicinity of pH 7.0 than other salts that had been used previously. In addition, the Parker procedure was a leaching procedure in which final equilibrium was attained between fresh solution of barium acetate and the relatively saturated soil.

Another class of methods involved treatment of the soil with a known amount of base in excess of that necessary for neutralization. By determining the excess, the capacity factor was calculated as the difference. Examples of this approach are the methods of MacIntire (25), Bradfield and Allison (4), and Mellich (29).

Titration procedures, with various modifications, present a fourth group of methods. Sharp and Hoagland (42) titrated soil directly with $\text{Ca}(\text{OH})_2$ to bring it to pH 7. These workers noted that the approach to equilibrium was slow, and that shaking was necessary. Crowthier and Martin (10) found that by using CaCl_2 as the suspension medium for titration with $\text{Ca}(\text{OH})_2$, a higher value for lime requirement was obtained than with the hydroxide alone. The dialysis-colorimetric method introduced by Pierre (37) permitted the use of indicators for determining the pH of soil systems.

Numerous comparisons have been made of the various procedures for determining the capacity factor of soil acidity. Parker (36) compared the barium acetate procedure with titration by the colorimetric procedure of Pierre (37) and found good agreement. Clark and Collins (9) compared lime requirement as determined by titration of the soil-water suspension with $\text{Ca}(\text{OH})_2$, and titration of the soil suspension in CaCl_2 with $\text{Ca}(\text{OH})_2$, and found that values obtained by titration in CaCl_2 suspension were 2.5 to 5.5 times as great as those obtained by titration in water suspension as measured at 90 hours.

Results of Liming Soils According to Lime Requirement

Determinations

Regardless of the method used to determine the capacity factor of soil acidity, it has been the almost universal experience that in order to neutralize soil acids it has been necessary to add a somewhat larger amount of lime to the soil than that indicated by the laboratory tests. Christensen and Jensen (7) found that to raise the pH of a field soil to neutrality, it was necessary to add three times as much CaCO_3 as was indicated by the titration curve. Part of this discrepancy was no doubt due to the fact that some of the CaCO_3 had not as yet reacted. Leaching losses would also account for some of the CaCO_3 added. These difficulties, however, were overcome in laboratory experiments where precipitated CaCO_3 was mixed with soil and permitted to react with the soil under controlled conditions. In an experiment of this type, Pierre and Worley (38) found that in order to raise the reaction of soil to pH 6.5, it was necessary to add CaCO_3 in amounts ranging from 1.3 to 1.7 times as great as those indicated by the dialysis-colorimetric titration method.

It was also found that liming soils to the extent of exchangeable hydrogen as measured by the barium acetate procedure did not bring soils to pH 7 as might have been expected. A number of possibilities were suggested as to the source of this discrepancy between the lime requirement determinations and liming results. It was suggested that some of the added CaCO_3 entered into reactions other than that with exchangeable hydrogen. The possibility that the barium acetate method did not measure all the hydrogen

was also advanced. Parker (38) had shown, however, that immediately after leaching soils with barium acetate, a pH of about 7 was obtained.

Prior to the development of methods for studying the exchangeable bases of the soil, inquiry into the fate of the CaCO_3 added to soils was necessarily limited to studies of leaching losses, changes in amounts of residual carbonates, and changes in lime requirement of limed soil.

It was shown by MacIntire (23) that when an excess of CaCO_3 was added to soil, it continued to break down over an extended period of time. From his early experiments that included study of the evolution of CO_2 from mixtures of variously treated soil, and of silica and alumina with lime, MacIntire (23) concluded that the continued breakdown of the carbonates in soil was due to a reaction with silica. It was emphasized that lime requirement methods that involved use of CaCO_3 took consideration of the lime-silica reaction, but that methods involving strong acid radicals did not do so.

Over a period of years, MacIntire, et al. (23, 24, 25, 26) conducted an extensive inquiry into the marked differential performance of MgCO_3 and CaCO_3 when added to the soil in excess of amounts necessary to neutralize soil acids. In a study of the solubility of the residue from heavy MgCO_3 and CaCO_3 treatments in carbonated water, 10 per cent ammonium carbonate and 1:1 HCl it was found that in soil exposed for five years, combined magnesium was held more tenaciously than in similar soil exposed under similar conditions for only a few weeks. Five years after treatment with

MgCO₃ at a rate equivalent to 28,100 pounds of CaCO₃ per acre, only very small increases in magnesium soluble in carbonated water were found in treated plots as compared to check plots. It was further noted that treatment with MgCO₃ had relatively little effect on calcium soluble in carbonated water, but that with CaCO₃ treatment, a substantial decrease took place in the magnesium soluble in carbonated water. By boiling for four hours with 1:1 HCl, a small fraction of the magnesium residue was brought into solution, whereas the major portion of the calcium added was dissolved.

The development of methods for studying the exchangeable bases in soils made possible a new approach to the study of the reactions between soils and CaCO₃. Using NaCl as a displacing agent, MacIntire and Sanders (25) investigated the fate of calcium and magnesium from various liming materials. It was found that a considerable portion of the non-carbonate residues from treatment of soil with calcium and magnesium-bearing liming materials were not recoverable by this procedure. It was concluded that either this procedure did not extract all the absorbed or exchangeable calcium and magnesium, or a part of the added calcium and magnesium assumed non-exchangeable form, probably as a result of reaction with soil components other than the exchange complex. In later work, MacIntire, Shaw, and Robinson (26) found that magnesium residues were resistant to prolonged leaching with normal ammonium chloride. Dilute acid was found to be a more effective extracting agent than normal ammonium chloride. Four overnight extractions with 0.02 N HNO₃ removed an amount of the residue comparable to that dissolved by digestion with 1:1 HCl, but was not capable of

effecting complete recovery of the added amounts. It was noted that the exchange capacity of the soil as measured by absorption of the ammonium ion was not altered by the magnesium fixation.

The work of Metzger (31), Pierre and Worley (38), Pierre and Searseth (39), and Walker, Brown and Young (47) are examples of another line of inquiry into the reaction of soil with CaCO_3 .

Metzger (31) studied the effect of increments of CaCO_3 upon the lime requirement as determined with the Jones calcium acetate method. It was found that initial increments of CaCO_3 reduced the lime requirement by an amount approximately equal to the amount of CaCO_3 applied, but that as the rate of liming increased, the lime requirement of the treated soil was not proportionately decreased. Pierre and Worley (38) found that upon liming soils to the extent of exchangeable hydrogen, the pH dropped to a point somewhat lower than would have been expected, a pH of about 6.5 being obtained in most cases. In an investigation of pH-base saturation relations of soils, Pierre and Searseth (39) limed soils at the rate of one ton per acre, measuring exchangeable hydrogen before and after liming. Their data show that the decrease in exchangeable hydrogen upon liming was considerably less than equivalent to the amount of lime added, reinforcing the view that when soil is limed, only part of the added lime enters into reaction with exchangeable hydrogen, the remainder being diverted into other reactions. Somewhat different results were obtained by Walker, Brown, and Young (47) in an experiment in which soils were limed at various rates, the highest rates somewhat greater than equivalent to the exchangeable

hydrogen determined by the barium acetate procedure. Liming of Shelby, Tama, and Grundy soils to the extent of exchangeable hydrogen would have resulted in pH values of about 6.9 to 7.4 according to their data. It may also be seen from their data, however, that the reduction in exchangeable hydrogen by liming was considerably less than equivalent to the amount of lime added, confirming the findings of Pierre and Worley (37) and Pierre and Scarsoeth (38).

Haftel (33) investigated the effect of various rates of liming on a number of chemical properties of eight Alabama soils. It was found that the reaction changed linearly through a point of 75 per cent of the calcium sorption capacity, as measured by a method of Bradfield and Allison (4), and approached a maximum of about 8.0 at the saturation point. At the lower levels of liming, the increase in exchangeable and water soluble calcium accounted for nearly all the CaCO_3 decomposed, but at higher levels of liming, a portion of the calcium from the decomposed CaCO_3 was converted to forms non-exchangeable with ammonium acetate. In six of the eight soils studied, an appreciable increase in exchange capacity occurred, which was attributed to increase in organic exchange material during the period of experimentation.

Dunn (11) determined pH values of soils limed to the extent indicated by titration curves to be necessary to bring soils to given pH levels. It was found that with a given application of $\text{Ca}(\text{OH})_2$, the pH of soils after three months was lower than that indicated by the titration curve.

The foregoing reveals that the results obtained by the various laboratory methods for measuring the capacity factor are not in good agreement

with the results of liming experiments. A number of reasons have been advanced for the discrepancy. MacIntire (23) advanced the view that with heavy applications of liming materials, considerable reaction occurred with silica in the soil, with the formation of silicates. Pierre and Worley (38) advanced the views that upon liming, part of the CaCO_3 reacts with materials other than the exchangeable hydrogen, or that the barium acetate procedure fails to measure all the exchangeable hydrogen. Naftel (35) showed that part of the calcium added in CaCO_3 was fixed; thus the effective addition was less than that calculated.

Secondary Reactions Upon Liming

The hypothesis that part of the added lime reacts with substances other than exchangeable hydrogen raises a question as to the combinations by which lime might be diverted from reaction with exchangeable hydrogen and the possible relations of such diversion to fixation. MacIntire (23) proposed that CaCO_3 reacts with silica to form silicates. It is known that soils contain silica and alumina in a state in which they might conceivably react with added lime, reducing the amount of lime available for neutralizing exchangeable hydrogen.

It would appear that this hypothesis might be tested by determining the performance of soils to which silica and alumina have been added, or by determining the effect of removing free silica and alumina. The difficulties in these approaches lie in producing conditions that permit conclusions to be drawn. It has been shown by MacIntire (23) that an interaction occurs in CaCO_3 -silica and CaCO_3 -alumina systems. It follows that if these sub-

stances were added to soil it might well be expected that an increase in reaction would occur over that of the original soil.

Interpretation of experimental results is greatly complicated by lack of information as to the amount and nature of the silica and alumina in the soil in a state that would react with bases upon liming. The efficacy of removing the free silica and alumina is also open to serious question, as there is no assurance that the system remains free from these substances over the period of experimentation. The amount of silica and alumina removed depends upon the severity of the treatment. Chueka (8) and Volk (46) reported results of Na_2CO_3 and HCl treatment of Colby colloid and of Miami and Hagerstown soils respectively. Chueka (8) found that boiling Colby colloid in 2 per cent Na_2CO_3 for one-half hour effected the removal of 0.57 per cent SiO_2 and 1.46 per cent Al_2O_3 . These amounts would combine with 18.8 m.e. of calcium and 28.6 m.e. of calcium in the formation of the mono-silicate and the aluminate respectively, a total of 47.4 m.e. per 100 gms. Volk (46) treated Miami silt loam and Hagerstown silt loam with normal HCl for 132 hours, and with normal Na_2CO_3 for 240 hours. The HCl removed 5.56 per cent SiO_2 from the Miami soil and 6.12 per cent SiO_2 from the Hagerstown soil. The Na_2CO_3 treatment removed 0.50 per cent SiO_2 and 1.35 per cent Al_2O_3 from the Miami soil, and 0.95 per cent SiO_2 and 0.71 per cent Al_2O_3 from the Hagerstown soil. The amounts of silica and alumina removed from these soils were thus in considerable excess of amounts necessary to combine with the bases that might possibly go into this combination. Britton (6) has shown that precipitation of the alkaline earth silicates occurs at pH values

of about 9.7 to 9.9 with solute compositions of about one part of calcium to five parts of silica. With large excesses of silica, buffer action is noted at pH values as low as 6.5. This would indicate that at pH values obtaining in soils, silica might combine with a certain small amount of base with formation of combinations of a wide base-silica ratio.

Britton (6) has shown that Al_2O_3 exhibits a buffering action toward bases at pH 8 and above. Magistad (27) found that solubility of alumina in NaOH solutions of varying pH was first noticeable at pH 7.55. MacIntire (23) demonstrated that lime-alumina systems react, which indicates that combinations of alumina and lime take place at pH values of saturated CaCO_3 solutions.

The fixation of part of the added lime would have the same net effect as failure to measure the exchangeable hydrogen fully. Fixation of a portion of the added lime may be at least a partial explanation for the presence of exchangeable hydrogen in soils limed to the extent of the exchangeable hydrogen, and for the decrease in pH of samples with the passage of time.

Effect of Heat Treatment on Soil, Soil Colloids, and Clay Minerals

The effect of heat upon the properties of soils, soil colloids, and clay minerals as reported by several investigators suggests the possibility that heat treatment might be a way of inactivating the base-consuming forces that are responsible for the discrepancy between laboratory methods and the results obtained by liming. Kelley, Dore and Brown (21) compared

the heat stability of bentonites, soil colloids and zeolites. They found that a temperature of 350°C had no effect on the exchange capacity of soil colloids and bentonites, but that zeolites were very materially affected by this treatment. A gradual decrease in exchange capacity of soil colloids was noted at temperatures above 350°C until at 750°C , exchange powers were practically destroyed. Mitchell (32) reported that subjecting soils to a temperature of 350°C to 450°C for six to eight hours had no effect on the inorganic exchange complex as measured by exchange capacity determinations. Grim and Bradley (13) made petrographic and X-ray analyses of illite and montmorillonite heated to various temperatures. These workers found that at 500°C modification of the lattice of montmorillonite took place. Lattice destruction was found to set in at 600°C and was complete at 850°C . Barker and Truog (2) studied a clay, the titration curve of which contained a dip between pH 6.5 and 8.0. This dip was attributed to aluminum. It was observed that after exposure to heat in brick formation, the dip in the titration curve disappeared.

Hofman and Endell (16) studied the effect of heating on the cation exchange and swelling properties of two bentonites, one a calcium bentonite in its native state, the other Wyoming bentonite, in which sodium is the predominant saturating cation. A sample of the calcium bentonite was saturated with sodium for experimental purposes. It was found that heating the calcium bentonite to 300°C reduced the exchange capacity to about half its original value. The decrease in the case of sodium bentonite was small.

At this temperature, innercrystalline swelling was retained; thus the change in exchange properties was regarded as evidence for the view that a more stable bond with the cation was formed, and that the sodium-clay bond is more heat-stable than the calcium-clay bond. At 700° C., exchange capacity was in all cases reduced to about 5 m.e.

From the foregoing it is apparent that there is general agreement regarding the destruction of the exchange properties of clays at temperatures above 600° C. The effect of temperatures up to 450° C is probably more diverse, depending on the particular material under consideration. The question as to the manner in which heat treatment affects the exchange properties of clay is open for speculation. No information is available as to the effect of heat on various types of forces capable of holding cations on the exchange complex. If the reduction in exchange capacity is the direct result of the formation of more stable bonds as suggested by Hofmann and Endell (16), then heat treatment might be looked to as a possible means of inactivating positions that may be responsible for the failure of laboratory methods to measure the extent to which lime reacts with the exchange complex. On the other hand, if reaction with alumina is responsible for the fixation of bases, the work of Barker and Truog (2) suggests the possibility that heat treatment might eliminate reactions of this type.

EXPERIMENTAL

Materials, Procedures, and Methods

MaterialsPrimary samples.

1. Soils - Four soils were selected for study. In order that the results might be related as closely as possible to the clay mineral makeup of the soils, sub-horizons low in organic matter were selected. Samples of the Iowa soils selected were obtained at type locations and are described as follows in the profile sample files.

P4-11

Weller B₂₂ 25" to 28" layer of virgin Weller silt loam.
Dull yellowish brown clay.

P32-6

Fayette B 13" to 16" layer of virgin Fayette silt loam,
consisting of a yellowish brown clay.

P5-8

Shelby C₁ 21" to 24" layer of Shelby silt loam.

It has been shown by Hadcock (14) that the clay mineral fraction of Weller soil is about 60 per cent montmorillonite, 30 per cent illite, and 10 per cent kaolinite. Montmorillonite is probably the dominant clay mineral in the Shelby and Fayette soils also.

A sample of Cecil clay loam obtained from J.W. Tidmore of the Alabama station was included. Black (3) has shown that the fraction of this sample of less than 2 μ effective diameter is kaolinite except for a small amount of gibbsite.

2. Soil colloids.- The colloidal fraction of less than 2μ effective diameter was separated by gravity sedimentation from portions of the Weller and Cecil samples described above. Following electro-dialysis until practically free from bases, these materials were washed with 95 per cent methyl alcohol, and dried from benzene. The dried samples were ground in an agate mortar to pass a 60 mesh screen.

3. Clay minerals - A kaolinite and a montmorillonite were included in order to compare the performance of these materials with that of soils and soil colloids known to contain minerals of these types in dominant amounts.

The kaolinite was part of a sample obtained from E.T. Vanderbilt Company, New York City, sold under the trade name of Peerless No. 1 clay. This clay came from mines operated by this company at Bath, South Carolina. Exchangeable bases were removed by electro-dialysis.

The montmorillonite was part of a sample obtained from the American Colloid Company, Chicago, Illinois, sold under the trade name of Panther Creek bentonite. This material is about 85 per cent montmorillonite, the remainder principally glauconite. This clay is obtained from mines in Monroe County, Mississippi. For use in this study 500 gms. of clay was electro-dialyzed until the rate of release of bases was so low that the liquor of the cathode gave a titre of only one m.e. after 12 hours' dialysis at 250 volts. The clay was then washed with methyl alcohol, followed by benzene,

dried, and ground in an agate mortar to pass a 60 mesh screen.

Secondary samples.

1. W (Na_2CO_3) - This sample was prepared from the primary sample of Weller soil by boiling for one hour with 2 per cent Na_2CO_3 . After filtration the sample was washed with hot 2 per cent Na_2CO_3 solution, followed by .02 N HCl until nearly free from exchangeable bases. The sample was then washed with portions of 80 per cent methyl alcohol followed with 95 per cent methyl alcohol. A final washing with benzene was given to remove alcohol and facilitate drying. The dry sample was passed through a 20 mesh screen.
2. WC (Weller soil, plus gibbsite) - This sample was prepared from the primary sample of Weller by adding gibbsite, ground to pass a 60 mesh screen, to the extent of 10 per cent of the amount of Weller soil.
3. Heat treated materials - Payette, Weller, and Cecil soil and Panther Creek bentonite were heat-treated at 250° C, 350° C, and 450° C for a period of six hours. Samples heated at 450° C were heated in an electric furnace. A gas oven was used for preparing samples at 250° C and 350° C. Under all sets of conditions temperature was indicated by a pyrometer. The heated samples were cooled, moistened with an excess of distilled water, air-dried and ground. The soil samples were ground to pass a

20 mesh screen. The bentonite samples were ground to pass a 60 mesh screen.

Heat treated samples are designated as follows:

	<u>Fayette soil</u>	<u>Weller soil</u>	<u>Cecil soil</u>	<u>Panther Creek bentonite</u>
Untreated	F 0	W 0	C 0	P.C.B. 0
250° C	F250	W250	C250	P.C.B.250
350° C	F350	W350	C350	P.C.B.350
450° C	F450	W450	C450	P.C.B.450
		W600		
		W800		

Procedure

Liming and care of primary samples. Soil samples were limed at the rate of 50, 75, 100, 125, 150 and 200 per cent of exchangeable hydrogen with C.P. CaCO_3 that had been passed through a 60 mesh screen. After addition of the lime, the samples were mixed in a mechanical mixer for not less than ten minutes. Soil samples were placed in tumblers, moistened with distilled water to about the moisture equivalent, and stored under bell jars. At the end of each four-week period the soils were air dried, ground to pass a 20 mesh screen, and mixed. After samples were taken for pH and other determinations, the soil was returned to the tumblers and again moistened as at the start of the experiment.

Soil colloid and clay mineral samples were limed at the rate of 50, 75, 100, 110, 125, and 150 per cent of exchangeable hydrogen with C.P. CaCO_3 that had been passed through a 60 mesh screen. Kaolinite was mixed in a mechanical mixer, but other samples were mixed in a stoppered wide-

mouthed bottle. After being mixed, samples were subdivided and placed in sample bottles for making studies of rate of reaction by determining the course of CO_2 evolution. Samples were air dried at four-week intervals, ground in an agate mortar, and a sample taken for pH determination. At the end of the reaction period, Weller colloid and Panther Creek bentonite were washed with methyl alcohol and benzene, air dried and ground in an agate mortar to pass a 60 mesh screen. Cecil colloid and kaolinite were air dried and ground to pass a 60 mesh screen.

Liming of secondary samples. Secondary samples were limed and the extent of reaction between the sample and CaCO_3 determined by determining the amount of CO_2 evolved.

Samples of Wc and WQ were limed at the rate of 200 per cent of exchangeable hydrogen as determined for Weller soil. Sufficient additional lime was added to the sample of $\text{W}(\text{Na}_2\text{CO}_3)$ to compensate for the difference in original exchangeable hydrogen in this sample.

Untreated and heat treated samples of Cecil soil were limed at a rate of 5.80 m.e. per 100 gms.

Untreated and heat treated samples of Fayette soil were limed at the rate of 13.50 m.e. per 100 gms.

Untreated and heat treated samples of Weller soil were limed at the rate of 200 per cent of exchangeable hydrogen.

Untreated and heat treated samples of Panther Creek bentonite were limed at a rate of 200 per cent of exchangeable hydrogen.

CO_2 evolution. To measure the extent of reaction between various materials and CaCO_3 limed samples were placed in jars or pint bottles.

A vial containing a known amount of NaOH was introduced to absorb the CO_2 evolved, and the sample moistened to about the moisture equivalent. Toluene was added to inhibit microbiological action, and the bottle securely stoppered. Determinations were made at 3, 10, and 21 days on all samples. The period was extended to 35 days for some samples.

Titration curves. To obtain the data for titration curves of the soils, soil colloids and clay minerals, samples of appropriate size were weighed and placed in centrifuge tubes. Varying amounts of 0.04 N $\text{Ca}(\text{OH})_2$ were added to the series of samples. The amount of water necessary to give a final soil/water ratio of 1:5 was added to each tube. Soil colloid and the bentonite samples were made to a volume giving a ratio of 1:10. Kaolinite was made to a mineral/water ratio of 1:5. The tubes were stoppered and shaken on an end-over-end shaker for twenty-four hours, after which they were removed and given occasional hand shaking. Determination of pH was made at 72 hours, after which exchangeable bases were displaced by repeated washings with normal ammonium acetate and determined by the procedure of Bray and Wilhite (5).

Because of the large amount of hydroxide needed in the case of Weller colloid and the bentonite when starting with the hydrogen-saturated material, it was necessary to partially titrate bulk samples in order to obtain the points on the curve at higher degrees of saturation and still adhere to the prescribed mineral/water ratio. The bulk sample was permitted to react with a known amount of calcium hydroxide for 12 hours, filtered, washed with alcohol and benzene. After the samples were dried and ground, exchangeable bases and moisture content were determined.

Methods

The principal chemical measurements made on samples in this study were pH, exchangeable hydrogen, total exchangeable bases, exchange capacity, exchangeable calcium and magnesium and evolution of CO_2 from reacting mixtures of carbonates and experimental materials.

All pH determinations were made with a glass electrode. pH determinations on soils were made at a soil/water ratio of 1:2.5. A ratio of 1:10 was used for soil colloids and bentonite. For kaolinite, a mineral/water ratio of 1:5 was used. Samples for pH determinations of soil colloids and clay minerals were ground to pass a 60 mesh screen.

Exchangeable hydrogen on soils was determined by leaching 10 gm. samples with 250 cc. of barium acetate, pH 7.0, over a period of eight hours, titrating with NaOH to an end point corresponding to that of a freshly prepared blank. To determine exchangeable hydrogen, soil colloids and clay minerals were washed with several portions of barium acetate in centrifuge tubes, other details of the procedure corresponding to that used on the soil samples.

Total exchangeable bases were determined on soils by leaching 10 gm. samples with 250 cc. of ammonium acetate, pH 7.0, and determining total bases according to the method of Bray and Wilhite (5). For soil colloids and clay minerals centrifugation was substituted for the leaching in this determination.

To determine the exchange capacity of soils, 10 gm. samples were leached with 250 cc. barium acetate, pH 7.0 followed with 250 cc. ammonium acetate, pH 7.0. Excess ammonium acetate was removed by leaching with

250 cc. 95% methyl alcohol. Exchangeable NH_4^+ was determined by distillation with MgO into an excess of .1 N HCl and back-titrating to the end point of a dichromatic indicator consisting of a mixture of methyl red and methylene blue. For soil colloids and the bentonite, centrifugation was substituted for leaching.

Calcium was precipitated as the oxalate and titrated with KMnO_4 . Magnesium was precipitated as MgNH_4PO_4 , the precipitate dissolved in an excess of standard HCl and back-titrated with standard NaOH to the end point of brom-cresol green. Manganese was determined colorimetrically as KMnO_4 .

To measure CO_2 evolved as an end product of reaction between CaCO_3 and various materials, CO_2 was absorbed in standard NaOH and determined as the decrease in titre after precipitation of the carbonate with BaCl_2 , as described by Treadwell and Hall (44).

To determine residual carbonates, the sample was treated with .1 N HCl while aspirated with CO_2 free air. The CO_2 was absorbed in NaOH in a Truog tower and CO_2 determined in the manner described above.

Presentation of Data

Unless otherwise stated, all results are expressed as m.e. per 100 gms. of oven dry material. Exchangeable bases as reported herein include all bases extractable by normal ammonium acetate, pH 7.0. These bases may derive from combination with the exchange complex, from dissolved CaCO_3 , or from ammonium acetate soluble combinations resulting from side reactions.

Exchangeable bases, calculated, represent the sum of the exchangeable bases in the original material and added calcium.

pH changes following liming

Changes in pH of soils with time after liming are given in Table 1 and are presented graphically in Figure 1. The Weller, Fayette and Shelby soils are characterized by small changes in the check samples. There was downward shift in pH of the Weller and Fayette samples limed at the 75 to 125 per cent rates during the 16-24 week period. The reaction of the Weller check sample declined quite steadily during the period, but the total change was only .3 pH unit. The pH of the Fayette and Shelby check samples rose quite consistently over the period though changes were small.

Table 1 shows that at eight weeks a slight upward trend in pH of the check, 50 and 75 per cent samples had taken place in Cecil soil. In the 8 to 12-week period a large rise in pH of the 75 per cent sample occurred. Determinations of exchangeable manganese at 18 weeks, as given in Table 2, show an increase of 0.31 m.e./100 gms. Almost twice this amount would

During most of the

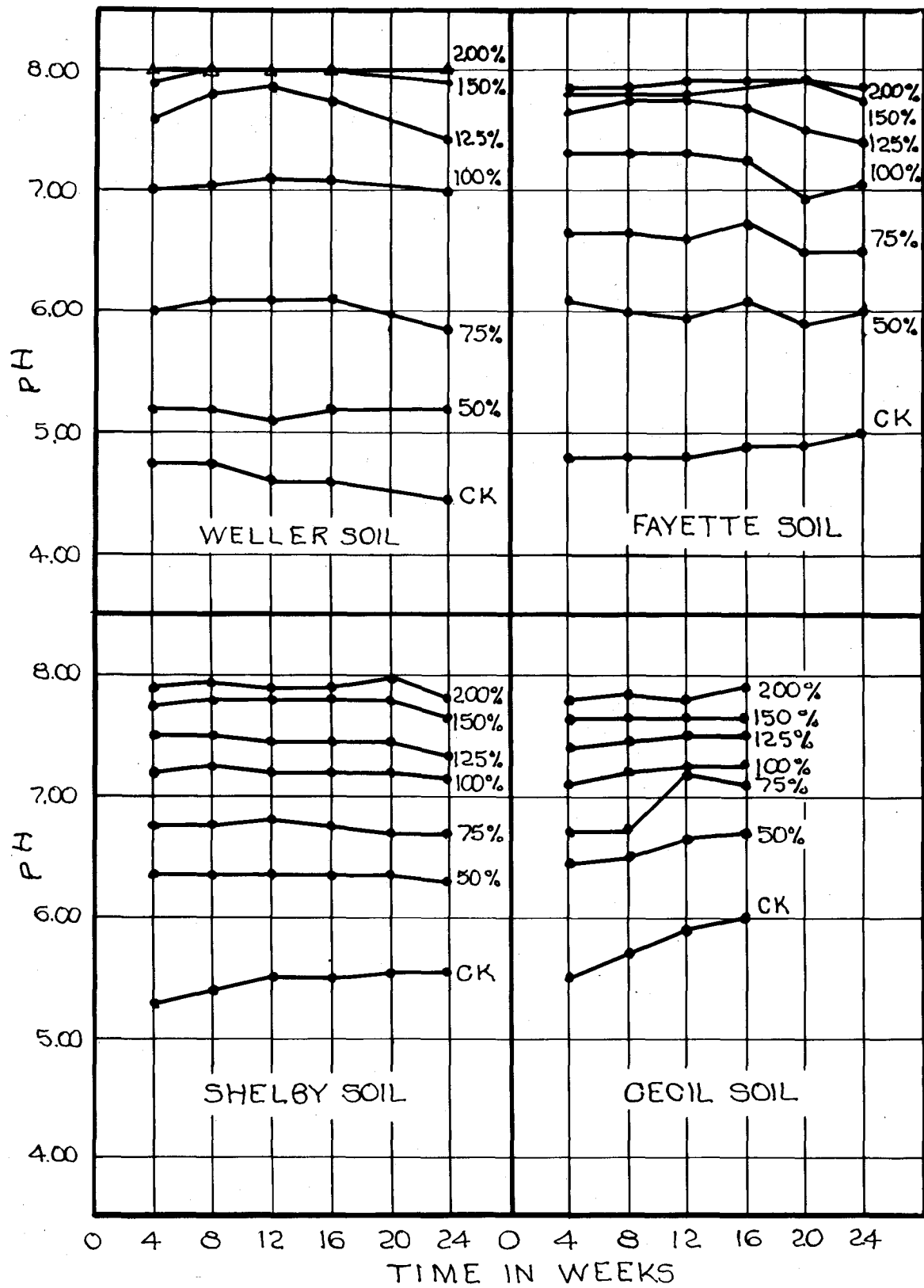


Fig. 1. pH of limed soils at four-week intervals during moist storage.

be necessary to explain the discrepancy in pH of the check sample. Comparatively small increases in manganese are noted for the 50 and 75 per cent samples. It is possible that reducing conditions may have brought about the reduction of iron so as to displace some exchangeable hydrogen and effect the pH increase.

Table 2. Effect of liming rate and moist storage on exchangeable manganese in Cecil soil

Original untreated	16 weeks			
	Untreated	50	75	100
0.12	0.43	0.22	0.18	0.13

As shown in Table 3 and Figure 2, the outstanding feature of the pH changes of soil colloids and clay minerals is the decided downward shift with time in pH of Panther Creek bentonite samples limed at rates up to 100 per cent. The probable significance of these changes will be discussed later.

The changes in pH of the check, 50 to 75 per cent treatments of Weller colloid are probably explainable on the basis of the physical condition of the sample as it was repeatedly wetted and dried. At the end of the period the samples were dried from benzene, whereas intermediate determinations were made on the air-dried sample ground to pass a 60 mesh screen, and were not as well dispersed.

Table 3. pH of limed soil colloids and clay minerals
at four-week intervals during moist storage

Material	Liming rate :		Time in weeks				
	% exchange-						
	able	hydrogen	4	8	12	16	20
Weller colloid	0		3.80	4.00	4.15		3.85
	50		4.50	4.60	4.70		4.50
	75		5.10	5.20	5.25		5.00
	100		6.90	6.80	6.90		6.90
	110		7.50	7.40	7.50		7.50
	125		8.00	8.00	8.00		8.00
	150		8.00	8.00	8.00		8.00
Cecil colloid	0		4.50	4.20	4.40	4.40	
	50		5.30	5.20	5.45	5.20	
	75		6.25	6.25	6.20	6.20	
	100		6.85	7.10	7.00	7.00	
	110		7.15	7.35	7.25	7.35	
	125		7.40	7.65	7.60	7.70	
	150		7.80	8.00	7.90	8.00	
Panther Creek bentonite	0		2.90	2.90		2.85	
	50		3.70	3.70		3.40	
	75		4.20	4.10		3.70	
	100		5.20	4.90		4.30	
	110		6.20	6.00		5.45	
	125		7.75	7.80		7.90	
	150		7.80	7.80		8.00	
Kaolinite	0		4.35	4.50	4.35	4.60	
	50		5.00	5.00	5.20	5.20	
	75		5.80	5.65	5.65	5.70	
	100		7.40	7.30	7.10	7.15	
	110		7.80	7.70	7.75	7.70	
	125		8.10	8.05	8.05	8.00	
	150		8.35	8.25	8.15	8.25	
	200		8.35	8.25	8.15	8.25	

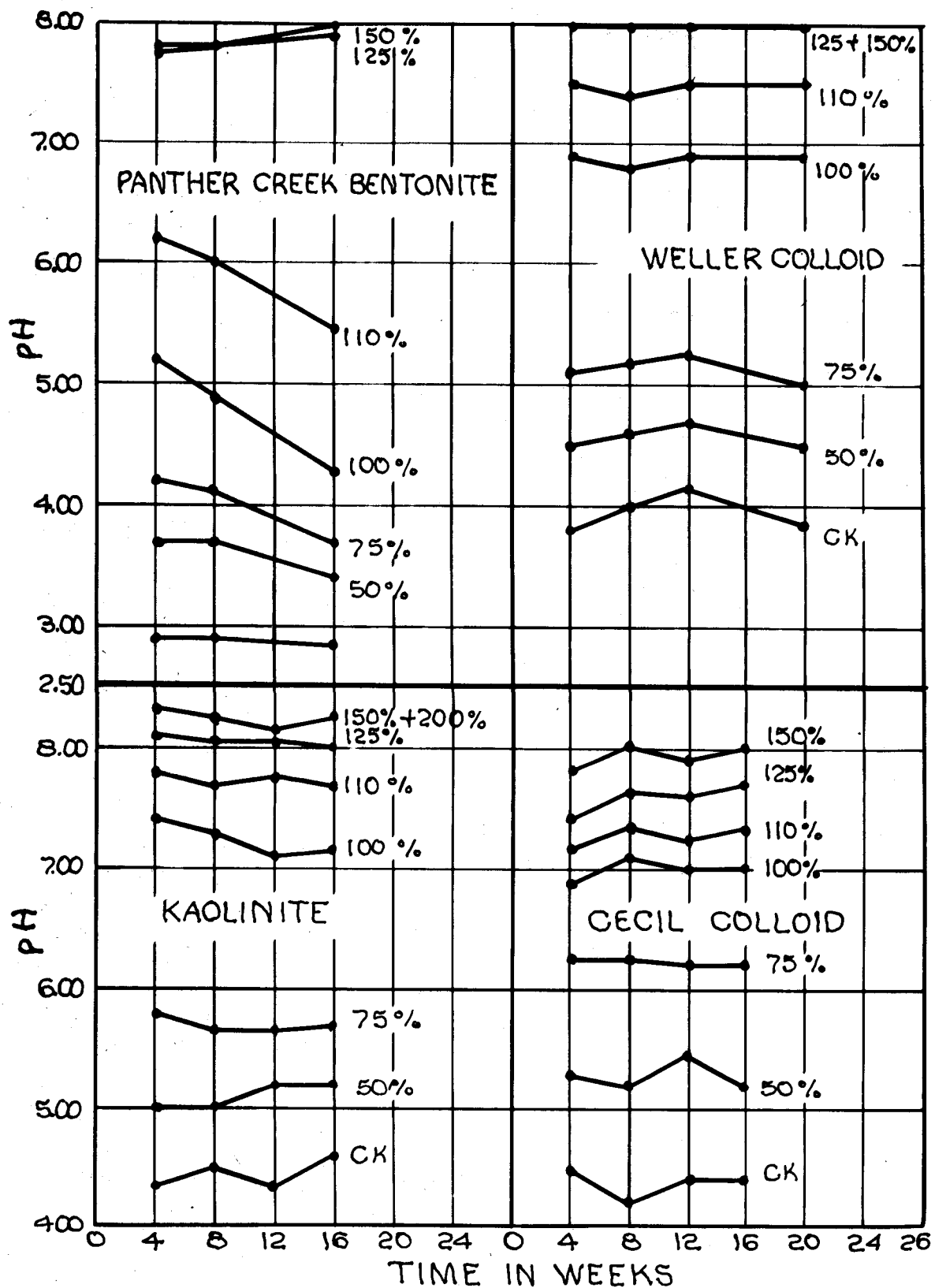


Fig. 2. pH of limed soil colloids and clay minerals during moist storage.

Except for the downward trend in pH of the kaolinite limed at the 100 per cent rate, no decided changes in pH occurred in this material.

From these data, it may be seen that the pH level attained by liming soils, soil colloids, and clay minerals to the extent of exchangeable hydrogen was close to neutrality in all cases except Panther Creek bentonite.

Rate of reaction of soil colloids, clay minerals and Cecil soil with CaCO_3

In order to obtain information as to the rate of the reaction between CaCO_3 and acid clays, the course of the reaction was followed by measuring the evolution of CO_2 at intervals of three, ten, and twenty-one days. The results of measurements of this type on the soil colloids, clay minerals and Cecil soil are given in Table 4 and are expressed graphically in Figures 3 to 7.

It was found that with rates of liming of ten per cent or more above exchangeable hydrogen, the amount of CO_2 given off in three days was equal to or slightly in excess of the exchangeable hydrogen value. With higher rates of liming the amount of CO_2 given off in three days was usually somewhat greater. Except in the case of Cecil soil and Panther Creek bentonite, only comparatively small increases were noted for the ten to twenty-one day interval at the highest rate of liming. Over the ten to twenty-one day period, the Weller colloid samples limed at the 125 and 150 per cent rates gave no additional CO_2 . The same was true of the Cecil colloid. Performance of the bentonite samples limed at the 125 and 150 per cent rates was parallel throughout the entire period. A small increase

Table 4. Rate of reaction of lime with soil colloids, clay minerals, and Cecil soil, measured as release of carbon dioxide and expressed as percentage of exchangeable hydrogen

Material	Time in days	50	75	100	110	125	150	200
Weller colloid	3	40	71	92	100	103	106	
	10	45	71	92	102	109	110	
	21			92	102	110	110	
	140*					117		
Cecil colloid	3	50	62	86	99	117	122	
	10		75	98	107	122	142	
	21			98	107	122	142	
	112*						139	
Panther Creek bentonite	3	49	72	94	103	108	108	
	10		72	100	108	118	118	
	21				110	125	126	
	112*						128	
Kaolinite	3	49	75	97	100	99	106	
	10			100	104	109	117	
	21				104	113	122	
	112*					123	124	
Cecil soil	3	50	70	94		106		112
	10		75	95		115	131	135
	21			99		119	150	162
	112*							172

*Calculated from residual carbonate determinations at end of moist storage period.

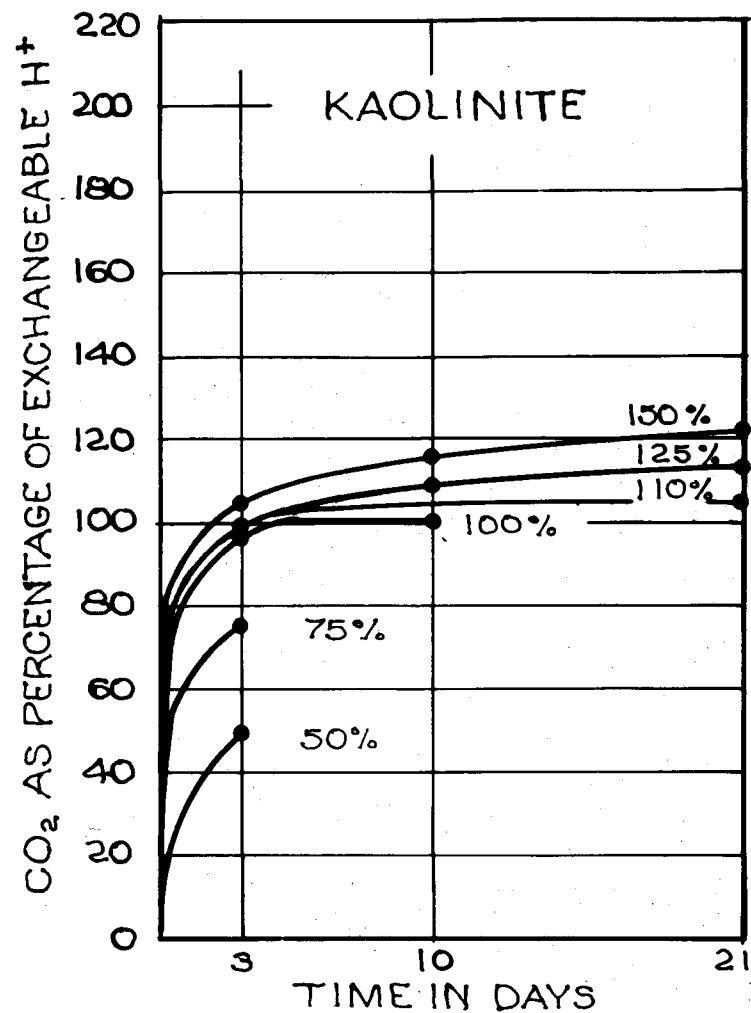


Fig. 3. Rate of evolution of carbon dioxide from limed kaolinite.

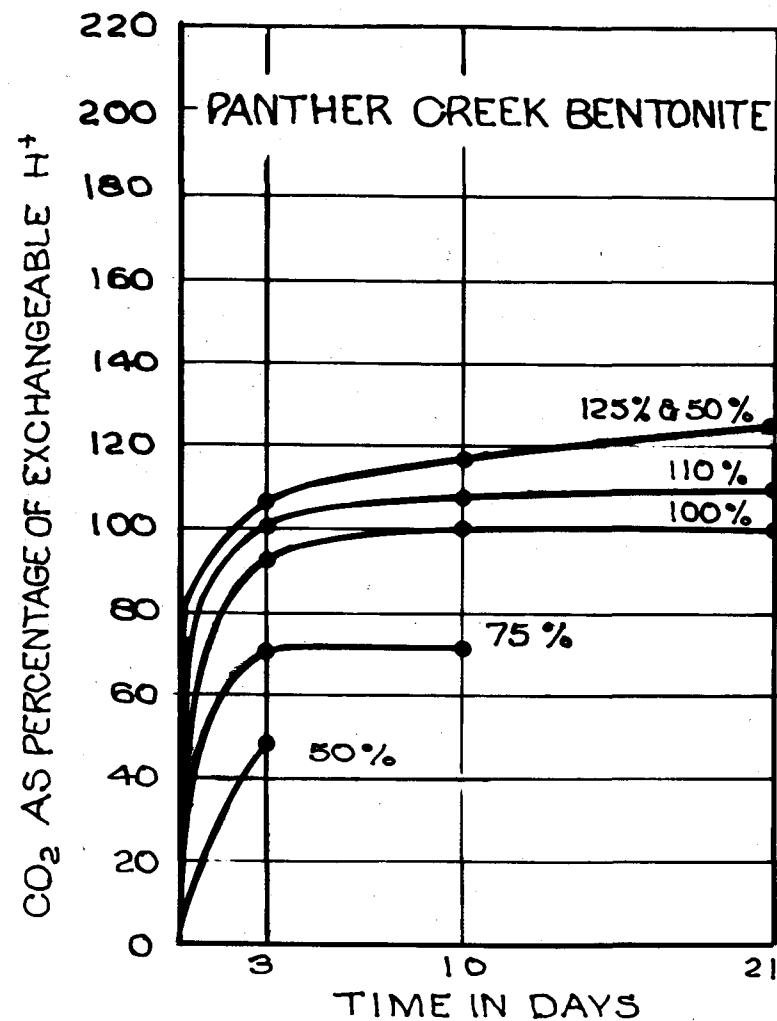


Fig. 4. Rate of evolution of carbon dioxide from limed bentonite.

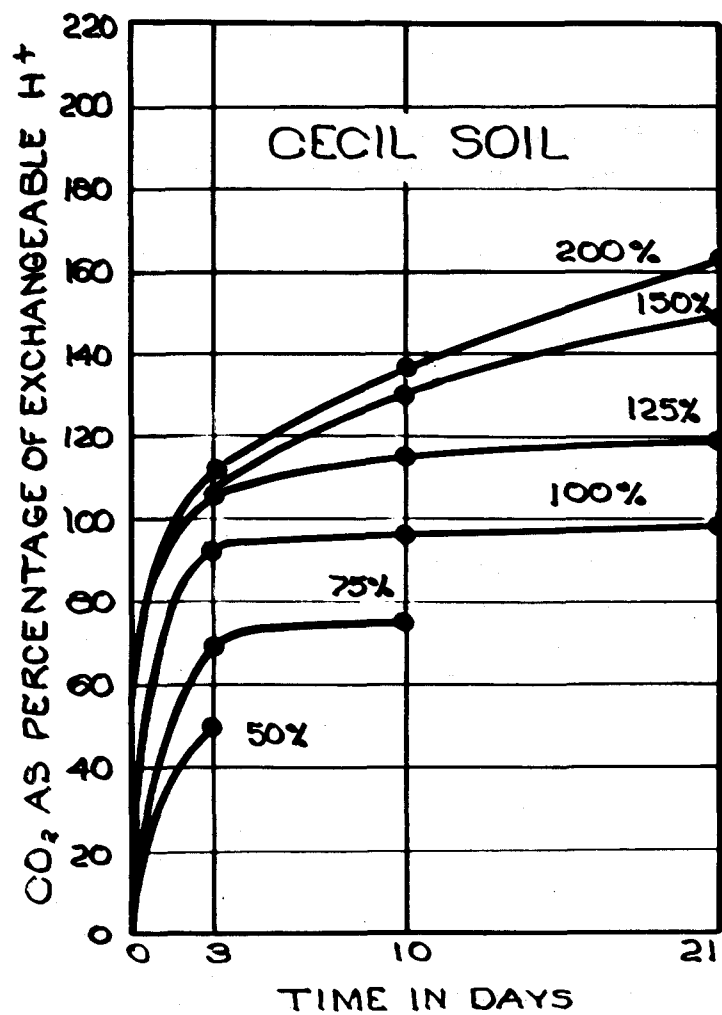


Fig. 5. Rate of evolution of carbon dioxide from limed Cecil soil.

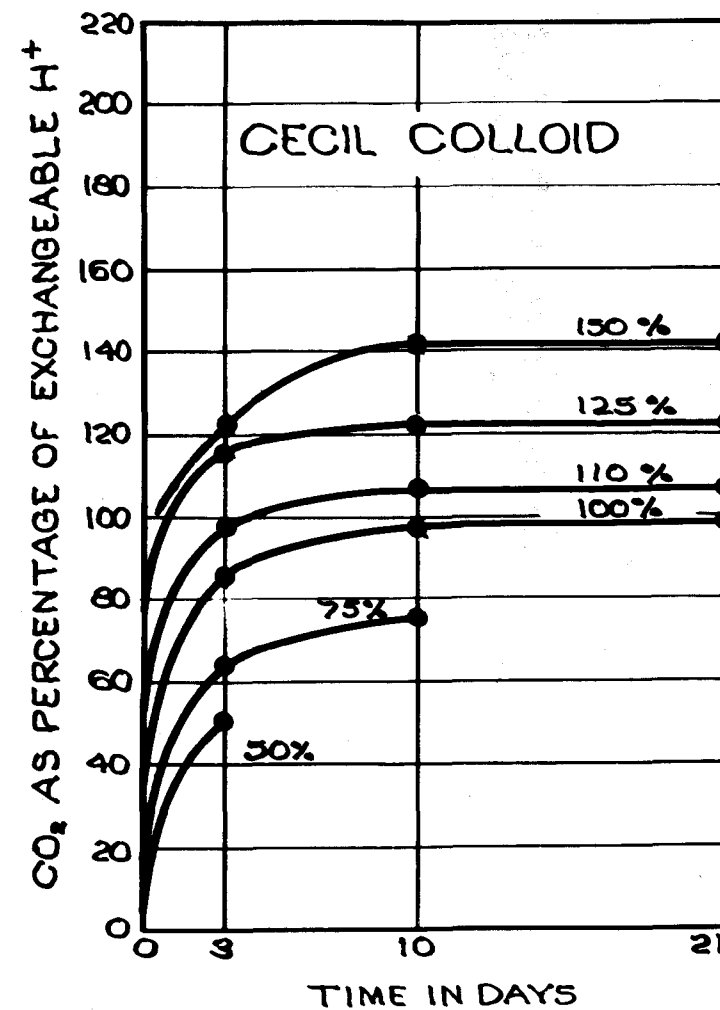


Fig. 6. Rate of evolution of carbon dioxide from limed Cecil colloid.

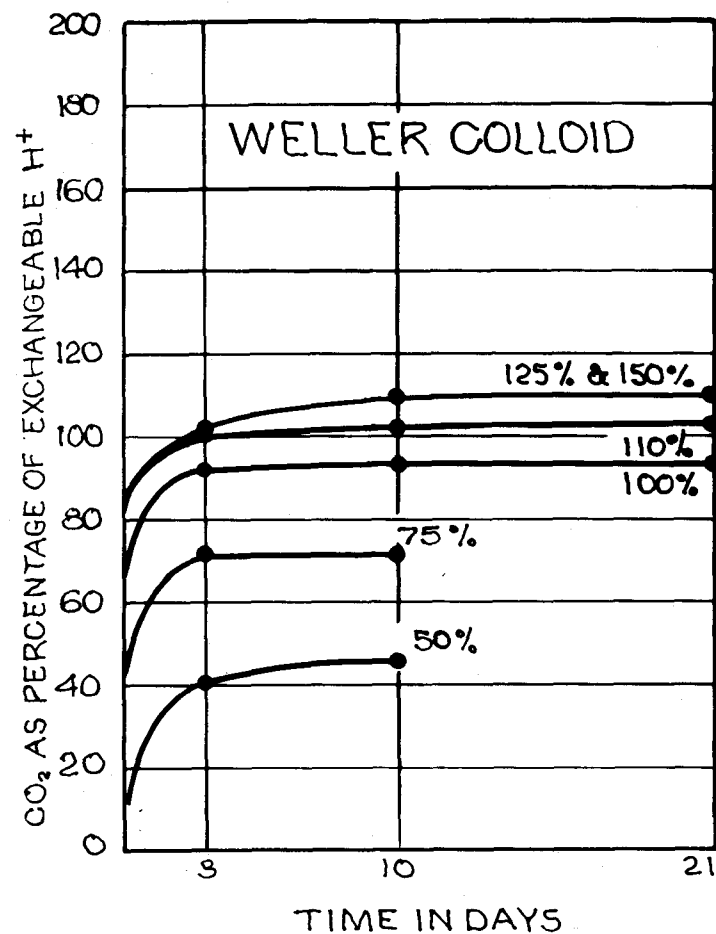


Fig. 7. Rate of evolution of carbon dioxide from limed Weller colloid.

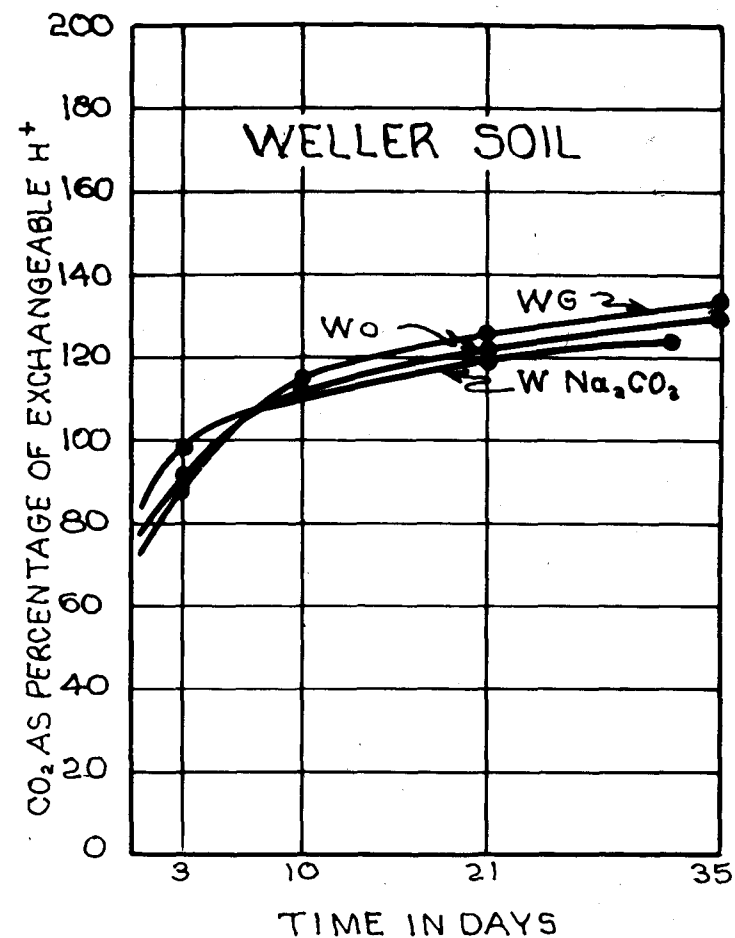


Fig. 8. The effect of addition of gibbsite and treatment with Na₂CO₃ on the evolution of carbon dioxide from limed Weller soil.

was obtained from kaolinite samples limed at the 125 and 150 per cent rates, while a larger increase was obtained from the Cecil soil during the ten to twenty-one day period. The Cecil soil was in a somewhat coarser condition than the other materials and this may in part explain the extension of the period of reaction of this material.

The reasons for the apparently low results obtained with the Weller colloid are not clear.

For purposes of comparison, the percentage decomposition of added carbonates at the end of the moist storage period was calculated from residual carbonate determinations, and is given in Table 4. This period was 140 days for the Weller colloid and 112 days for all other materials. From these data it is apparent that the decomposition occurring after twenty-one days is relatively small. Additional evidence of completeness of reaction is given in Table 5 which shows exchangeable bases in Weller soil limed at two rates, as determined after four, sixteen, and twenty-four weeks' moist storage. These data show that comparatively small changes took place after four weeks.

Table 5. Exchangeable bases in limed Weller soil after four, sixteen, and twenty-four weeks' moist storage

Liming rate:	Time in weeks		
	4	16	24
% exchange- able hydrogen:			
150	40.4	39.6	39.5
125	36.0	35.6	35.1

Effect of gibbsite addition and treatment with Na_2CO_3 upon the evolution of CO_2 from Weller soil

Data with respect to the evolution of CO_2 upon liming Weller soil, untreated, upon addition of 10 per cent gibbsite, and upon treatment with two per cent Na_2CO_3 are given in Table 6, and are presented graphically in Figure 8. In this work the reaction period was extended in order to get as complete information as possible on the effect of treatment upon the reaction between lime and the variously treated systems. Initially, the sample treated with Na_2CO_3 contained much more exchangeable hydrogen than the other samples. In the table and the figure, corrections have been made so as to place all the materials upon a common basis with respect to exchangeable hydrogen. It is noted that addition of ten per cent gibbsite effected a slight increase in the amount of reaction, while a decrease resulted from treatment of Weller soil with sodium carbonate.

Table 6. Effect of gibbsite addition and treatment with Na_2CO_3 upon the evolution of CO_2 , expressed in m.e./100 gms. and as percentage of the exchangeable hydrogen from limed Weller soil

Material	Time in days							
	3		10		21		35	
	%		%		%		%	
	m.e.	Ex. H.	m.e.	Ex. H.	m.e.	Ex. H.	m.e.	Ex. H.
Wo	15.6	91	19.5	112	21.0	121	22.3	128
WG	15.4	89	20.0	115	21.3	125	23.2	133
WNa ₂ CO ₃ *	17.2	99			20.5	118	21.2**	122**

*This sample contained 29.36 m.e. exchangeable hydrogen per 100 gms. compared to 17.35 m.e. per 100 gms. in the other samples. To place all samples on a common basis, 12.01 m.e. was subtracted from the CO_2 evolved by the Na_2CO_3 treated sample during the first three days.

**Terminated at 32 days.

Cation status of soils, soil colloids and clay minerals after liming

Determinations of exchangeable hydrogen were made on the soils, soil colloids, and clay minerals at the beginning of the experiment, and serve as a basis for liming the various materials.

Determinations of total exchangeable bases, exchangeable hydrogen and base exchange capacity were made on limed soils, soil colloids, and clay minerals at the end of the period of moist storage.

The results for Weller, Fayette, Shelby and Cecil soils are given in Table 7 and are presented graphically in Figures 9 to 11 in terms of pH vs. total exchangeable bases (determined), pH vs. total exchangeable bases (calculated), and pH vs. exchangeable hydrogen. The results for the soil colloids and clay minerals are given in Table 8 and are presented graphically in Figures 9 to 12. In these figures, exchangeable hydrogen is plotted with respect to the same pH scale as the other functions, but the scale of quantities is reversed. Orientation is effected by adjusting the value for native exchangeable hydrogen to coincide with the value for native exchangeable bases.

Data in Table 7 show that in the course of moist storage, a considerable increase in exchangeable bases occurred in the unlimed samples of Weller and Shelby soils. The exchangeable bases in the unlimed sample of Weller soil increased from 16.6 to 17.4 m.e. per 100 gms., while in Shelby soil, an increase from 13.8 to 14.1 m.e. per 100 gms. took place.

In the case of Weller colloid, exchangeable bases in the unlimed sample increased from 2.88 to 7.57 m.e. per 100 gms., a gain of 4.69 m.e.,

Table 7. Cation status of limed soils after sixteen weeks' moist storage

Liming rate :	:Exchange-:	:Exchange-:	:Exchange-:	:Exchange-:	:Ex-:	:Ex-:
Per cent :	:able bases:	:able bases:	:Calcium:	:Calcium:	:change-:	:change-:
exchangeable: pH	:calculated;determined;	:fixed;calcium	:calcium	:fixed ;magnesium;	:able :	:capac-:carb.
hydrogen :	:	:calculated;determined;	:	:fixed ;hydrogen:	:ity :	:
Payette						
0*	4.80	9.78	6.14	3.60	6.77	14.88
0 ₁ **	4.90	9.78	6.06	3.60	5.89	14.57
50	6.10	13.20	9.52	3.55	3.09	14.73
75	6.75	14.86	.21	3.55	2.08	
100	7.25	16.55	.44	3.30	1.13	
125	7.70	18.24	1.14	2.99	.46	0.20
150	7.85	19.94	1.43	2.68	.92	0.95
		18.51	16.30			
Weller						
0*	4.60	16.62	7.28	8.93	17.35	31.97
0 ₁ **	4.60	17.38	7.46	9.23	16.47	32.00
50	5.20	25.30	15.96	9.02	8.22	32.05
75	6.10	29.63	20.29	8.98	4.94	
100	7.10	33.97	.23	8.35	2.48	
125	7.75	38.31	.94	7.07	.58	0.30
150	8.00	42.64	2.71	6.83	1.86	2.67
		39.65	32.08		2.10	
Shelby						
0*	5.30	13.80	10.22	3.50	5.03	17.87
0 ₁ **	5.50	14.11	10.37	3.62	4.84	17.80
50	6.35	16.31	12.73	3.50	2.73	17.54
75	6.80	17.57	.45	3.36	2.07	
100	7.20	18.83	.73	3.08	.14	
125	7.45	20.09	.99	2.79	.42	
150	7.80	21.35	1.38	2.55	.71	0.20
200	8.00	23.83	1.50	2.48	.95	2.17
		22.01	17.22		1.02	
		20.28	19.30			

Table 8. Cation status of limed soil colloids and clay minerals after moist storage.

		:Liming : :rate as: pH :% ex. H:	: Ex. : : bases : : calo. :	: Ex. : : bases : : det'n. :	: Bases : : fixed : :	: Ex. : : H : :	: Base : : ex. : : capacity:	: Resid. : : carb. : :
Weller colloid	0*	3.75		2.88		65.50	69.51	
	0 ₁ **	3.85		7.57		62.16		
	50	4.50	35.63	38.53		29.76		
	75	5.00	52.00	52.64		16.72		
	100	6.90	68.38	65.76	2.62	6.79		
	110	7.50	74.93	71.04	3.89	3.57		
	125	8.00	84.75	79.32	5.43		70.72	5.24
	150	8.05	101.13	95.16	5.97		70.18	19.36
Cecil colloid	0*	4.40		0.86		12.75	12.24	
	0 ₁ **	4.40		1.03		11.85		
	50	5.20	7.23	7.18	0.05	5.94		
	75	6.20	10.42	9.59	0.73	4.20		
	100	7.00	13.61	12.19	1.42	1.61		
	110	7.35	14.88	13.19	1.69	1.20		
	125	7.70	16.80	14.99	1.81		13.50	
	150	8.00	19.98	18.02	1.96		13.63	1.54
Panther Creek bentonite	0*	2.90		13.46		71.56	88.72	
	0 ₁ **	2.85		12.82		66.78		
	50	3.40	49.24	44.64	4.60	39.29		
	75	3.70	67.13	60.66	6.47	22.23		
	100	4.30	85.02	76.59	8.43	7.73		
	110	5.45	92.18	83.19	8.99	5.69		
	125	7.90	102.91	96.11	6.80		87.99	1.74
	150	8.00	120.80	110.96	9.84			15.12
Kaolinite	0*	4.60		0.08		3.14	2.93	
	0 ₁ **	4.60		0.18		2.83		
	50	5.20	1.65	1.62	0.03	1.44		
	75	5.70	2.44	2.36	0.08	0.67		
	100	7.15	3.22	3.18	0.04	0.18		
	110	7.70	3.53	3.43	0.10		3.19	
	125	8.00	4.01	3.81	0.20		3.15	0.18

*Untreated material.

**Unlimed check sample after moist storage.

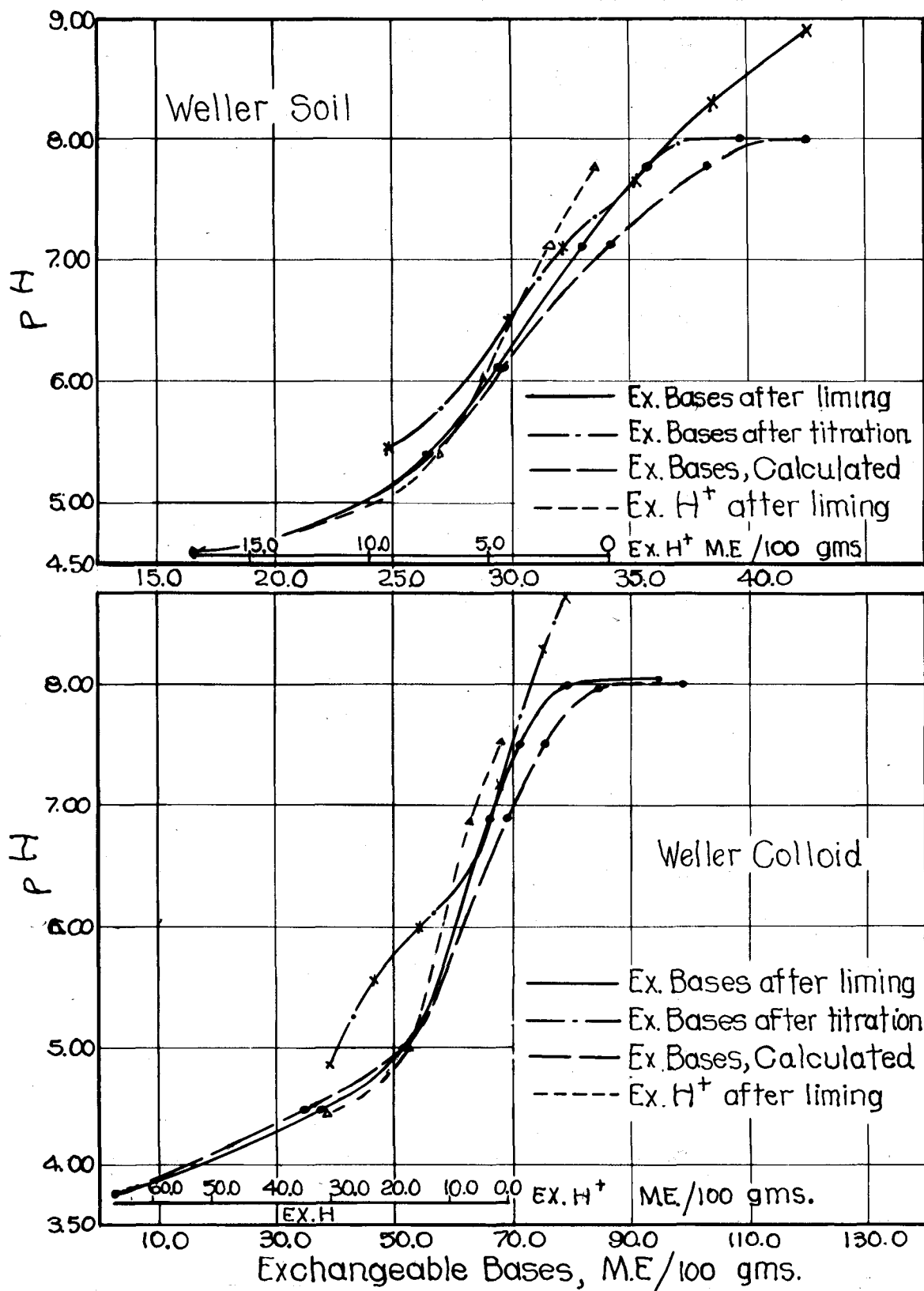


Fig. 9. The relation between pH and the cation status of lined and titrated Weller soil and colloid.

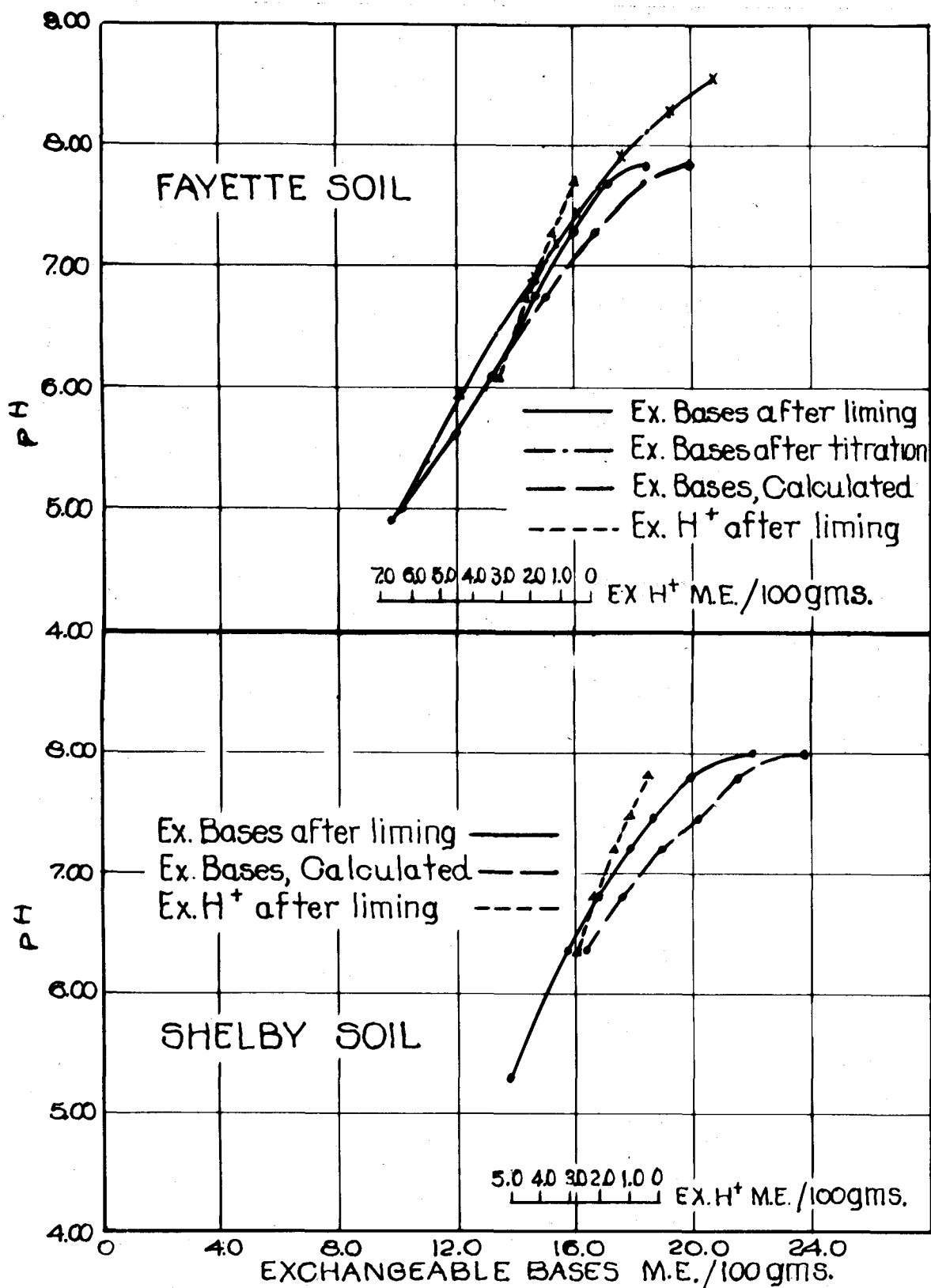


Fig. 10. The relation between pH and the cation status of limed and titrated Fayette and Shelby soil.

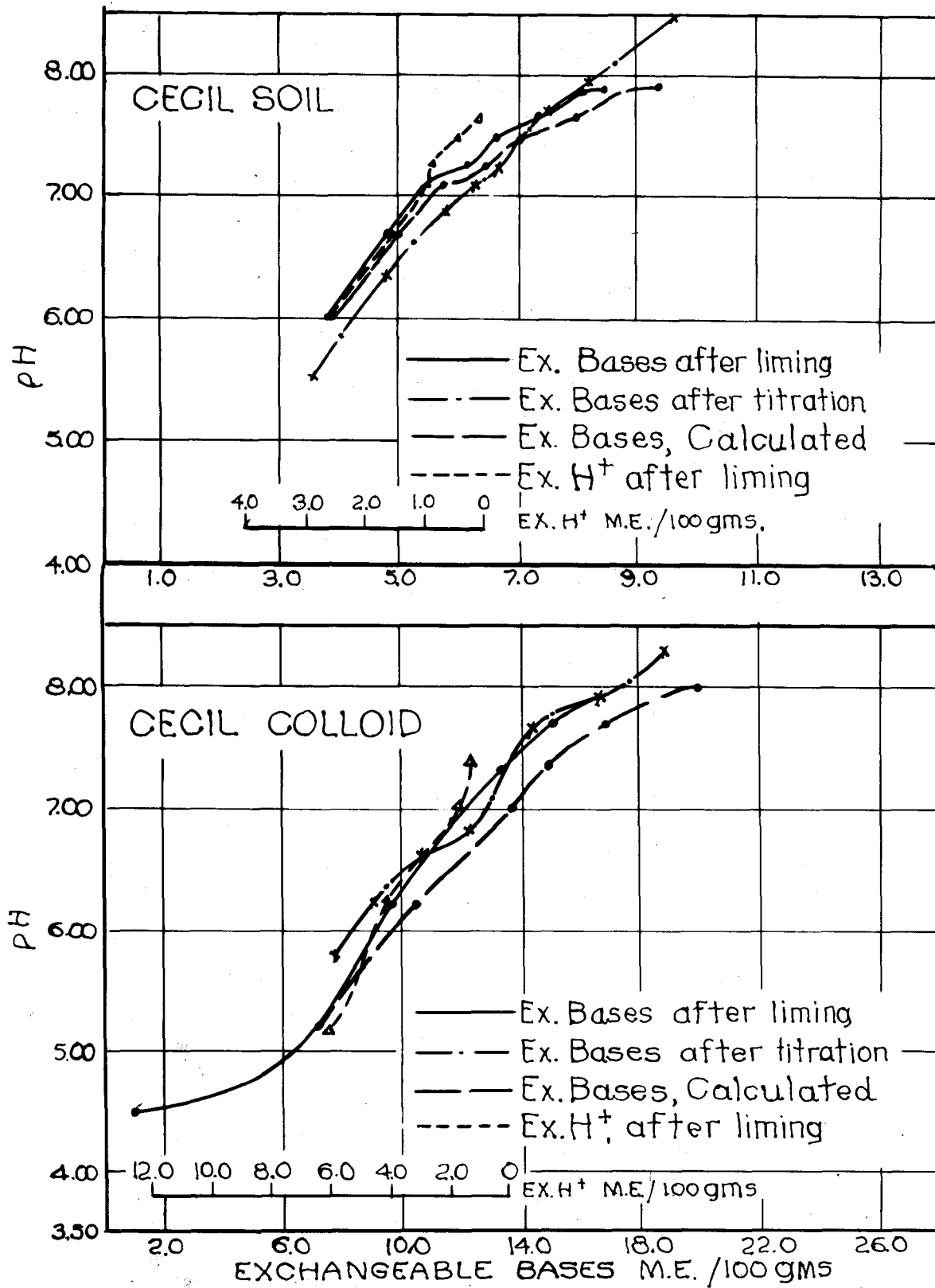


Fig. 11. The relation between pH and the cation status of limed and titrated Cecil soil and colloid.

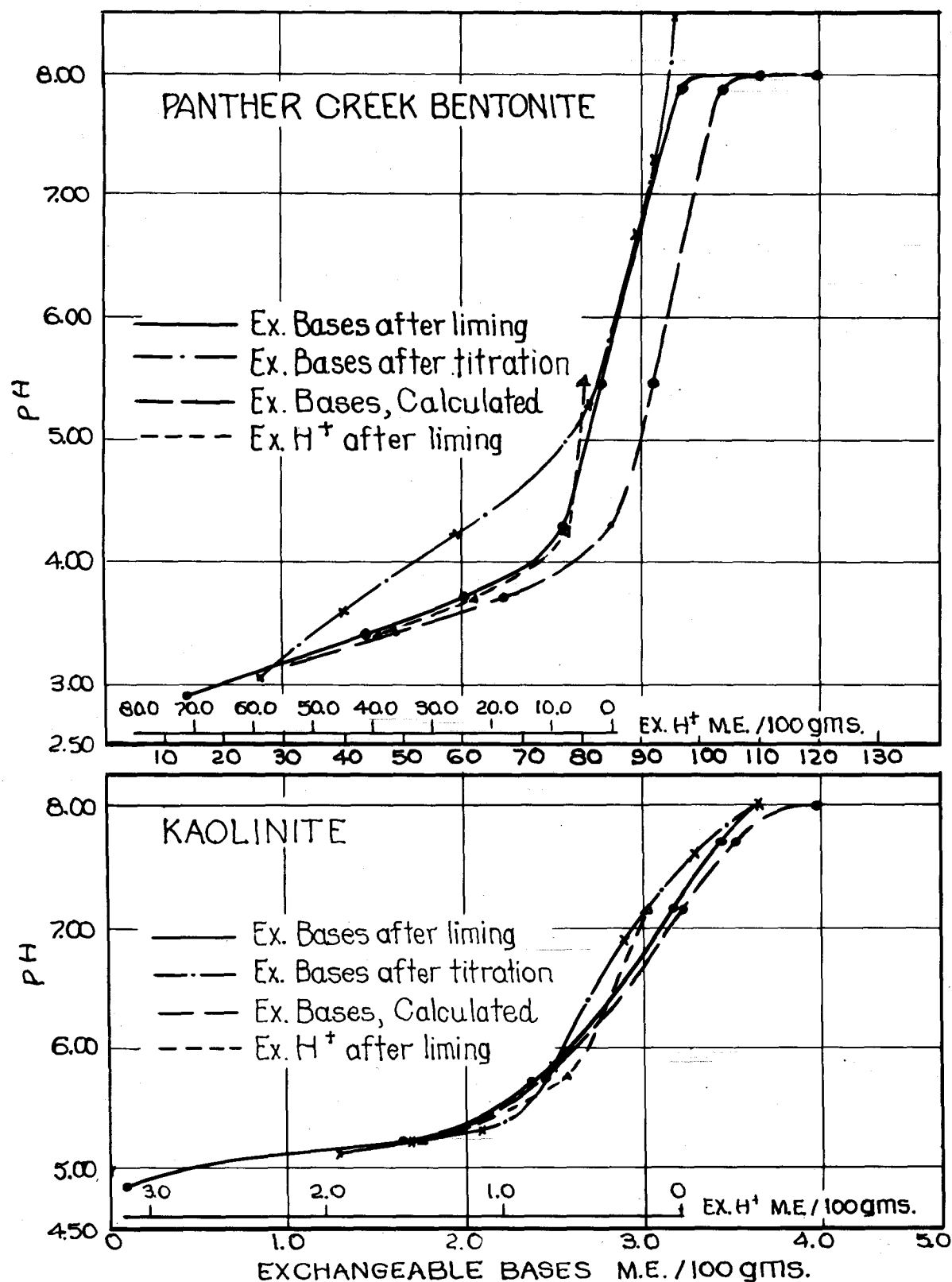


Fig. 12. The relation between pH and the cation status of limed and titrated bentonite and kaolinite.

while the sample limed at the rate of 50 per cent of exchangeable hydrogen gained 2.90 m.e. per 100 gms. in addition to that added as lime. In view of the unlikelihood that the weathering processes taking place in the unlimed samples would proceed in like manner in samples limed at higher rates, all calculations have been based on exchangeable hydrogen and exchangeable bases as given for the original material.

The outstanding features of this phase of the study are the reversion of bases into forms non-exchangeable with ammonium acetate, and the persistence of exchangeable hydrogen in materials with reaction substantially above pH 7.0.

As measured by failure to recover the original exchangeable bases, plus increments of calcium added as calcium carbonate, reversion of bases into forms non-exchangeable with ammonium acetate occurred in all the soils in the experiment. In the Shelby and Cecil soils, a small amount of fixation appeared in the samples limed at the rate of 50 per cent of the exchangeable hydrogen, while in the Weller and Fayette soils, fixation did not occur at the 50 per cent liming rate, as measured by differences in total exchangeable bases. With increasing rates of liming, fixation increases in all of these soils.

Determinations of calcium and magnesium in the ammonium acetate leachates were made to determine the extent to which these elements enter into non-exchangeable combinations at various liming rates. As measured by failure to recover the original exchangeable calcium plus calcium added as calcium carbonate, calcium fixation sets in at a pH somewhat lower than that of

magnesium fixation measured as a decrease in magnesium from its original value. This is true in all the soils studied. Although a small amount of magnesium appears to have been fixed at the 50 per cent rate in Fayette, the results with the 75 per cent rate indicate that the fixation of calcium is occurring in advance of magnesium fixation in this case also. It is noted that magnesium fixation begins at a rate somewhere between the 75 and 100 per cent rates, except in Shelby, where fixation occurs with the 75 per cent rate. Magnesium fixation may be regarded as beginning at a pH of about 6.75 or slightly higher in some cases. It is noted that as the liming rate increases, the rate of magnesium fixation increases proportionately much more rapidly than the rate of calcium fixation.

The outstanding features of the results pertaining particularly to soil colloids and clay minerals are the fixation of bases by bentonite at low pH values, and the virtual absence of fixation by kaolinite.

At a pH of 3.40, the bentonite fixed 4.60 m.e. of bases. This increases to 8.43 m.e. at a pH of 4.30. Comparatively small increases in fixation occur in bentonite at higher liming rates in spite of the sharp increase in pH that occurs with rates of liming over 100 per cent of exchangeable hydrogen.

In kaolinite, the amounts of bases are small, because the exchange capacity of this material is low. The values that emerge for fixation are within experimental error with the possible exception of the sample limed at the rate of 125 per cent of exchangeable hydrogen. It is clear that the magnitude of fixation that occurs in kaolinite is small if it

occure at all. Inspection of the graphs reveals that at the lower rates of liming, bases that are not fixed replaced hydrogen. In the case of bentonite this holds true within experimental error for all rates of liming on which an exchangeable hydrogen measurement was obtainable. With increasing rates of liming, there is a divergence of the curves for exchangeable bases and exchangeable hydrogen, which shows that a portion of the bases enters into reactions other than the neutralization of exchangeable hydrogen, but nevertheless remains in combinations that are soluble in ammonium acetate. The divergence of the curves expressing exchangeable bases after liming and exchangeable bases, calculated, is an expression of fixation of part of the bases of the system in forms that are not extractable by ammonium acetate.

The divergence of the curve for exchangeable hydrogen, and the curve for exchangeable bases, calculated, is an expression of the total extent to which added bases were diverted into reactions other than the neutralization of exchangeable hydrogen. It would appear that the curve described by plotting pH vs. exchangeable hydrogen is the true curve of neutralization of the exchangeable hydrogen in soils and that the curve for exchangeable bases is a composite of bases held by unsatisfied valence bonds of the complex and bases dissolved by ammonium acetate from other than exchange combinations.

Exchangeable bases of soils, soil colloids and clay minerals after titration

Exchangeable bases after titration, as determined by displacing bases from titrated samples with ammonium acetate, are given for Weller, Fayette

and Shelby soils in Table 9 and are presented graphically in Figures 9 to 11, in connection with data on exchangeable bases and exchangeable hydrogen. Similar data for soil colloids and clay minerals are given in Table 10, and are presented graphically in Figures 9 to 12. The outstanding feature of these experiments is the close agreement between the pH-exchangeable base curves after liming and after titration. This agreement indicates that reactions with components other than exchangeable hydrogen that give rise to ammonium acetate soluble substances are short term reactions and that they take place to about the same extent in both limed and titrated systems.

Effect of moist storage on fixation of bases

Since periodic wetting and drying have been shown to be important factors in the fixation of other ions (46, 34), a comparison was made of fixation of bases in two types of limed systems, identical except that one had been kept perpetually moist whereas the other had been wetted and dried at four-week intervals. These data, presented in Table 11, show that fixation of bases by Weller and Shelby soils limed at the rate of 150 per cent of exchangeable hydrogen, are increased slightly by periodic drying and wetting. The effect, however, is much less pronounced than that reported for potassium (46).

Effect of time of leaching on the determination of exchangeable hydrogen

In order to study the effect of time of leaching on the determination of exchangeable hydrogen, 10 gm. samples of Weller, Fayette, Shelby and

Table 9. Exchangeable bases and pH of Weller, Fayette and Cecil soils after titration

Material	cc. $\text{Ca}(\text{OH})_2$ added	Exchangeable bases calculated	Exchangeable bases determined	pH
Weller soil	0	16.6	16.6	4.60
	10	24.9	25.0	5.45
	16	29.9	29.9	6.50
	19	32.4	32.1	7.10
	21	34.0	33.8	7.60
	23	35.7	35.2	8.30
	27	39.0	38.6	8.90
	32	43.2	42.7	
Fayette soil	0	9.67	9.67	4.90
	3	12.2	12.2	5.85
	6	14.6	14.5	6.90
	7	15.4	15.4	7.20
	8	16.2	16.1	7.45
	9	17.0	16.9	7.65
	10	17.8	17.6	7.90
	12	19.5	19.3	8.30
	14	21.1	20.8	8.55
	0	3.52	3.52	5.50
	3.5	4.94	4.75	6.35
	6	5.98	5.77	6.85
	7	6.36	6.10	7.10
	8	6.77	6.59	7.20
	10	7.58	7.35	7.70
	12	8.39	8.07	7.90
	16	10.01	9.65	8.50

Table 10. Exchangeable bases and pH of soil colloids and clay minerals after titration

Material	cc. $\text{Ca}(\text{OH})_2$	Exchangeable bases : calculated	Exchangeable bases : determined	pH
Weller colloid	0	39.0	39.0	4.85
	5	46.7	46.4	5.55
	10	54.3	54.0	6.00
	15	61.9	61.1	6.35
	20	69.5	68.8	7.20
	22	72.6	71.3	8.05
	24	75.6	75.1	8.30
	27	80.2	79.6	8.70
Panther Creek bentonite	0	13.4	13.4	2.85
	8	25.5		3.05
	20	43.5		3.60
	0*	59.1	59.1	4.20
	15*	82.1	81.9	5.30
	20*	89.8	89.5	6.70
	22*	92.8	92.6	7.25
	26*	99.0	96.9	8.50
Cecil colloid	0	.86	.86	4.40
	5	7.71	7.84	5.75
	6	9.08	9.05	6.30
	7.2	10.7	10.6	6.60
	8.5	12.5	12.3	6.80
	10	14.6	14.2	7.70
	12	17.3	16.6	7.90
	14	20.0	18.9	8.15
Kaolinite	0	.08	.08	4.60
	3	1.29		5.10
	4	1.69		5.20
	5	2.10		5.30
	6	2.50		5.65
	7	2.90		6.90
	8	3.30		7.60
	9	3.71		8.00
	11	4.51		8.70
	13	5.52		9.20

*These samples were partially calcium-saturated prior to this experiment.

Table 11. Exchangeable bases in limed Weller and Shelby soils, with and without periodic drying
(Limed at the rate of 150 per cent of exchangeable hydrogen)

Soil	Treatment	Exchangeable	Exchangeable	
		bases calculated	bases determined	Bases fixed
Weller	Dried at 4-week intervals for 24 weeks	42.64	39.54	3.10
	Perpetually moist for 24 weeks	42.64	39.60	2.84
Shelby	Dried at 4-week intervals for 24 weeks	21.35	19.73	1.62
	Perpetually moist for 24 weeks	21.35	20.10	1.25

Table 12. Effect of time of leaching on exchangeable hydrogen obtained from four soils with 250 cc. N barium acetate

Time	Weller	Fayette	Shelby	Cecil
1½ hr.	15.20	5.85	4.70	2.47
8 hrs.	17.35	6.77	5.03	2.90

Cecil soil were leached with 250 cc. normal barium acetate pH 7.0, limiting the leaching period to one and one-half hours by applying suction. In Table 12, these results are compared with those obtained by the eight-hour leaching period used in exchangeable hydrogen studies in this investigation. It will be seen from these results that the shorter leaching period gave exchangeable hydrogen values that were on the average 12 per cent lower than those obtained by the longer period of leaching.

Effect of heating on the behavior of limed soils and bentonite

Samples of Weller, Fayette and Cecil soils, and Panther Creek bentonite were heat-treated at 250, 350 and 450° C and the effect on the exchange properties determined. Values for exchangeable hydrogen, exchangeable bases, and exchange capacity are given in Table 13. These changes are presented graphically in Figure 13.

Changes in exchange properties reflect great differences in the heat stability of the various materials. The exchangeable hydrogen of the Weller soil underwent comparatively little change, while exchange capacity decreased about 20 per cent and exchangeable bases decreased to about half the original value upon heating to 450° C.

The major changes in the bentonite occurred between 250° C and 350° C. Heating to 450° C did not effect any changes that were not also effected at 350° C. At 350° C, the exchangeable hydrogen and exchangeable bases declined to about one-third the original value, indicating a relatively low order of heat stability in this mineral.

Table 13. The effect of heat on the cation status of Weller, Fayette and Cecil soils and bentonite

Temp. °C		pH	Exchangeable hydrogen	Exchangeable bases	Exchange capacity
Weller	0*	4.60	17.35	16.62	31.97
	250	4.45	16.35	13.51	30.08
	350	4.55	16.15	9.55	26.79
	450	4.50	15.28	8.60	26.12
Fayette	0*	4.80	6.77	9.78	14.88
	250	5.45	5.25	7.25	13.79
	350	5.55	4.20	5.77	11.95
	450	5.70	4.21	4.10	9.76
Cecil	0*	5.55	2.90	3.52	5.69
	250	6.00	2.15	1.70	4.14
	350	6.05	1.91	1.39	4.26
	450	6.00	1.57	2.00	4.41
Panther Creek bentonite					
	0*	2.90	71.6		88.7
	250	3.05	46.8		59.4
	350	3.50	22.6		29.9
	450	3.50	22.9		29.8

*Not heat treated.

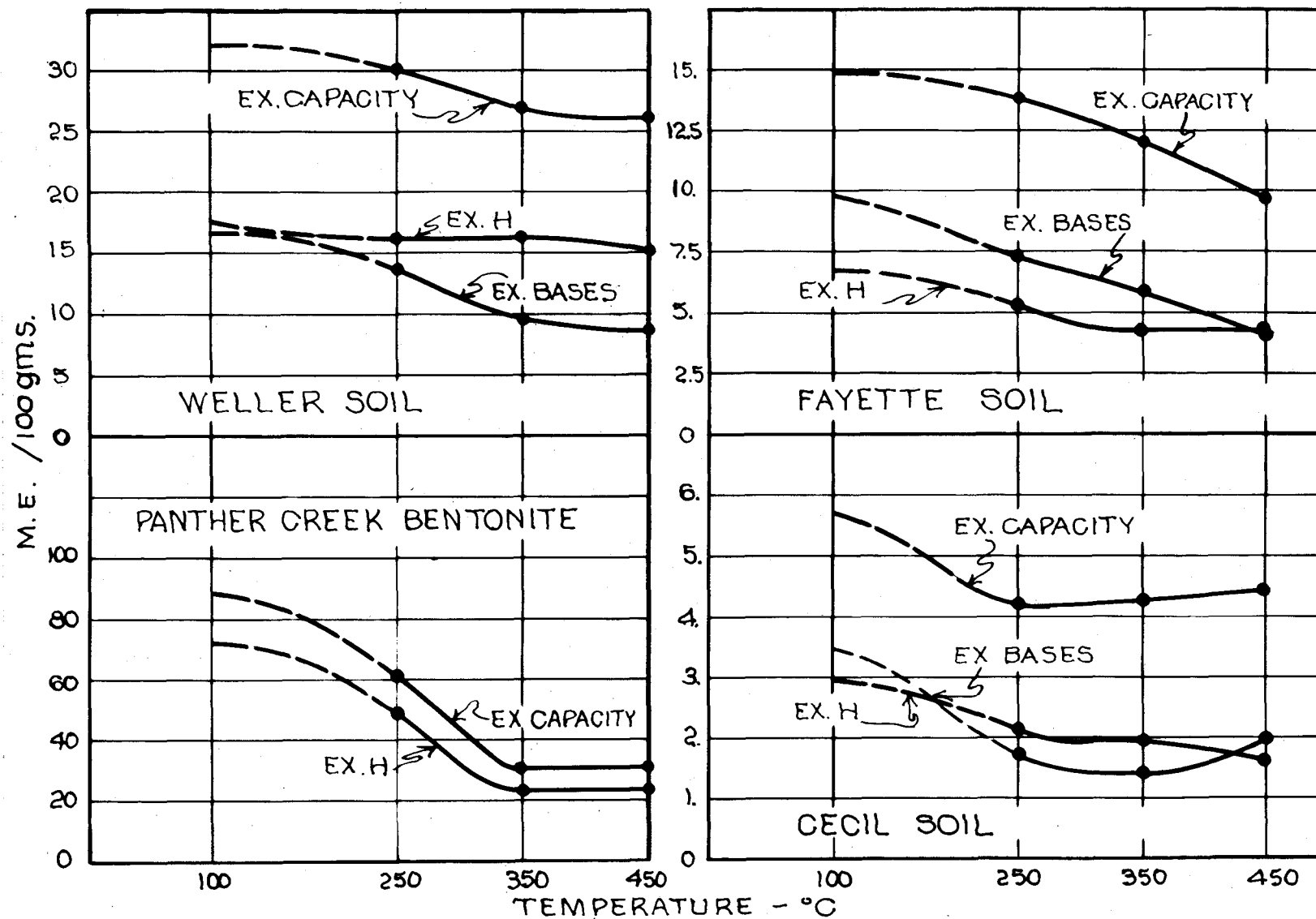


Fig. 13. The effect of heating on the cation status of Weller, Fayette and Cecil soils and bentonite.

The percentage changes in the exchange properties of Fayette soil are substantially greater than those of Weller, but less than the changes in the bentonite, indicating an intermediate stability of this material toward heat. The effect of heat treatment on the Ceoll soil is similar to the other materials studied in the range up to 250°, but above that temperature exchange capacity rises slowly, and exchangeable bases decline slowly, increasing slightly at 450° C.

Reaction between heat-treated material and lime was evaluated by measuring the evolution of CO₂ from limed samples at three, ten, twenty-one, and thirty-five days. Data with respect to CO₂ evolution from these samples are given in Tables 14 and are shown in graph form in Figure 14. The data from the variously treated Weller soil, expressed as per cent of exchangeable hydrogen, gives rise to a family of curves of similar general form differing only by the amount of CO₂ given off in the first ten days of the period, the ten to thirty-five day portions of the curve being essentially parallel. A somewhat similar but less consistent relationship appears in the Fayette data. In the bentonite, the untreated sample and the sample heated at 250° C gradually converge in the late stages of the period, while the materials heated to 350 and 450° C perform in very similar manner. The parallel performance of the 350 and 450° C samples confirm the findings earlier referred to with respect to the similarity in exchange relations of the samples heated at these temperatures. In the case of Ceoll soil, two groups of performance are noted, the untreated and the 250° C samples forming one group, and the 350 and 450° C materials forming the other.

Table 14. Reaction between heat-treated materials and lime, measured as release of carbon dioxide. (Expressed as per cent of exchangeable hydrogen)

Material	Time in days			
	3	10	21	35
W O	110	120	128	133
W250	105	115	123	128
W350	91	102	110	114
W450	62	85	95	102
F O	104	121	133	139
F250	63	87	106	120
F350	91	117	135	146
F450	80	105	119	128
C O	72	114	142	169
C250	44	97	144	177
C350	79	146	198	238
C450	78	140	193	242
P.C.B.O	109	117	122	126
250	93	109	118	124
350	89	115	128	136
450	88	120	129	137

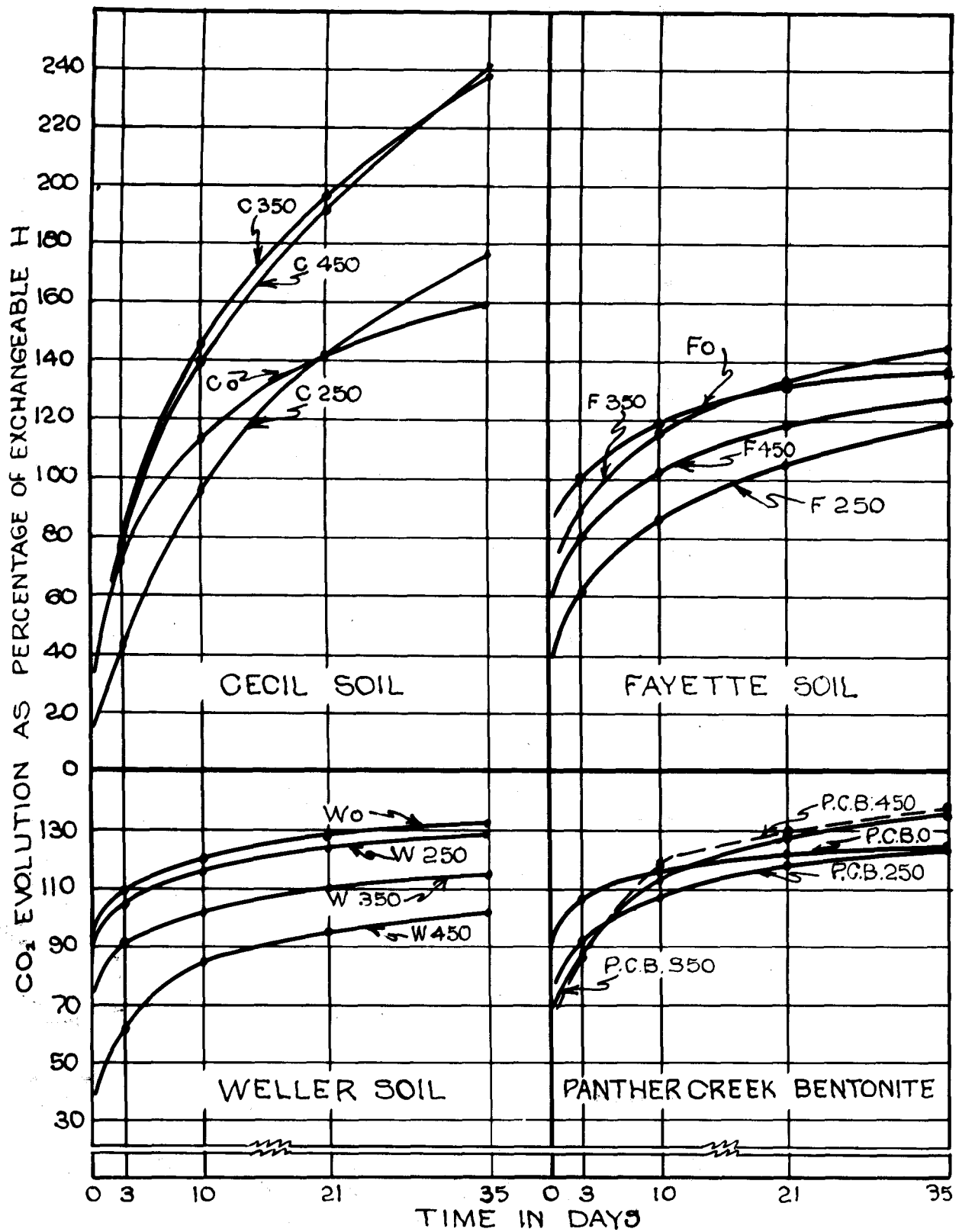


Fig. 14. The effect of heating on the evolution of carbon dioxide from limed Cecil, Fayette and Weller soils and bentonite.

Evaluation of these data is difficult in view of the limited information as to the characteristics of these particular samples. Except in the Weller soil, differences in performance cannot be resolved on the basis of long and short-run behavior. It is possible that a certain amount of re-hydration occurs during the course of the period of moist storage. These data do not permit any inferences with respect to the nature of reactions with lime.

Increase in exchange capacity of Cecil colloid following liming and following titration

Increase in exchange capacity of Cecil colloid resulted at the higher rates of liming and titration.

Table 15. Changes in exchange capacity of Cecil colloid following liming and following titration

Material	Treatment	pH	Exchange- able bases	Exchange capacity
Cecil colloid	None	4.40	0.86	12.2
"	Liming	7.70	15.0	13.5
"	Liming	8.00	16.5*	13.6
"	Titration	7.70	14.2	12.3
"	Titration	7.90	16.6	12.5
"	Titration	8.30	18.9	13.5
"	Titration	8.65	22.3	13.3

*Adjusted for content of CaCO_3 .

These data show that when Cecil colloid is titrated, the increase in exchange capacity is coincident with higher pH and exchangeable base values than is the case in liming.

DISCUSSION

pH Relationships of Limed Soils, Soil Colloids, and Clay Minerals

The pH level attained by liming soils to the extent of exchangeable hydrogen as determined by barium acetate was close to neutrality in all cases except that of the bentonite. This is in good agreement with the results of Walker, Brown, and Young (47) who found that Shelby, Tenn. and Grundy soils limed to the extent of exchangeable hydrogen as determined by barium acetate gave pH values ranging from 6.9 to 7.4 after six months' incubation.

These data vary from the data of Pierre and Worley (38), who found that soils limed to the extent of exchangeable hydrogen characteristically gave pH values of about 6.5. Differences in experimental conditions such as the method used in determining the exchangeable hydrogen (Table 12) may partially account for this discrepancy. In the case of Keller soil, the reduction in exchangeable hydrogen when the short leaching period was used was sufficiently great that a pH of about 6.7 would have resulted if soil had been limed on the basis of the short period value. Smaller decreases were found with the Fayette, Shelby, and Cecil soils.

Accumulation of nitrates also may account for part of the failure of exchangeable hydrogen to be reduced by an amount equivalent to the added lime. The soils in this experiment were very low in organic matter; thus this would not be a factor in this study. Schollenberger (41)

found, however, that from 0.008 to 0.038 per cent of CaCO_3 or 0.16 to 0.76 m.e. of nitrate per 100 gms. of soil was accumulated in soils in a somewhat similar experiment. On soils of low exchange capacity, this would have an appreciable effect.

Examination of the data for bentonite reveals that in order to obtain an initial pH of 7.0, it would have been necessary to add 77.5 m.e. of lime (Figure 12). It is noteworthy that the exchangeable hydrogen determinations at the end of the period of moist storage are uniformly low in comparison to the amount required to attain a pH of 7.0. The magnitude of fixation at low pH values and rapid rate of change of pH with degree of base saturation as shown by the steepness of the pH-exchangeable bases curve are additional factors contributing to the low pH level found upon liming this soil to the extent of exchangeable hydrogen. From the CO_2 evolution data it would appear that in this clay the fixation process took place during the 10 to 21 day period in the samples limed at 125 and 150 per cent rates. The pH data suggest that in samples limed at rates below 125 per cent, fixation was a gradual process of diversion of exchangeable bases to fixed form accompanied by a gradual decrease in pH.

Absence of any very great changes in pH of other limed samples may be regarded as an indication that changes in cation status of these materials had for the greater part been accomplished within four weeks, as was shown for Weller soil in Table 5. Changes after four weeks were correspondingly small in other samples analyzed. The intimate mixing of carbonate and soil at the outset of the experiment may be responsible for the rapid reaction obtained.

Cation Status of Soils, Soil Colloids and Clay Minerals

After Liming

From the curves in Figures 9 to 12 it was seen that exchangeable bases after titration compared very well with exchangeable bases after liming in most cases, except at low pH values, especially in Weller colloid and bentonite. The divergence of the titration and liming curves at low pH values may be explained on the basis of failure to attain equilibrium in the titrated systems to which only small amounts of base were added. Upon the addition of base, surface positions are probably the first to be neutralized. It may be assumed that hydrogen ions in surface positions have relatively more effect than those in more deeply seated positions in determining the pH of the system. Establishment of equilibrium between surface and more deeply seated positions apparently requires more than three days. At the time of measurement, the pH determining positions were apparently neutralized to an extent greater than that characteristic of the clay as a whole, and somewhat higher pH values resulted than would have been the case if equilibrium had been established.

The persistence of exchangeable hydrogen, at pH values up to 7.75 in some cases, is compatible with the results reported by Walker, Brown, and Young (47) and indicates that for the materials in this experiment, excluding bentonite, barium acetate measures exchangeable hydrogen that dissociates at pH values considerably above 7.0. In view of the effect of the duration of the leaching period on the amount of exchangeable hydrogen obtained (Table 12) it is possible that the extension of the period of

contact between barium acetate and bentonite to twenty-four hours or longer would have given a more adequate measure of exchangeable hydrogen.

The divergence of the curves for exchangeable hydrogen and exchangeable bases after liming may be regarded as evidence that a portion of the bases extracted by ammonium acetate are derived from sources other than exchange positions, and that a portion of the added lime is diverted from reaction with exchangeable hydrogen into other forms, which, however, are soluble in ammonium acetate.

It is noticed that at low pH values, exchangeable hydrogen is reduced to the same extent that ammonium acetate soluble bases are increased.

Divergence of the exchangeable hydrogen and exchangeable base curves begins at reactions between pH 6.00 and pH 7.00. It was noted by Britton (6) that silica exerts a slight buffering effect at pH 6.5. It is considered probable that the bases that do not neutralize exchangeable hydrogen are combining with clay breakdown products. This explanation is supported by the data presented in Table 6 in which it was shown that addition of gibbsite increased and the removal of silica and alumina decreased the liming factor of Weller soil.

The close agreement of the curves of exchangeable bases after titration and after liming indicates that whatever the side reactions may be, they proceed to about the same extent under titration and liming conditions. The main differences between titrated and limed systems appear to be the failure in some cases to attain equilibrium at low pH values and the virtual absence of fixation under the conditions of titration. The failure of

titration curves as a means of estimating lime requirements appears to derive in the main from the fact that no estimate is given of the amount of lime needed to satisfy fixation reactions.

Consideration of the data with respect to exchangeable hydrogen after liming, and exchangeable bases after titration and after liming prompts the view that the pH-exchangeable hydrogen curve represents the true neutralization curve and that the titration curve is essentially a composite of reaction with exchangeable hydrogen and side reactions, disregarding the very small amount of fixation that may occur under titration conditions.

It was noted (Table 15) that Cecil colloid demonstrated an increase in exchange capacity at the higher rates of liming and titration. Jackson and Truog (18) have explained increase in the exchange capacity of soil colloids by grinding on the basis of rupture of $X-Si-O-Si-X$ bonds. Mehlich (30) has explained parallel adsorption of barium and hydroxyl ions by kaolinite at pH above 9.6 on the basis of rupture of $X-Si-O-Si-X$ bonds under the influence of high hydroxyl ion concentration. It should be noted that the amount of ammonia held by the complex at the time of determining exchangeable bases is considerably less than the amount of bases held by the same system prior to saturation with ammonia. This difference may be due to differences in dissociation with increasing pH.

Comparison of the amount of base held at pH 7.70 shows that the titrated system contained 0.8 m.e. less than the limed system. This suggests the

possibility that as yet the system contained some hydrogen ions embedded where they exerted no effect on pH, and that upon saturation with ammonia the hydrogen still persisted, giving a low value for exchange capacity. At pH 7.9, however, the titrated colloid contained 16.6 m.e. base, compared to 16.5 m.e. in the limed sample at pH 8.0. Still no increase in exchange capacity resulted. Additional evidence is necessary to determine the manner in which the observed increase in exchange capacity occurs, but the data suggest the possibility that the increase in exchange capacity with ammonia may be a hysteresis effect in the cycle of dissociation of $X-Si-O-Si-X$ bondings.

The Liming Factor of Soils, Soil Colloids, and Clay Minerals

In Table 16, the liming factor, calculated as the ratio of lime added to the reduction in exchangeable hydrogen and as percentage of calcium added that did not neutralize exchangeable hydrogen has been calculated for the four soils used in this experiment. Similar calculations have been made for soil colloids and clay minerals and are given in Table 17. These data show that at low rates of liming, all or nearly all the added lime neutralizes exchangeable hydrogen. As the liming rate increases a progressively larger proportion of the added lime enters into reactions other than that with exchangeable hydrogen. It has been shown (Tables 7 and 8) that with increasing rates of liming, an increasing amount of base was fixed by soils, soil colloids and bentonite. It was also shown that

Table 16. Lime factors of four soils at various rates of liming

Soil	Liming rate : % exchange- able hydrogen	pH	m.e. calcium added	Exchange- able hydrogen reduction	Calcium added Reduction in exchangeable hydrogen	Per cent of added calcium not neutral- izing Ex.H.
Weller	50	5.20	8.68	9.13		
	75	6.10	13.01	12.40	1.05	5
	100	7.10	17.35	14.87	1.16	14
	125	7.75	21.65	16.99	1.27	22
Fayette	50	6.10	3.38	3.68		
	75	6.75	5.08	4.69	1.08	8
	100	7.25	6.77	5.64	1.20	17
	125	7.70	8.46	6.31	1.34	25
Shelby	50	6.35	2.51	2.39	1.04	5
	75	6.80	3.77	3.01	1.26	20
	100	7.20	5.03	3.79	1.32	24
	125	7.45	6.29	4.25	1.48	32
	150	7.80	7.55	4.66	1.62	38
Cecil	50	6.70	1.45	1.38	1.05	5
	75	7.10	2.17	1.91	1.14	12
	100	7.25	2.90	1.95	1.40	33
	125	7.50	3.62	2.46	1.47	32
	150	7.65	4.35	2.81	1.55	36

Table 17: Lime factors of soil colloids and clay minerals at various rates of liming

Soil	Liming rate: % exchange- : able hydrogen	pH	m.e. : calcium added	Exchange-: : able reduction	Calcium added : Reduction in exchangeable hydrogen	Per cent of added calcium not neutralizing : Ex. H.
Weller colloid	50	4.50	32.75	35.74		
	75	5.00	49.12	48.78	1.01	
	100	6.90	65.50	58.71	1.12	10
	110	7.50	72.05	61.93	1.16	14
Cecil colloid	50	5.20	6.37	6.81		
	75	6.20	9.56	8.55	1.11	11
	100	7.00	12.75	11.14	1.14	13
	110	7.35	14.02	11.55	1.21	18
Panther Creek bentonite	50	3.40	35.78	32.3	1.10	10
	75	3.70	53.67	49.4	1.09	8
	100	4.30	71.56	63.9	1.11	11
	110	5.45	78.72	67.67	1.16	14
Kaolinite	50	5.20	1.57	1.70		
	75	5.70	2.36	2.37		
	100	7.15	3.14	2.96	1.06	6

with increasing rates of liming, a considerable portion of the bases entered into side reactions, forming combinations that were soluble in ammonium acetate. It was shown (Table 6) that addition of gibbsite increased the reaction with lime, while removal of free alumina and silica by treatment with sodium carbonate reduced the amount of reaction that was not attributable to neutralization of exchangeable hydrogen.

With the exception of kaolinite, all the materials in this experiment demonstrated fixation of bases when limed and kept in moist storage. The rate at which the fixation reaction proceeds has already been discussed. The data from the soils afford an opportunity to compare the fixation of calcium and magnesium in various soils at several rates of liming. It is noted (Table 7) that fixation of calcium occurs in each case at a lower point on the liming curve than does fixation of magnesium. Magnesium fixation first asserts itself at a pH of about 6.75 and as the pH rises, increases in magnitude at a rate somewhat greater than the fixation of calcium.

A number of lines of evidence bear proof that fixation of calcium is not merely the outcome of a failure to dissolve calcium in the carbonate form. In the first place, determination of residual carbonates on soils and colloids shows that calcium fixation values are much too large to be explained on this basis, even if it were assumed that no calcium derived from solution of carbonate.

The calcium carbonate used in this experiment was found to dissolve in ammonium acetate to the extent of over 4 m.e. per 250 cc. ammonium acetate in much shorter time than that used for displacing bases from these systems.

Additional evidence on this point may be gained by considering the recovery of bases from the sample of Weller colloid (Table 8) lined at the 125 and 150 per cent rates, both samples containing carbonate. The difference in residual carbonate to be expected would be approximately the difference in amount added, or 16.38 m.e./100 gms. It is noted that the difference in fixation is only 0.54 m.e.; thus the failure to dissolve residual carbonates in this sample would be at most not over 0.54 m.e./100 gms. out of a total of over 16 m.e./100 gms. Fixation of calcium cannot then be attributed to failure to dissolve residual carbonates.

The fixation of bases, the detection of differences in the pattern of fixation of calcium and magnesium, and the failure of kaolinite to effect any fixation of base prompts speculation as to the manner in which these elements may be held. That the phenomenon is not merely an expression of exchangeability of the ions is borne out by the fact that under similar pH and base saturation conditions in the titration systems, almost full replacement of native and added bases occurred. Riecken (40) has shown that at the pH values obtaining in this experiment, magnesium is more exchangeable than calcium. In addition, exchange capacity, as determined by distillation of exchangeable ammonia is not changed upon fixation of calcium and magnesium by the systems investigated. This is contrary to the observations that have been made with respect to the fixation of potassium. Joffe and Kolodny (19) and Truog and Jones (45) have pointed out that a decrease in exchange capacity accompanies fixation of potassium. The mechanism of calcium and magnesium fixation is therefore probably not

the same as that which effects the fixation of potassium. MacIntire and Sanders (25) noted that fixation of magnesium did not affect the exchange capacity. Additional evidence to this effect is provided by data on fixation under conditions of periodic wetting and drying, as compared to fixation in samples kept perpetually moist. In Table 11 data are given on Weller and Shelby samples that afford this comparison. It is seen that fixation was only slightly greater in the periodically dried samples. This behavior is contrary to that obtaining in the fixation of potassium.

Comparison of the data for Weller colloid and Weller soil (Tables 7 and 8) reveals at least a certain degree of substitutability of calcium for magnesium in the fixation reaction. Weller colloid was relatively free from magnesium, whereas half the native base in Weller soil was magnesium. Despite this fact the magnitude of fixation of base by these systems was approximately the same per unit of exchange capacity. These data would indicate that the manner of fixation of these bases is essentially the same, and would suggest the probability that the differences in the fixation characteristics of the two ions are the result of differences in conditions under which they precipitate. The data with respect to the tenacity with which the fixed calcium and magnesium are held seem to preclude explanation of this phenomenon as a simple precipitation, however. MacIntire and Young (24) were unable to recover fixed magnesium by subjecting the soil to boiling 1:1 HCl for four hours, whereas the major portion of the fixed calcium was recoverable by this procedure. A further difference was noted, in that additions of magnesium had no effect on the amount of

calcium soluble in carbonated water, but that additions of calcium materially reduced the amount of magnesium soluble in carbonated water. In later experiments, MacIntire, Shaw and Robinson (26) found that NH_4Cl was unable to effect recovery of added magnesium, but that upon extraction with .02 N HNO_3 , as much magnesium was recoverable as with 1:1 HCl . It was proposed by these workers that magnesium enters the colloidal complex.

Consideration of the size of the magnesium ion, the dimensions of the apertures through which it would enter the complex, and the views with respect to the occurrence of magnesium in the crystal lattice of clays of the montmorillonite type suggests the possibility of a penetration of magnesium into the crystal lattice and its retention there without change in the exchange capacity. The magnesium ion has been assigned an ionic radius of 0.71 Å, or a diameter of 1.42 Å. This ion would be easily accommodated in the space formed by the hexagonally arranged oxygen ions which has been assigned a diameter of 2.8 Å. Calcium, with an ionic diameter of 1.96 Å might also move freely in this space. Penetration into the brucite sheet would be dependent on ability to pass through the sheets, however, and it is considered probable that the magnesium ion might enter, whereas the considerably larger calcium ion probably would not. Additional magnesium could be accommodated in the brucite sheet without change of exchange capacity if three magnesium⁺⁺ ions replaced two aluminum ions, a possibility suggested by Marshall (28). Ions held in this manner might be as invulnerable to the action of reagents as the clay itself. The recovery of the major portion of calcium residues, as noted by MacIntire

and Young (24), suggests that calcium is held in a less tenacious manner. It was found, however, that .02 N HNO_3 was unable to remove either fixed calcium or magnesium from the bentonite limed at the 110 per cent rate, which indicates that fixed calcium is also very resistant to the action of reagents.

In the case of Cecil soil, fixation of bases was at a low but nevertheless, consistent level. The fixation of bases by Cecil colloid was considerably greater per unit exchange capacity. Dialysis of the colloid may have increased its capacity for fixing bases.

The absence of fixation in kaolinite would appear to preclude explanation of fixation by Cecil soil and Cecil colloid on the basis of crystal structure. The currently popular view (15) with respect to the structure of kaolinite does not admit of the development of a scheme to account for fixation of bases. In speaking of clays of the kaolinite-halloysite type, Marshall says,

There would seem to be no reason why there should not be substitution of magnesium for aluminum, and of aluminum for silicon in this type, which would lead to clays with appreciable cation content and possibly also to base exchange clays.

SUMMARY AND CONCLUSIONS

The purpose of the investigation was to obtain more information as to the reactions that occur following liming. Calcium carbonate was added at several rates, based on the exchangeable hydrogen content, to four soils, two soil colloids and two clay minerals. pH was measured at four-week intervals following liming. At the end of 16 weeks, determinations of exchangeable bases, exchange capacity, exchangeable hydrogen and residual carbonates were also made. From these data the pH-exchangeable base curve was established for each material and compared with a similar curve determined by a 72-hour titration method.

Failure of all the added lime to react with exchangeable hydrogen indicated the existence of side reactions. Factors affecting these side reactions were studied by treating some of the experimental materials with gibbsite, sodium carbonate and by heating.

On the basis of these studies the following statements and conclusions can be made.

1. Under the conditions of this experiment, the pH attained by liming soils, soil colloids and kaolinite to the extent of exchangeable hydrogen, as determined by barium acetate pH 7.0 was close to neutrality. In the case of Panther Creek bentonite, the barium acetate procedure as used here did not fully measure exchangeable hydrogen.

2. As measured by CO_2 evolution and changes in the status of exchangeable bases, the reaction between lime and soils, soil colloids and clay minerals was practically complete by four weeks.
3. Downward trends in pH of limed samples with time are regarded as evidence of redistribution of bases on the exchange complex.
4. When an amount of lime equivalent to the exchangeable hydrogen as measured by barium acetate was added to the soils, soil colloids, and clay minerals a portion entered into reactions other than the neutralization of acidity. This portion averaged 22 per cent for the soils and 10 per cent for colloids.
5. A portion of the base entering into reactions other than the neutralization of exchangeable hydrogen remains in forms that are extractable with ammonium acetate. The remainder is fixed in forms that are not extractable with ammonium acetate. No fixation occurred in limed kaolinite.
6. Wetting and drying effected a comparatively small increase in the fixation of bases in limed systems.
7. Calcium fixation sets in at lower pH values than does magnesium fixation.
8. Magnesium fixation set in at a pH value of about 6.75. As the pH was increased, magnesium fixation increased at a greater rate than calcium fixation. At the highest rates of liming, about one-fourth of the total amount of magnesium present entered forms non-replaceable with ammonium acetate. (fix. of $\text{Mg}(\text{OH})_2$ at high pH)

9. With some exceptions at low pH values, the pH-exchangeable base relationships of soils, soil colloids, and clay minerals are essentially the same in limed and titrated systems.
10. Normal barium acetate of pH 7.0 replaces hydrogen from some soils with pH values considerably above 7.0. The barium acetate appears to be able to replace hydrogen from positions from which it normally does not dissociate sufficiently to influence pH measurements.
11. By extending the leaching time from one and one-half to eight hours, an average increase of 12 per cent resulted in the exchangeable hydrogen obtained, as measured by barium acetate pH 7.0.
12. Treatment of Weller soil to remove free silica and alumina reduced the extent to which this soil reacted with lime in excess of reaction attributable to exchangeable hydrogen. Addition of 10 per cent of gibbsite to Weller soil effected a small increase in the extent of reaction.
13. Heating to 450° C reduced the exchange capacity of the Weller, Fayette and Cecil soils by approximately one-third. Similar treatment reduced the exchange capacity of Panther Creek bentonite from 89 to 30 m.e. per 100 gms.

LIST OF REFERENCES

1. Albrecht, Wm. A., Pettyjohn, Wm. J., and McLean, E.O. Magnesium depletion in relation to some cropping systems and soil treatments. *Soil Sci.* 55:447-455. 1943.
2. Barker, G.J. and Truog, E. Further investigations in the improvement of clays through control of pH and character of base exchange saturation. *Jour. Amer. Ceram. Soc.* 24(10):317-322. 1941.
3. Black, Charles A. Phosphate fixation by kaolinitic and other clays. Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1942.
4. Bradfield, R., and Allison, W.H. Criteria of base saturation of soils. *International Soc. Soil Sci. Trans. Second Comm.* A:63-79. 1933.
5. Bray, R.H. and Willhite, F.M. Determination of total replaceable bases in soils. *Ind. & Eng. Chem. (Anal. Ed.)* 1:144. 1929.
6. Britton, Hubert T.S. *Hydrogen Ions*, Vol. II. 3rd ed. New York, D. Van Nostrand Co. 1943.
7. Christensen, H.R. and Jensen, S.T. On the quantitative determination of the lime requirement of the soil. *International Soc. Soil Sci. Trans. Second Comm.* A:94-115. 1925.
8. Chuska, J.A. The mineral constituents of the colloidal fraction of soils. *Jour. Amer. Soc. Agron.* 24:421-434. 1932.
9. Clark, N.A. and Collins, E.R. Equilibrium between soil and electrolytes, and its influence upon some lime requirement methods. *Soil Sci.* 29:417-427. 1930.
10. Crowther, E.M. and Martin, W.S. Studies on soil reaction. VI. The interaction of acid soils, calcium carbonate, and water in relation to the determination of "lime requirements". *Jour. Ag. Sci.* 15:237-255. 1925.
11. Dunn, L.E. Lime-requirement determination of soils by means of titration curves. *Soil Sci.* 56:341-351. 1943.

12. Graham, E.R. Soil development and plant nutrition. I. Nutrient delivery to plants by the sand and silt separates. *Soil Sci. Soc. of Amer. Proc.* 6:259-262. 1941.
13. Grim, R.E. and Bradley, W.F. Investigation of the effect of heat on the clay minerals illite and montmorillonite. *Jour. Amer. Ceram. Soc.* 23(8):242-248. 1940.
14. Haddock, J.L. Identification of clay minerals in some Iowa and New England soil profiles. Unpublished Ph. D. Thesis. Ames, Iowa, Iowa State College Library. 1943.
15. Hofmann, U., Endell, K., and Wilm, D. Kristallstruktur und Quellung von Montmorillonit. *Zeit. Krist.* 86:340-348. 1933.
16. Hofman, U. and Endell, K. Die Abhängigkeit des Kationenaustausches und der Quellung bei Montmorillonit von der Verwitterung. *Angewandte Chemie* 52:708-709. 1939.
17. Hopkins, C.G., Knox, W.H. and Pettit, J.H. A quantitative method for determining the acidity of soils. U.S. Bur. of Chem. Bul. 73:114-119. 1903.
18. Jackson, M.L. and Truog, E. Influence of grinding soil minerals to near molecular size on their solubility and base exchange properties. *Soil Sci. Soc. of Amer. Proc.* 4:135-145. 1939.
19. Joffe, J.S. and Kolodny, L. The effect of alternate drying and wetting on the base exchange complex with special reference to the behaviour of the K-ion. *Soil Sci. Soc. of Amer. Proc.* 3: 107-111. 1938.
20. Jones, C.H. Method of determining the lime requirement of soils. *Amer. Fert.* 39 (11):28-29. 1913.
21. Kelley, W.P., Dore, W.H., and Brown, S.M. The nature of the base exchange material of bentonites, soils, and zeolites, as revealed by chemical investigation and X-ray analysis. *Soil Sci.* 31:25-55. 1931.
22. McIntire, W.H., Willis, L.G., and Hardy, J.I. The non-existence of magnesium carbonates in humid soils. *Tenn. Agr. Exp. Sta. Bull.* 107. 1914.
23. McIntire, W.H. Factors influencing the lime and magnesia requirements of soils--a method for the determination of the immediate lime requirements. *Tenn. Agr. Exp. Sta. Bul.* 115. 1916.

24. MacIntire, W.H. and Young, J.B. The transient nature of magnesium--induced toxicity and its bearing upon lime-magnesia ratio studies. *Soil Sci.* 15:427-471. 1923.
25. MacIntire, W.H., and Sanders, K.B. The relation between the absorbed and exchangeable calcium and magnesium content of a soil four years after additions. *Soil Sci.* 28:289-304. 1929.
26. MacIntire, W.H., Shaw, W.M., and Robinson, B. Distinction between magnesium absorbed and that exchangeable, four years after lysimeter incorporations of oxides and carbonates. *Soil Sci.* 37:289-303. 1934.
27. Magistad, O.C. The aluminum content of the soil solution and its relation to soil reaction and plant growth. *Soil Sci.* 20:181-225. 1925.
28. Marshall, C.E. Layer lattices and base-exchange clays. *Zeit. Krist.* 91:433-449. 1935.
29. Mehlich, Adolf. Use of triethanolamine acetate-barium hydroxide buffer for the determination of some base exchange properties and lime requirements of soils. *Soil Sci. Soc. of Amer. Proc.* 3:162-166. 1938.
30. Mehlich, Adolf. Adsorption of barium and hydroxylions by soils and minerals in relation to pH. *Soil Sci.* 53:115-124. 1942.
31. Metzger, W.H. Behaviour of the Jones lime requirement determination with progressive decrease in soil acidity. *Jour. Amer. Soc. Agron.* 25:789-796. 1933.
32. Mitchell, John. The origin, nature, and importance of soil organic constituents having base exchange properties. *Jour. Amer. Soc. Agron.* 24:256-275. 1932.
33. Naftel, James A. Soil liming investigations. III. The influence of calcium and a mixture of calcium and magnesium carbonates on certain chemical changes of soils. *Jour. Amer. Soc. of Agron.* 29:526-535. 1937.
34. Page, J.B. and Eaver, L.D. Ionic size in relation to fixation of cations by colloidal clay. *Soil Sci. Soc. of Amer. Proc.* 4:150-155. 1939.
35. Parker, F.W. Methods for the determination of the amount and avidity of exchangeable hydrogen in soils. *First Internat'l. Cong. Soil Sci. Proc.* 2:164-174. 1927.

36. Parker, F.H. The determination of exchangeable hydrogen in soils. Jour. Amer. Soc. Agron. 21:1030-1039. 1929.
37. Pierre, W.H. Buffer capacity of soils and its relation to the development of soil acidity from the use of ammonium sulfate. Jour. Amer. Soc. Agron. 19:332-351. 1927.
38. Pierre, W.H. and Worley, S.L. The buffer method and the determination of exchangeable hydrogen for estimating the amounts of lime required to bring soils to definite pH values. Soil Sci. 25:363-375. 1928.
39. Pierre, W.H. and Searseth, G.D. Determination of the percentage base saturation of soils and its value in different soils at definite pH values. Soil Sci. 31:99-114. 1931.
40. Riecken, F.P. Some considerations in the magnesium cycle of weathering in Solonchaks soils. Soil Sci. Soc. of Amer. Proc. 8:391-395. 1943.
41. Schellenberger, C.J. Lime requirement and reaction of lime materials with soil. Soil Sci. 11:261-276. 1921.
42. Sharp, L.T. and Hoagland, D.R. Acidity and adsorption in soils as measured by the hydrogen electrode. Jour. Ag. Res. 7:123-145. 1916.
43. Tacke, B. Ueber die Bestimmung der freien Humussäuren in Moorboden. Chem. Ztg. 21:174-176. 1897.
44. Treadwell, F.P. and Hall, W.T. Analytical Chemistry. Vol. II. Seventh Ed. New York, John Wiley and Sons. 1930.
45. Truog, E. and Jones, R.J. Fate of soluble potash applied to soils. Ind. & Eng. Chem. 30:882-885. 1938.
46. Volk, N.J. The fixation of potash in difficultly available form in soils. Soil Sci. 37:267-287. 1934.
47. Walker, R.H., Brown, P.E., and Young, A.W. Some chemical and bacteriological effects of various kinds and amounts of lime on certain southern Iowa soils. Part I. Laboratory and greenhouse experiments. Ia. Agr. Exp. Sta. Res. Bul. 148. 1932.
48. Wheeler, H.J., Hartwell, B.L., and Tucker, G.M. The recognition of the acidity of upland soils and its bearing upon agricultural practice. Rhode Island Agr. Exp. Sta. Report 8:232-280. 1884.
49. Whitt, D.M. and Swanson, C.L.W. Effect of erosion on changes in fertility of the Shelby loam profile. Jour. Ag. Res. 65:283-298. 1942.

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