University of Arizona

COLLEGE OF AGRICULTURE

AGRICULTURAL EXPERIMENT STATION

THE HYDROLYSIS OF CALCIUM CARBONATE AND ITS RELATION TO THE ALKALINITY OF CALCAREOUS SOILS

BY

T. F. BUEHRER AND J. A. WILLIAMS

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TABLE OF CONTENTS

ILLUSTRATIONS

THE HYDROLYSIS OF CALCIUM CARBONATE AND ITS RELATION TO THE ALKALINITY OF CALCAREOUS SOILS

BY

T. F. BUEHRER AND J. A. WILLIAMS

INTRODUCTION

Most arable soils, excepting those which are definitely acid, possess "reserve alkalinity" in greater or lesser amounts, chiefly in the form of calcium carbonate. It may be present in certain horizons of most soil profiles, and even those soils whose A horizon is acid may have a calcareous B horizon. The highly laterized soils of the tropics, because of proximity to or location upon the coral reefs, may be more or less calcareous. In soils which developed from limestones or marls and whose A horizons have not yet been completely leached of their limestone content, we may still find calcium carbonate disseminated in varying degrees throughout this horizon. The calcareous soils of the desert, formed under conditions favorable to the thermal decomposition of calcium bicarbonate, frequently have calcium carbonate disseminated throughout the entire profile or localized in a highly calcareous hardpan.

Whether genetically present from the weathering of basic parent rock or more recently formed by deposition from lime-bearing waters, calcium carbonate is closely related to the fertility of the soil. By reason of its wide distribution in soils, it has received extensive consideration at the hands of soil scientists. It has been found to be closely associated with such soil processes as pan formation, reversion of phosphates, and the existence of free alkalinity in arid soils. For many years it has been used in humid regions to correct acidity and calcium deficiency in soils.

Inasmuch as calcium carbonate may thus exist in the soil, either by virtue of its natural origin or as a result of direct application, the equilibria in which it takes part and which determine both the chemical and physical behavior of the soil will be essentially the same in all soils. We are therefore dealing with a perfectly general type of phenomenon, which, though concerned with alkaline calcareous soils primarily, deals with the principles governing the behavior of calcium carbonate in all soils.

Referring to the calcareous soils of arid regions, McGeorge (16) in a recent bulletin suggests that calcium carbonate may be in large measure responsible for the high alkalinity of such soils, inasmuch as "it is distributed in some areas rather uniformly

3

throughout the soil profile, in others as a cemented layer or hardpan, and in still others as a soft mushy layer or stratum." Comparatively little seems as yet to be known concerning the hydrolytic behavior of calcium carbonate. A soil may be alkaline and yet not highly calcareous, though such cases are doubtless rare; on the other hand a soil might be calcareous and yet not actually alkaline. This fact emphasizes the possibility of other substances affecting the hydrolysis of calcium carbonate.

Although usually considered to have the simple, elementary composition, $CaCO_3$, calcium carbonate may exist in various chemical as well as physical (that is amorphous or crystalline) forms, and it may in its various states exhibit properties which are fundamental to soil fertility. Certainly the typical mineral forms, which resulted from extremely slow geological processes, will exhibit a behavior profoundly different from those finely divided, loosely coherent forms that may be deposited in the interstices of the soil as a result of reactions of calcium bicarbonate or carbonic acid with the free alkalinity of the soil. They will differ particularly in such properties as solubility and hydrolytic behavior. The exact nature of the equilibria in which calcium carbonate may take part is still quite obscure. A study was therefore undertaken in the hope of throwing some light upon this important problem.

REVIEW OF THE LITERATURE

The present investigation concerns itself with calcium carbonate only. It is recognized that magnesium carbonate is usually present in the soil as well, but its properties are in many respects similar to those of calcium carbonate. The extensive literature on this problem has in the past dealt primarily with the results of field experiments on the application of lime to soils, its effect on physical properties, composition of the soil solution, bacterial activity, and crop yields, and in arid regions with the relation of calcium carbonate to alkali soil reclamation.

The literature on the theoretical aspects of the hydrolysis of calcium carbonate is limited in extent. The investigation by Cameron and Bell (6) in 1907 dealing with the effect of various salts upon the solubility of calcite and aragonite in water is the most exhaustive one thus far published. Wiegner (34) has shown that calcium carbonate hydrolyzes to give different pH values in water solution, depending upon the partial pressure of carbon dioxide in the atmosphere in equilibrium with it. Moberg, Greenberg, Revelle, and Allen (19) in their studies on the buffer mechanism of sea water have shown that at 34 per cent salinity, sea water having a pH of 8.20 is saturated with calcium carbonate. Shipley and McHuffie (29) by electrometric titration methods studied the formation of calcium carbonate and established the pH value of 9.4 at which calcium carbonate is in hydrolytic equilibrium with water. As will be shown later, however, this value is not absolute but varies with dilution of the calcium carbonate suspension.

The forms in which calcium carbonate may exist in the soil and the conditions under which the transition of one form to another occurs are fundamental to a complete understanding of its hydrolytic behavior. Cameron and Bell (6) have pointed out that since aragonite is more soluble than calcite in water at a given temperature, the latter must be the more stable phase and hence probably the dominant form in soils. Aragonite can undergo transformation to calcite, as Watson (32) has shown, for when calcium carbonate is prepared at temperatures above 30 degrees C., crystals corresponding to aragonite are formed, while below this temperature calcite crystals appear. Hence aragonite is unstable at temperatures below 30 degrees. The transformation is influenced by numerous other factors, notably the kind and concentration of salts present. Dana (8) states that "aragonite will form when calcium carbonate solutions are evaporated at temperatures between 80 and 100° C; it will form at lower temperatures if the solution contains some sulfate or small amounts of the carbonates of strontium or lead."

However, as Rastall (23) points out, the interrelations between calcite and aragonite are still very obscure. It is not unlikely that differences in hydrolytic behavior of calcium carbonate in soils are attributable in large measure to differences in the crystalline modifications of this mineral. However, it must be borne in mind that calcium carbonate may also precipitate in the soil as more or less amorphous agglomerates from colloidal suspension and as such may be in a much more reactive state. There is reason to believe, as will be shown later, that calcium carbonate may exist in still other forms. It is therefore not surprising to find a wide discrepancy between the results of various authors on the hydrolytic pH of pure calcium carbonate. For the purpose of the present investigation, various natural and synthetic carbonates of calcium were studied in order to ascertain the extreme limits of variation in properties resulting from chemical composition.

THEORETICAL CONSIDERATIONS

The fundamental reaction which forms the basis of this study is as follows:

$$CaCO_3 \text{ (solid)} + H_2O \text{ (l)} = Ca^{++} + HCO_3^- + OH^-.$$
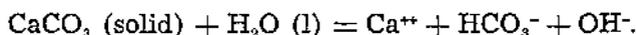
It will be observed from this equation that the nature of the solid phase is an inherent condition for the equilibrium and will largely determine to what extent the reaction will take place. Then, the ratio of $CaCO_3$ to water may be expected to play an important rôle. The effect of neutral salts, whether with or without a common ion, as Cameron and Bell (6) have shown, will be to increase the solubility of the calcium carbonate, but the hydrolysis should, if the carbonate is at all in colloidal dispersion, be reversed. The same should be true if colloidal impurities were present. These and other considerations constituted the basis of the present study.

EXPERIMENTAL METHODS

The extent of hydrolysis was followed by determining the pH of carbonate suspensions by means of the glass electrode (17, 19) in conjunction with an Aminco pH Meter (No. 851-02, manufactured by the American Instrument Company, Washington, D.C.). This instrument is equipped with a highly sensitive galvanometer, so that vacuum tube amplification is unnecessary. The electrode bulbs were blown from No. 015 Corning glass to about 14 mm. in diameter, somewhat ellipsoidal in shape, and of wall thickness about 0.05 mm. They were fitted with a silver-silver chloride electrode in N/10 HCl solution. They were very sensitive and reproducible. The instrument was so constructed that 1 mv. was equivalent to 0.02 pH unit, which was considered sufficie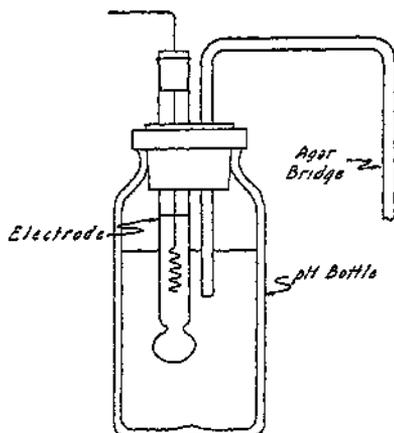ntly accurate for the problem under consideration. The measurements were carried out in a wide-mouthed bottle as shown in Figure 1. This technique made it possible to make measurements in the absense of carbon dioxide or other acid fumes in the laboratory. The graph of E.M.F. as ordinates against pH as abscissae gave a perfect straight line throughout the pH range from 3 to 11.

In all cases where variables other than dilution were being studied, a constant dilution of 1:10 in carbon-dioxide-free water was employed as suggested by McGeorge (16). The time of equilibration prior to the pH measurements was kept constant at one hour on the mechanical shaking machine.

Figure 1.—Glass electrode assembly for pH measurements.

EXPERIMENTAL RESULTS

pH OF PURE CALCIUM CARBONATE SUSPENSIONS

In the preliminary experiments it was noted that different samples of calcium carbonate showed widely varying pH values. Some gave values considerably above 10, while others were as low as 7.5. It was also found that no two samples of calcium carbonate as taken from stock bottles coming from different supply houses agreed in their pH values in 1:10 dilution. Samples coming from even the same supply house showed large differences. Under these circumstances it was decided to prepare calcium carbonate very carefully and locate the cause of the discrepancy. Several different methods were employed as follows:

1. Precipitation by slowly mixing filtered solutions of calcium chloride and ammonium carbonate. The resulting product was

filtered by suction and washed free from chlorides with 50 per cent alcohol.

2. Bubbling carbon dioxide through a filtered solution of calcium hydroxide until the precipitate which formed redissolved. It was then filtered, and the solution decomposed by boiling. The product thus formed was washed repeatedly by suction using 95 per cent alcohol and kept in a desiccator under an atmosphere of dry carbon dioxide until used.

3. Treatment of C.P. calcium carbonate with a solution of ammonium carbonate to convert the particles which may have undergone superficial hydrolysis (with loss of carbon dioxide in drying) back to the normal carbonate. The product thus obtained was washed with alcohol and kept in a vacuum desiccator until dry. The pH values obtained for these precipitated forms of calcium carbonate in 1:10 dilution are shown in Table 1.

TABLE 1.—pH OF CALCIUM CARBONATE AS A FUNCTION OF METHOD OF PREPARATION.*

No.	Sample	pH
1	$CaCl_2 + (NH_4)_2CO_3$	9.35
2	Same	9.40
3	Same	9.68
4	Same	9.55
5	$Ca(OH)_2 + CO_2$	9.55
6	$CaCO_3 + (NH_4)_2CO_3$	9.43

*1:10 suspension in CO_2-free water.

These results indicate that the true pH of calcium carbonate appears to lie between 9.3 and 9.7. They agree closely with that of Shipley and McHuffie (29) obtained electrometrically, namely 9.32, but are at variance with that of Wiegner (34) who reported a value of 10.23. The variations may be due in part to occluded ions of the neutral salts in the presence of which they were precipitated but perhaps principally to the physical conditions of their preparation. It is quite possible that calcite and aragonite may have been present in varying proportions in the products obtained.

CALCULATION OF HYDROLYTIC pH OF CALCIUM CARBONATE FROM IONIZATION CONSTANTS OF CARBONIC ACID AND WATER

In view of the foregoing results it was considered of interest to calculate from the known constants for water and carbonic acid the pH of calcium carbonate in carbon-dioxide-free water. We are here concerned with the reactions:

1. $CaCO_3$ (s) = $CaCO_3$ (x-molal) = Ca^{++} (x-molal) + CO_3^{-} (x-molal)
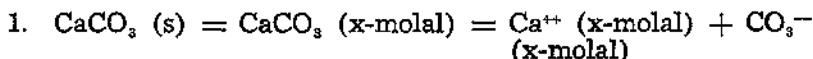
for which we know the solubility of 25 degrees C. from Seidell (28, p. 193) to be 5.1×10^{-4} mol per 1,000 gm. water. In this equation,

x represents the solubility concentration in terms of mols per 1,000 gm. of water.

2. The hydrolytic reaction:

$$CO_3{}^{--} \text{ (y-molal)} + H_2O \text{ (l)} = HCO_3{}^- \text{ (y-molal)} + OH^- \text{ (y-molal)}.$$
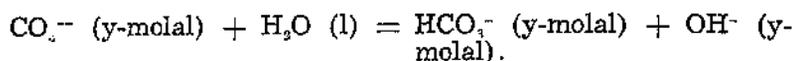
We may calculate the hydrogen-ion concentration resulting from such a hydrolysis at equilibrium in two ways: (1) by obtaining the hydrolysis constant and degree of hydrolysis from the ionization constant of water and the second ionization constant of carbonic acid and (2) by basing the calculations upon the second ionization constant of carbonic acid and expressing the various concentrations in terms of the hydrogen-ion concentration. We shall use the latter procedure.

The second ionization constant of carbonic acid according to Lewis and Randall (12, p. 578) is equal to 3.7 x 10^{-11}. The ionization constant of water according to the same authors (12, p. 486) is 1.005 x 10^{-14} at 25 degrees C.

$$\text{Let } (H^+) = x$$
$$\text{Then } (OH^-) = \frac{1.005 \times 10^{-14}}{x}$$
$$(HCO_3{}^-) = (CO_3{}^{--})_{init.} - (CO_3{}^{--})_{equil.}$$
$$= 5.1 \times 10^{-4} - (CO_3{}^{--})_{equil.}$$
$$(Ca^{++}) = 5.1 \times 10^{-4}.$$

$(CO_3{}^{--})_{equil}$ = concentration of carbonate ion present at equilibrium. This quantity can be calculated by use of the principle that the total equivalents of positive ions present must equal the total number of equivalents of negative ions. Whence

$$x + 2 \ (5.1 \times 10^{-4}) = 2 \ (CO_3{}^{--}) + (5.1 \times 10^{-4} - CO_3{}^{--}) +$$
$$\frac{1.005 \times 10^{-14}}{x}.$$

Simplifying, we obtain:

$$(CO_3{}^{--})_{equil.} = x \frac{1.005 \times 10^{-14}}{x} + 5.1 \times 10^{-4}.$$

Substituting the expressions for the hydrogen-, bicarbonate-, and carbonate-ion concentrations in the second ionization constant for carbonic acid, which is as follows:

$$\frac{(H^+) \ (CO_3{}^{--})}{(HCO_3{}^{--})} = 3.7 \times 10^{-11}$$

and solving for x, we obtain

$$x = 1.95 \times 10^{-11}$$
$$\text{whence pH} = 10.70.$$

The value thus obtained represents the limiting value theoretically possible in the hydrolysis of calcium carbonate. This should be the maximum pH value which was obtained at the highest dilutions. However, the range of pH values obtained by experiment was from 9.3 to 9.7. In some instances samples of calcium carbonate were obtained which showed a pH value of 10.3, but in all cases the actual pH found was considerably less than that calculated from theory. It is true that certain assumptions were involved in the calculations, particularly that all constituents of the equilibrium solution were completely ionized. This was considered justifiable since the solution at best is very dilute. The value of 10.23 obtained as a maximum by Wiegner (34) is more nearly in accord with the theoretical value than are our experimental values.

EFFECT OF LEACHING ON pH OF CALCIUM CARBONATE

The question next arose: If the variation in pH of calcium carbonate be due to adsorbed or occluded salts, can these be removed by continued leaching, or are they chemically combined so as to resist leaching with water? It was found by preliminary experiments that leaching did in fact tend to lower the pH of a calcium carbonate suspension. Samples of synthetic calcium carbonate were chosen from various sources and the pH values of their 1:10 suspension in carbon-dioxide-free water measured. The solutions were then filtered off and the solid materials re-equilibrated with like volumes of fresh carbon-dioxide-free water. The pH was again measured, and the same procedure was repeated until some five or six such leachings had been made. The results are assembled in Table 2.

TABLE 2.—EFFECT OF LEACHING ON THE pH OF CALCIUM
CARBONATE.

Sample	Number of leachings					
	1	2	3	4	5	6
1. Baker's C.P. CaCO₃	8.86	9.35	9.65	9.67	9.70	
2. Synthetic CaCO₃ from (NH₄)₂CO₃+CaCl₂	7.50	8.68	9.56	9.63	9.70	
3. Synthetic CaCO₃ prepared same as (2) but different batch	9.85	9.62	9.65	9.67	9.70	
4. Baker's C.P. CaCO₃ leached with (NH₄)₂CO₃	7.65	8.43	9.39	9.54	9.63	9.70

These data show that while the initial pH values of the carbonates varied rather widely, it was possible by successive leaching to bring them all to a constant value of 9.70. Those below this equilibrium value increase, and those above decrease to it. It appears from these results that adsorbed salts are slowly removed by leaching and may have a significant effect upon the pH of calcium carbonate suspensions.

pH OF SUSPENSIONS OF VARIOUS CARBONATES AS A FUNCTION OF DILUTION WITH WATER

As pointed out before, calcium carbonate undoubtedly exists in the soil in various forms, as the naturally occurring minerals and in precipitated form resulting from the interaction between calcium bicarbonate in irrigation waters and the free alkalinity of the soil. It was therefore deemed of interest to compare the hydrolytic behavior of these classes of carbonates. Since the soil contains magnesium carbonate in analogous forms, these were also included in the study. The naturally occurring carbonates would be expected to be less soluble than the synthetic ones and very probably also hydrolyze to a lesser degree. Those of calcium included calcite, aragonite, precipitated calcium carbonate, and a naturally occurring limestone. Those of magnesium included the mineral magnesite, precipitated magnesium carbonate, and dolomite. For comparison, the pH values of analogous solutions of sodium carbonate were also determined.

The results are shown graphically in Figure 2. Two general relations are deducible from the curves: first, in every case the pH is seen to increase with dilution, rather sharply at first and gradually approaching a constant value at higher dilutions. This is a rather surprising result in view of the fact that the solid phase in each case was present in great excess of its solubility. The method of equilibrating the suspensions allowed sufficient time for the solid to come to equilibrium with the solution, hence the solutions should in all cases have been saturated. If saturated, one should be justified in assuming a constant degree of hydrolysis, hence a constant pH throughout the range of dilutions. This was not found to be the case. The pH was found to rise in one case from 6.86 to 8.28, in passing from a dilution of 1:1 to 1:100. This difference is far in excess of the experimental error of measurement. Similar results on the effect of dilution on the pH in the case of soils have been reported by Baver (2), McGeorge (16), Salter and Morgan (26), and others.

Such an increase in hydrolysis with dilution is normally to be expected in the case of dissolved salts, and we find this to be true in the case of sodium carbonate. In the case of the slightly soluble compounds we must assume the equilibrium which is set up to be in part a surface equilibrium. It is probable that the particles of solid, $CaCO_3$ for example, as soon as they come in contact with water hydrolyze off the surface layer of molecules, forming a less soluble basic carbonate, for example $CaCO_3.Ca(OH)_2.xH_2O$ (33). Hence, when a constant weight of 10 grams of solid is taken in each determination, and the amount of water varied to give the range of dilutions measured, obviously, the same absolute amount of calcium carbonate would go into solution in each case. However, since the volume of water varied considerably, the degree of hydrolysis and hence the pH increased as the volume of water increased, finally become constant with further dilution. It thus seems logically necessary to postulate a change in composition of
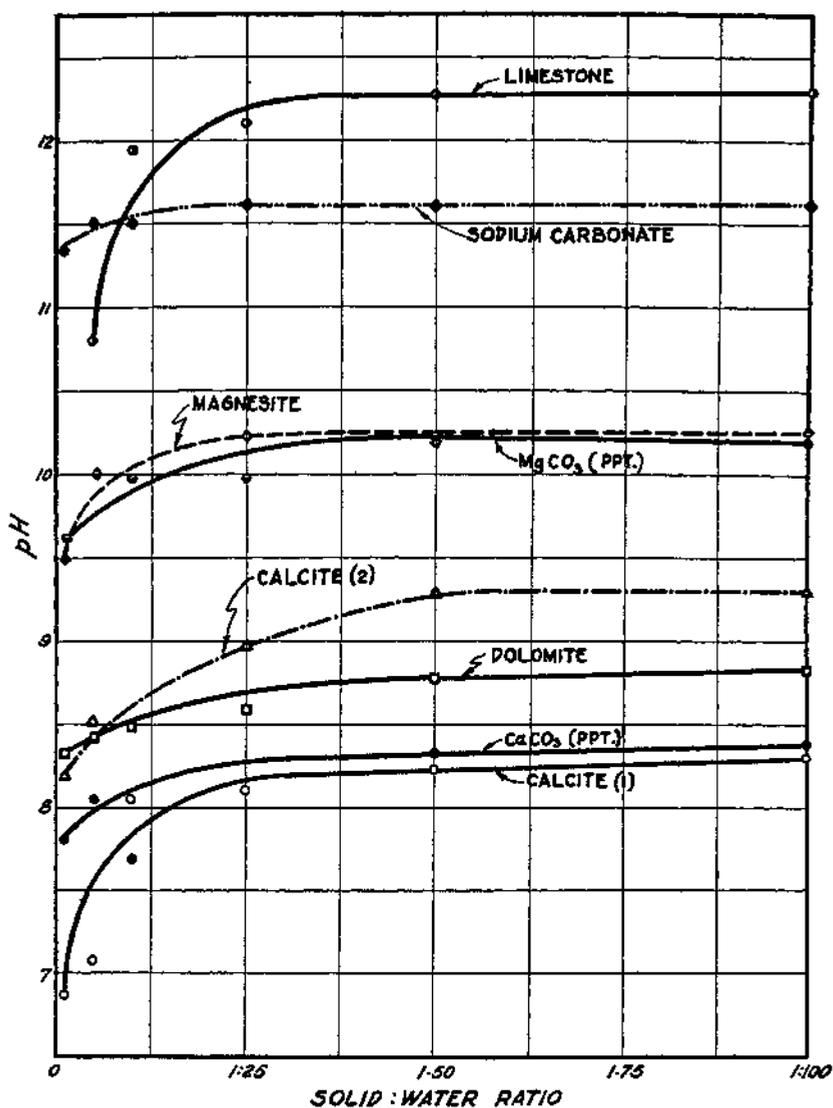
Figure 2.—pH of suspensions of various carbonates as a function
of dilution with water.

the surface of the particles. Such a phenomenon is also observed
when soils are made up to different soil-water ratios and their pH
values determined. It is likely that such a surface effect may be
important in other soil processes.

Secondly, we observe from the graph that the pH of the freshly precipitated compounds is invariably higher than that of the corresponding naturally occurring carbonates. It is probable, of course, that differences in the size of particles may account in part for this discrepancy. The minerals calcite and aragonite were finely pulverized in the ball mill and passed through a 100-mesh screen. The synthetic materials undoubtedly contained particles of much smaller size. The data for limestone are quite surprising and suggest the presence of adsorbed readily hydrolyzable compounds, such as sodium carbonate, and since the material itself was impalpably fine, it was highly dispersed in suspension. These results also indicate that in field practice these carbonates may be precipitated in the interstices between soil grains, and, approximating colloidal dimensions in size, they may contribute materially to the alkalinity of a soil by virtue of their increased hydrolysis. Winchell (36) classifies this form as μ-$CaCO_3$ whose physical properties, such as density, are very different from those of calcite and aragonite.

pH OF SOIL CARBONATES AS A FUNCTION OF NEUTRAL SALTS PRESENT IN SOLUTION

That soluble salts are capable of exerting an effect upon the hydrolysis of calcium carbonate has been demonstrated by the previously discussed leaching experiment. On the assumption that part of this effect may be attributed to the adsorption of neutral salts present, an experiment was conducted to determine the effect of neutal salts at various concentrations upon the pH of calcium carbonate. While the $CaCO_3$-water ratio was kept constant, the neutral salt concentration was varied from N to N/10,000. The pH data so obtained are shown graphically in Figure 3.

It is seen from the curves that the effect of neutral salts in general is to reduce the hydrolytic alkalinity of calcium carbonate suspensions, whether the neutral salt contains a common ion or not. This effect has been observed on soils by Christensen and Jensen (7) and also by McGeorge (16) working with acid and alkaline soils, respectively. However, it does not appear to have been observed that neutral salts have similar effects on the carbonates. The curves further show that the effects of the various chlorides of sodium, calcium, magnesium, and potassium are approximately in the order of the lyotropic series of the respective positive ions when considered at the higher salt concentrations. Calcium chloride gives the greatest reduction in pH, and while this effect may be attributed in part to a common-ion effect, it is also true that calcium has the strongest coagulating effect on colloids, being above the other ions in the lyotropic series. If such a flocculating effect occurred, it should reduce the surface and hence the tendency of the solid to hydrolyze.

A rather interesting result is obtained in the case of sodium sulfate, namely that this salt has practically no effect on the hy-
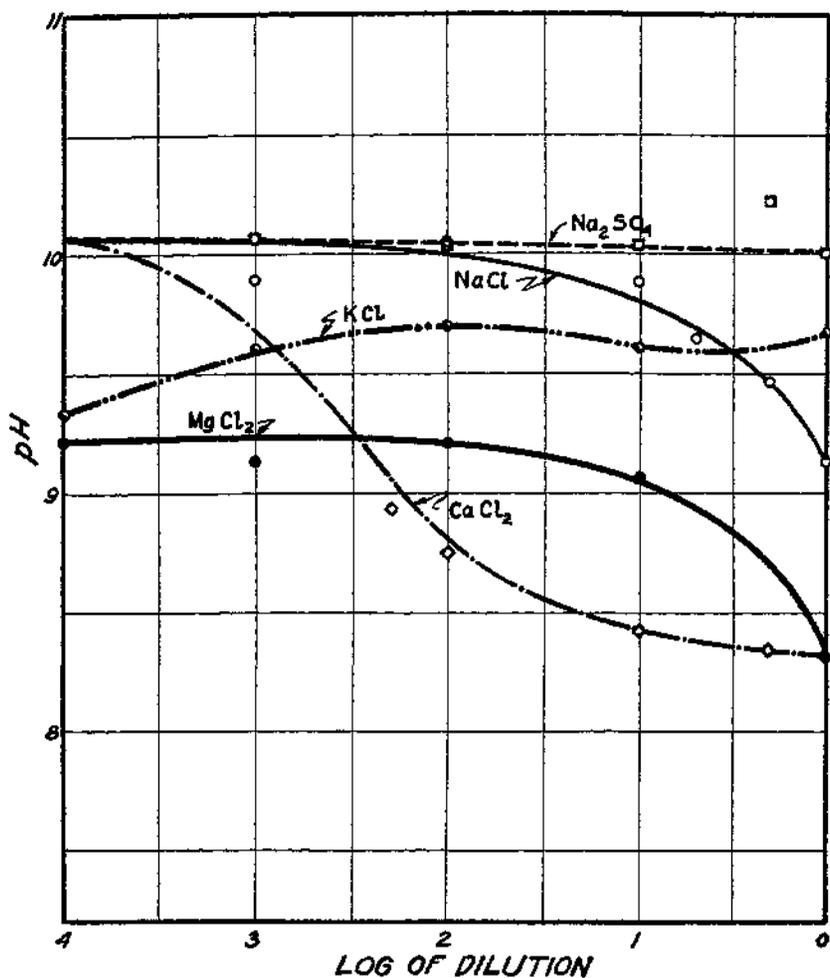
Figure 3.—Effect of neutral salts on hydrolysis of calcium carbonate
(CaCO₄-water ratio, 1:10).

drolysis of calcium carbonate. Lewis, Squires, and Thompson
(13) have found that sodium sulfate is likewise without effect on
the pH of clay suspensions. In Figure 4 the analogous effect of
neutral salts on soil suspensions is illustrated. The order of the
effect of the various ions is the same as in the case of calcium car-
bonate alone, and the magnitude of the reduction is also of the
same order.

However, an explanation of the effect of neutral salts in terms
of coagulation of the colloidal particles is only a partial one. There
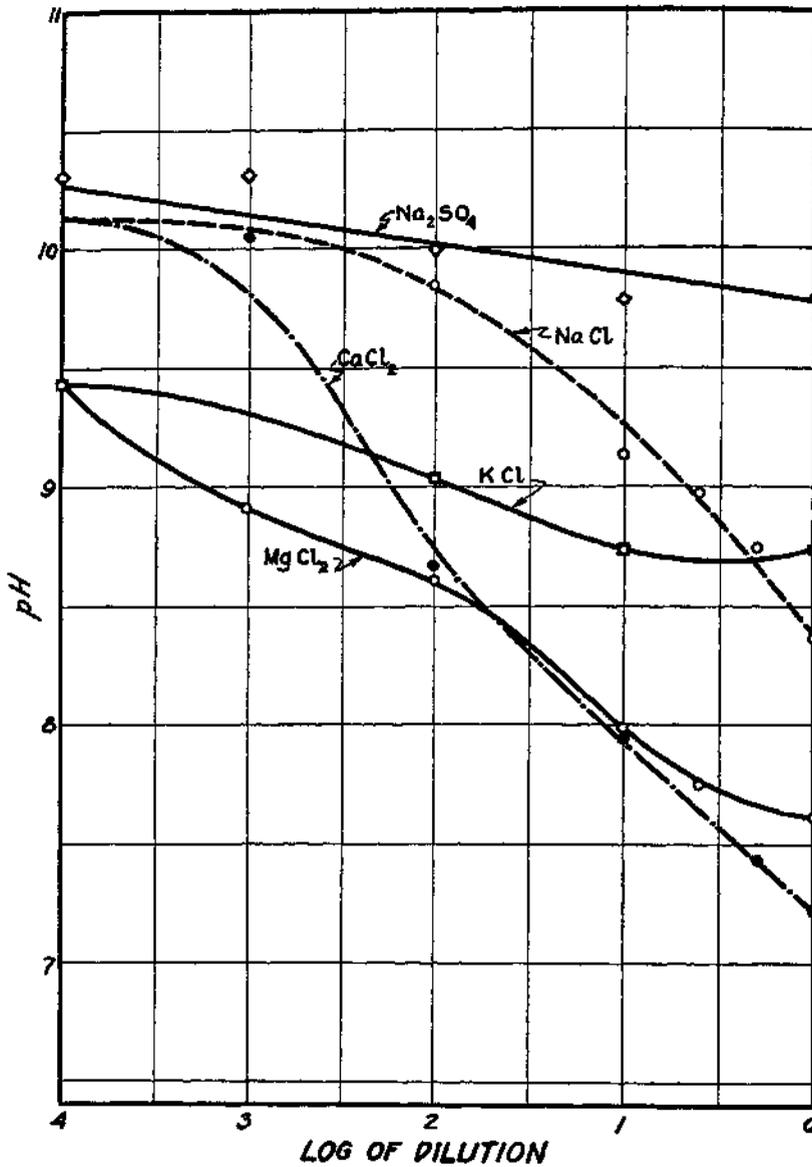is reason to assume that an appreciable amount of the calcium

Figure 4.—Effect of neutral salts on pH of soil suspensions (soil-water ratio, 1:10). Sunrise composite.

carbonate is in the colloidal state, although the methods of synthesis and washing fairly completely flocculate any colloidal particles that may be present. It is true that when the solid is mixed with pure neutral water, it is peptized to some extent, but

calcium carbonate does not seem to pass into the dispersed state very readily.

An interesting paper by Breazeale (5) contains results which are apparently at variance with the above findings. In Figure 1 of the paper cited are plotted the amounts of free alkalinity in terms of p.p.m. of Na_2CO_3 produced when calcium carbonate is treated respectively with solutions of sodium chloride, sodium nitrate, and sodium sulfate at various concentrations from 1 to 30 per cent. The alkalinity was determined by titration after filtering off the equilibrium solution from the calcium carbonate. It is found to *increase* markedly as the concentration of neutral salt is increased, reaching a maximum at 5 per cent in the case of NaCl and at 20 per cent in the case of $NaNO_3$. The sodium sulfate curve showed the most pronounced effect, increasing sharply up to the saturation concentration.

A comparison of the results cited with those of the present paper shows obvious disagreement in all cases. We are dealing with pH measurements in the one case and with total titratable alkalinity in the other. These quantities are necessarily not the same. The pH value indicates the active, ionized OH^- (or H^+) ion concentration in the equilibrium solution at the beginning, while the titratable alkalinity gives the total alkalinity measured at the end point in a titration. Obviously during titration the equilibrium is continuously shifted. The alkalinity thus determined is actually a carbonate alkalinity and the pH at which it exists in equilibrium would actually be considerably less than that of a pure sodium carbonate solution of equal normality because of the reversal of the hydrolysis.

A second reason for the lack of agreement lies in the fact that the salt concentrations were much higher than those used by the present authors, varying from N to about 6N in the case of sodium chloride and 7N in the case of sodium nitrate. It is common knowledge that neutral salts will increase the solubility of calcium carbonate. Usually this effect is accounted for by the equation

$$CaCO_3 + 2\,NaCl = Na_2CO_3 + CaCl_2$$

which at first glance would not be expected to take place. However, there is a marked difference in the activity coefficients as Lewis and Randall (12) have shown; for NaCl at 0.1N concentration it is 0.798, while for $CaCl_2$ it is 0.501. In more concentrated solutions the difference is even greater. In other words, the reaction proceeds because calcium chloride, which is relatively less dissociated, is formed. However, it does not proceed to any great extent, since the titration data of Breazeale (5) indicate that at 20 per cent NaCl concentration only .00318 gm. of carbonate alkalinity is present in 100 cc. of solution, whereas there should have been 1.06 gm., if the entire 1 gm. sample of calcium carbonate had reacted.

This effect of neutral salts on the solubility of calcium carbonate is shown also by the curves in Breazeale's paper, for if we plot

the solubility of calcium carbonate, as given by Seidell (28) in the presence of sodium chloride and sodium sulfate respectively, we find that the curves so obtained are closely concordant and practically coincide with the titratable alkalinity curves. In other words, the titrations give the amounts of carbonate alkalinity which had gone into solution by interaction with the neutral salt.

However, as stated before, the titratable alkalinity affords no index as to the active alkalinity as measured by pH under these conditions. The pH depends upon the degree of hydrolysis and dissociation of the hydrolytic products and would doubtless be greatly reduced by the salt concentrations such as Breazeale used. Hence the pH as measured in the presence of neutral salts should be less, as the authors of the present paper have found.

It is possible that the reaction cited above may be in part a surface desorption of hydroxyl ions from calcium carbonate particles by chloride or sulfate ions. There is some evidence to show that calcium carbonate particles when they come in contact with water hydrolyze off the surface layer of molecules or ions, and a certain number of hydroxyl ions take the place of carbonate ions. The film thus produced is of the nature of a basic calcium carbonate. Such a condition may also result from the adsorption of OH^- ions from solution by calcium carbonate particles, a mechanism which would explain why the pH of calcium carbonate suspensions decreases with the time to a limiting or minimum value. When Cl^- ions are added by way of sodium chloride, there may be a replacement of OH^- by Cl^- in a manner similar to anion exchange in zeolites as Ravikovitch[1] has shown. If such a replacement occurred, there may conceivably be an increase in pH by virtue of the OH^- liberated. This point has not yet been established with certainty, and the entire mechanism is doubtless quite complicated.

The effect of neutral salts may, however, be accounted for in still another way. When we consider the hydrolytic reaction:

$$CaCO_3 \ (s) + H_2O \ (l) = Ca^{++} + HCO_3^- + OH^-$$
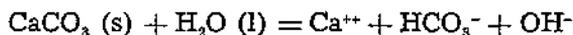
it should be noted that water enters as one of the reacting components. Any substance which tends to reduce the activity (12) (or effective concentration) of the water would tend to reduce the extent to which the hydrolytic reaction will take place. The neutral salts used in this experiment reduce the activity of the water very markedly and to a greater extent in the more concentrated solutions. This point of view is confirmed by the foregoing results, for the pH is, in fact, found to be lowest in the case where the solutions are the most concentrated and vice versa. In field practice the effect would not be noticeable except where the soil itself was strongly saline, or the irrigation water carried a high content of soluble salts.

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[1] S. Ravikovitch, "Anion Exchange: Liberation of the Phosphoric Acid Ions Adsorbed by Soils," *Soil Science*, XXXVIII (1934), 279-90.

pH OF CALCIUM CARBONATE IN THE PRESENCE OF COLLOIDAL MATERIALS

It has frequently been observed that a soil which shows a neutral or slightly acid reaction in neutral water will effervesce vigorously when treated with acid. In other words, the soil contains a considerable amount of carbonate which is not amenable to hydrolysis. It seems to be coated with a film of material which must first be dissolved by the acid. When nodules of calcium carbonate in heavy clay soils are examined, it is found that they are surrounded by such a coating of clay, iron oxide, or organic matter. It seemed of interest to investigate this phenomenon by studying the effect of various colloidal sols upon the hydrolysis of calcium carbonate. Accordingly, sols of the following materials were made up in a series of concentrations by weight: dialyzed ferric hydroxide, starch, agar, gelatine, and a clay. These were equilibrated with calcium carbonate, the total weight of calcium carbonate as well as the ratio of $CaCO_3$ to volume of sol being held constant at $1:10$. These mixtures were equilibrated on the mechanical shaker for one hour, and the pH values determined. The data obtained are given in Table 3 and are represented graphically in Figure 5.

TABLE 3.—EFFECT OF COLLOIDAL SOLS ON THE pH OF SUSPENSIONS OF PRECIPITATED CALCIUM CARBONATE.*

Colloid	Per cent colloid						Initial pH of sol	pH of CaCO₃
	1	0.5	0.1	0.05	0.01	0.001		
Agar	......	......	6.84	......	7.64	7.88	5.85	9.98
Starch	......	7.77	7.90	......	8.70	8.96	7.80	9.98
Gelatine	......	8.78	8.80	......	8.89	8.78	8.63	9.98
Fe(OH)₃	7.46	......	8.78	......	9.70	9.79	6.22	9.98
Clay	8.05	8.05	8.54	8.28	......	......	8.16	9.98

*Ratio of $CaCO_3$ to sol $= 1:10$.

The foregoing results show that colloidal materials are capable of materially reducing the hydrolysis of calcium carbonate. Such an effect would evidently result if the sol itself were initially acid. However, it will be observed that three of these sols were definitely on the alkaline side of neutrality, and in the case of the clay the resulting pH in the 1 and 0.5 per cent suspensions was less than that of either component before mixing. In this case, as in the experiment on the effect of neutral salts, the reduction in pH is greater the more concentrated the sol.

The mechanism by which the hydrolysis is reversed must be quite different from the effect induced by neutral salts. In this case the effect of the sol on the activity of the water is practically nil, as we may judge from the fact that in dilute lyophobic sols the freezing point of water is but slightly affected. There may, however, be an appreciable amount of water "bound" or rendered "inactive" by such hydrophiles as gelatine or agar, even in con-
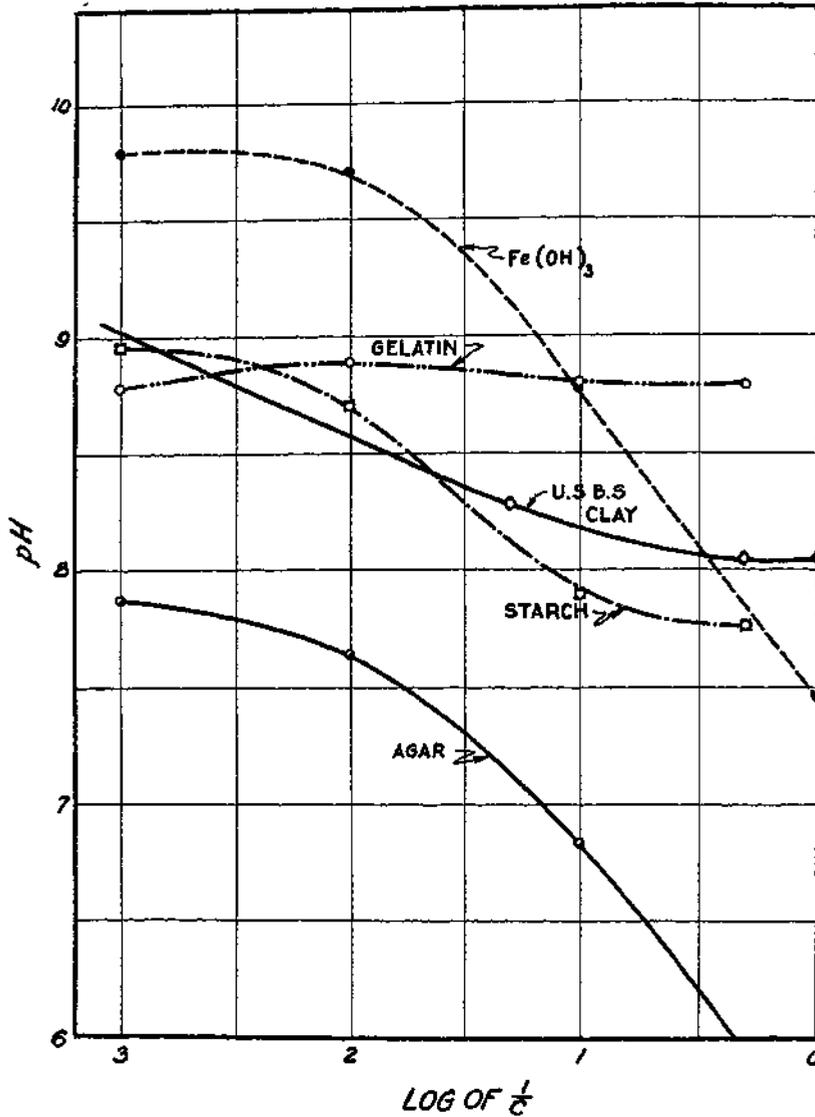
Figure 5.—Effect of colloidal solutions on the hydrolysis of calcium carbonate.

centrations as low as 0.1 per cent. It seems more convincing to assume that the colloidal material is adsorbed on the surface of the particles, forming a coating or protective film. When such a film is formed, hydrolysis is momentarily arrested, and the only process by which hydroxyl ions can be released into the solution, or water reach the calcium carbonate particle, would be

by diffusion through this protective film. Such a diffusion process would be very slow, as shown by experiment, for the pH does not change appreciably with the time, once the particle has been coated. Usually, as independent determinations on soils have shown, there is a marked decrease in the pH of a suspension with the time. The lowering of pH by the organic compounds cannot be attributed to the formation of carbon dioxide by bacterial action, for the time was too short for any appreciable oxidation to occur.

The data of Table 3 are significant also in that they indicate that any colloidal matter which may be present in the soil, whether organic or inorganic, will have the effect of reducing the pH of calcium carbonate. This is shown convincingly by Scarseth (27) working with highly organic Alabama soils, in which the pH was constant in spite of widely varying calcium carbonate content. His data are quoted as follows:

Soil type	Per cent CaCO$_3$	pH
Sumter clay	51.9	7.7
Sumter clay	9.3	7.6
Sumter clay	48.8	7.5
Houston clay	3.3	7.5
Houston clay	0.6	7.5
Houston black clay	17.6	7.5

These soils were all heavy clays, practically saturated with bases and would very probably have yielded the above pH value even if calcium carbonate had not been present.

The situation is markedly different, however, in the alkaline calcareous soils of arid regions. The organic matter content is very slight or nil, and the clays usually contain considerable amounts of replaceable sodium. Several Arizona soils from different localities were analyzed for total carbonate and the pH of 1:10 suspensions determined. The results of this study are shown in Figure 6, in which values of pH of soil suspensions are plotted against percentages of calcium carbonate in the soils. It will be observed that no correlation exists between the calcium carbonate content and the hydrolytic pH of these soils. When, however, the same soils were leached with neutral calcium chloride, washed with water until free from chlorides, and the pH of 1:10 suspensions determined, it was found that the pH became constant in all of the soils at a value of about 8.67. This is indicated by the horizontal straight line across the graph.

When the percentage of calcium carbonate was redetermined on these soils after leaching, it was found that it had not measurably changed. In other words, the leaching with calcium chloride simply converted the sodium clay to calcium clay and thus reduced the hydrolytic alkalinity to the equilibrium value for calcium zeolite. It seems logical to assume that the calcium carbonate in the case of these soils is likewise coated with a film or coating of
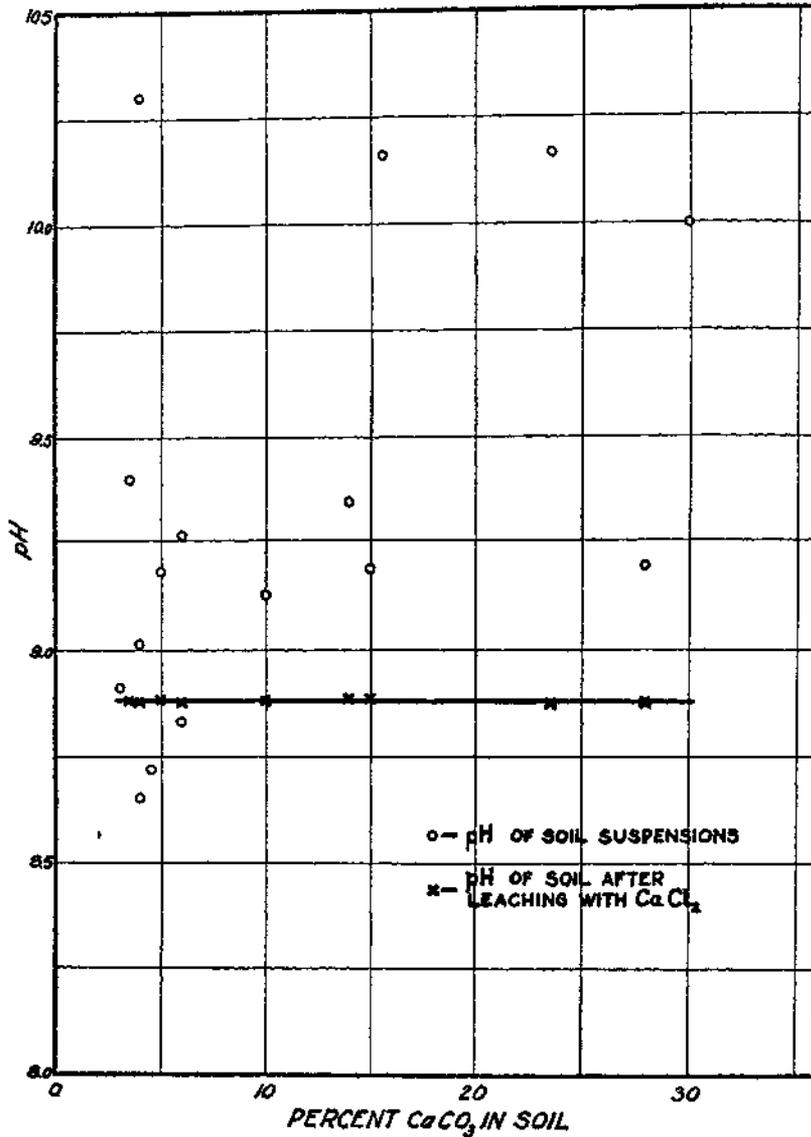
Figure 6.—Relation between calcium carbonate content and pH of calcareous soils.

clay which prevents its hydrolysis, and the alkalinity in such cases is the result of hydrolysis of the zeolites. This deduction is also substantiated by the results of McGeorge (16) on the effect of grinding in which he found that the pH continuously increased with the degree of fineness to which the material was ground.

Evidently the grinding exposed some of the previously coated particles, allowing them to hydrolyze.

EFFECT OF CALCIUM CARBONATE ADDITIONS ON THE pH VALUES OF SOILS

In order to throw further light on the effect of colloids on the hydrolysis of calcium carbonate, a series of experiments was carried out in which calcium carbonate was added to some acid and alkaline soils. Taking 10 grams as the weight of soil plus added calcium carbonate, four different alkaline soils and two acid soils were mixed in various proportions with precipitated calcium carbonate. These samples were made up to 1:10 soil-water ratios with neutral water, equilibrated as before and the pH determined. The results are shown graphically in Figure 7, in which pH values are plotted as ordinates and percentages of calcium carbonate as abscissae. The pH of the pure $CaCO_3$ was in all cases 9.70. It will be seen, as might have been anticipated, that the effect would be slight or nil in the case of alkaline calcareous soils but quite pronounced in the case of acid soils.
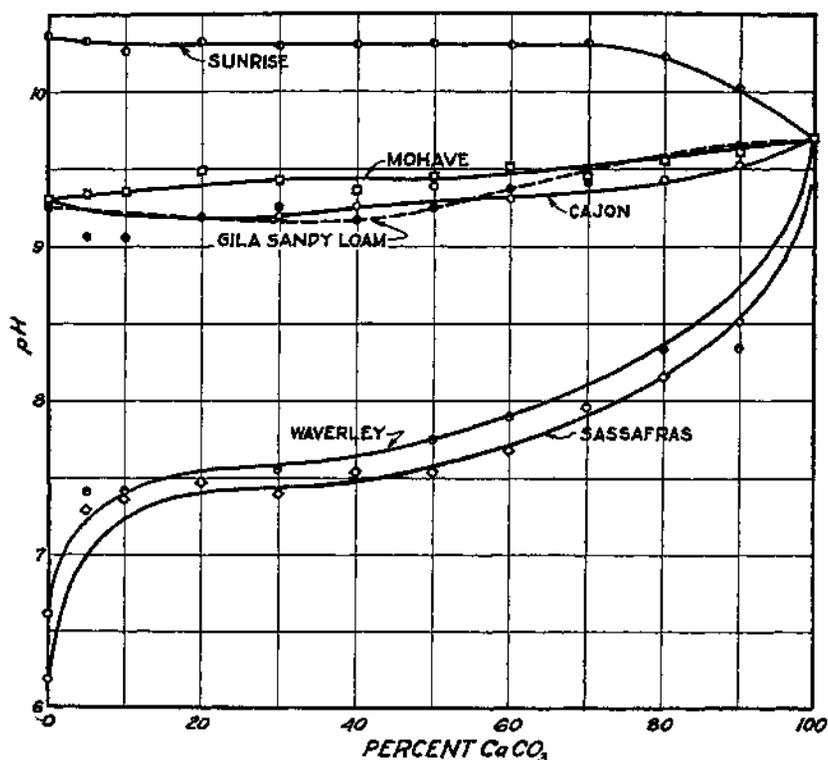

Figure 7.—Effect of calcium carbonate additions on pH of soils.

The intent of this experiment was to simulate by direct addition the formation of calcium carbonate in the soil, as may doubtless occur when an irrigation water high in calcium carbonate is applied to an alkaline soil. It was thought that possibly the pH of the three soils—Mohave, Cajon, and Gila sandy loam from the New University Farm—would be immediately increased to the pH of calcium carbonate when the percentage reached, say, 30 per cent. However, such was not the case, and a plausible explanation of this effect may be the salinity of these soils, which is sufficient to reduce the pH by 0.5 pH unit. It is likely that the reactivity of the carbonate, so far as hydrolysis and solubility are concerned, is not affected. It is still as readily soluble in carbonic acid as ever. Furthermore, it seems improbable that the calcium carbonate particles would be very extensively covered with an adsorbed film of clay or organic material, since under alkaline conditions the colloids all carry a negative charge. It should be pointed out that in the case of Figure 5, in which no correlation was obtained between the calcium carbonate content and the pH values, the soils considered were all *virgin* soils. The conditions might be fundamentally different in the case of calcium carbonate freshly precipitated on the surfaces of soil grains.

BUFFER CAPACITY OF SOME ALKALINE CALCAREOUS SOILS

A study of the buffer capacity of some alkaline calcareous soils and of calcium carbonate was made to determine its relation to the pH of these materials. The pronounced buffer action manifested by the carbonate-bicarbonate and the bicarbonate-carbonic acid systems is well known. Undoubtedly these buffer pairs function to some extent in soils to control their pH values. Numerous investigations have been carried out in this field, notably by Bradfield (3), Baver (1), Pierre (22), Meyers and Gilligan (18), and Wilson and Plice (35), but they have concerned themselves primarily with eastern humid soils. In the present experiments, electrometric titrations were carried out on four characteristic arid soils: Sunrise clay loam, Cajon silty loam, Gila sandy loam, and Gila sandy loam from the New University Farm. These soils vary widely in their calcium carbonate content and originate from totally different sources. The samples used were tube borings taken to a 4-foot depth and carefully composited to secure representative samples.

Since the clay complexes of these soils contain both exchangeable sodium and calcium, separate samples were first leached with calcium chloride before the electrometric titrations were made. The experimental procedure was as follows: 10 grams of the finely ground material was placed in the pH bottle, 100 cc. of carbon-dioxide-free water added, the mixture equilibrated for one hour and the pH measured. Tenth-normal hydrochloric acid was then added a few cc. at a time, and the mixture equilibrated on the shaking machine after each addition and the pH determined. The additions of acid were continued until the pH had been re-

duced to 4.5. The data so obtained for pure calcium carbonate are shown in Figure 8. The curve shows a sharp drop in pH after the first addition of acid, after which it remains constant over a wide range of acid additions. This constancy is obviously due to the bicarbonate-carbonic acid buffer system.
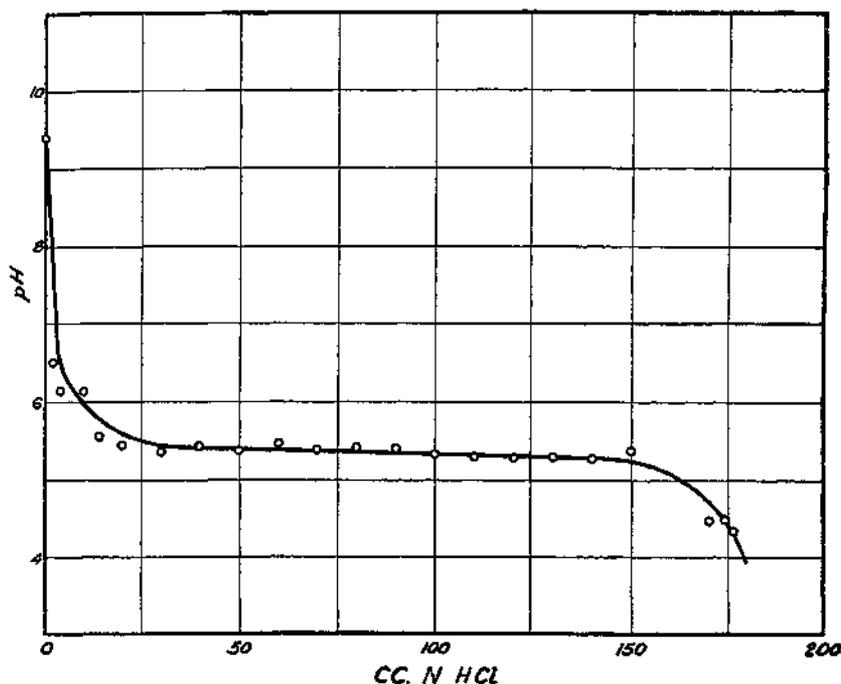

Figure 8.—Electrometric titration curve of pure calcium carbonate.

Corresponding curves for soils are shown in figures 9, 10, 11, and 12. In each case there is only one well-defined inflection point. Even in the case of pure calcium carbonate it was possible to realize only one inflection point. Usually the soluble carbonates yield two characteristic inflections. It follows that calcium carbonate, when titrated with hydrochloric acid, yields carbon dioxide immediately after the first addition of acid, and since the rate of reaction between the solid carbonate and the carbonic acid to form the bicarbonate is extremely slow, the first inflection point usually realized in carbonate titrations is entirely obliterated. At least it does not occur at the point corresponding to the volume of acid required for the conversion of all of the carbonate to the bicarbonate. The slight solubility of calcium carbonate is largely responsible for this effect. Presumably the bicarbonates would be formed only after long equilibration. It is significant, however, from a practical standpoint, that when acid is applied to the soil

Figure 9.—Electrometric titration curve for Sunrise clay.
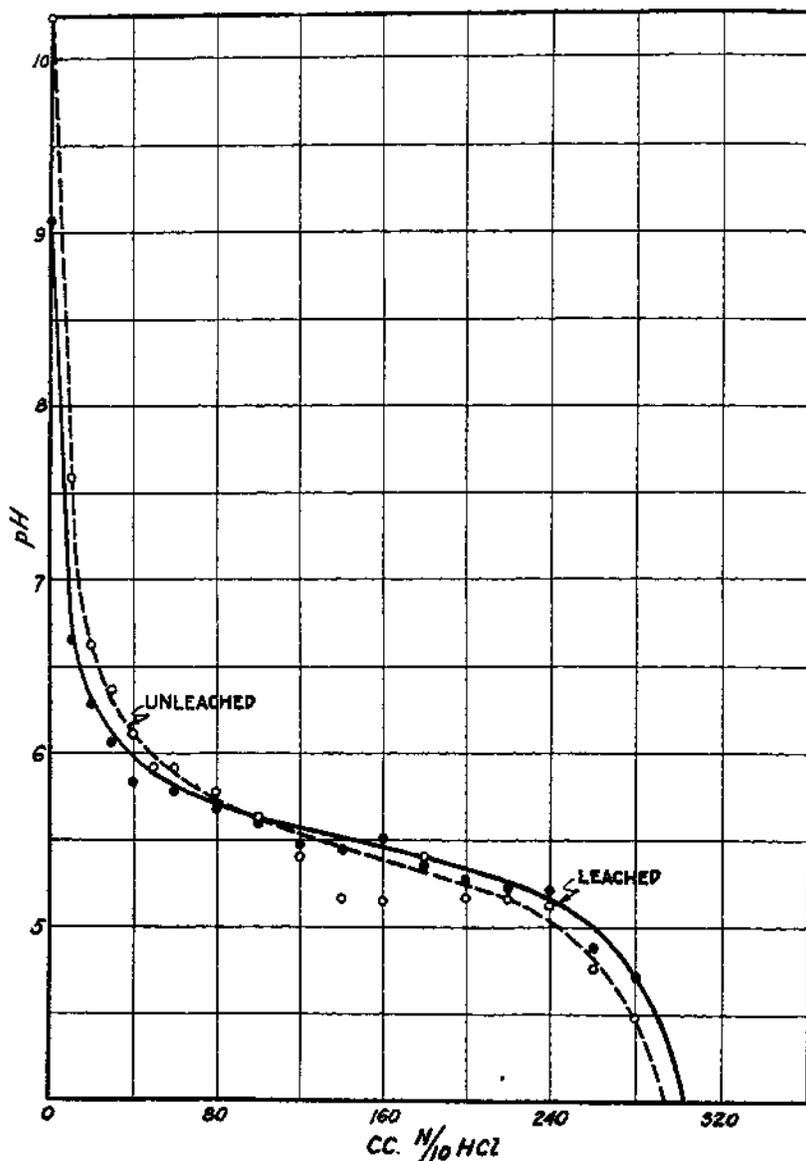
to reduce its pH, if the soil is high in calcium carbonate, a considerable proportion of the carbon dioxide formed will be liberated and lost from the soil as such, before it has had an opportunity to be converted to the bicarbonate.
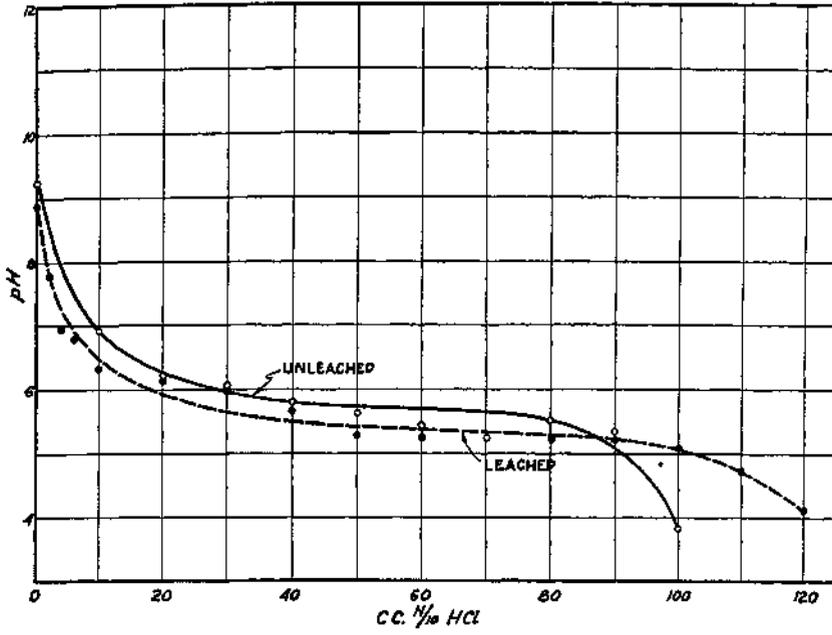
Figure 10.—Electrometric titration curves of Mohave clay loam.
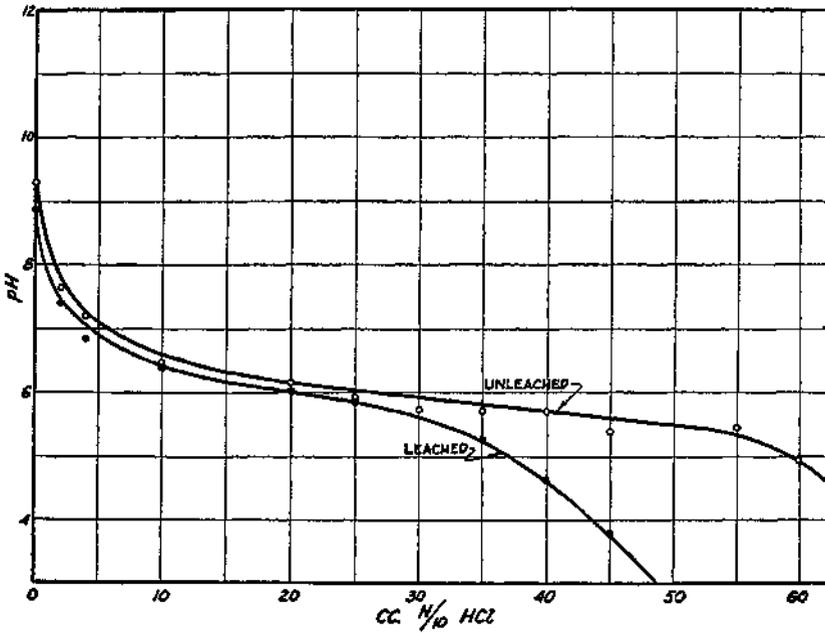

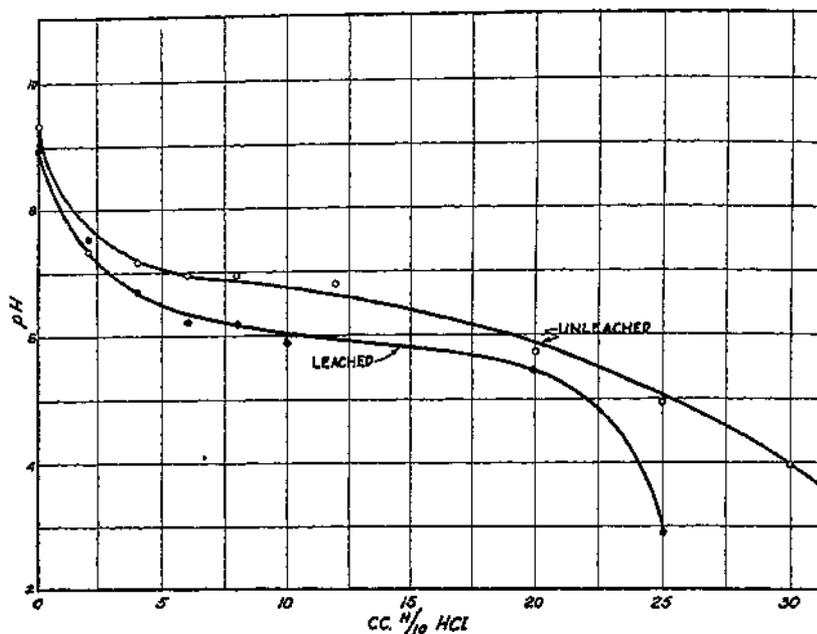Figure 11.—Electrometric titration curves of Cajon silty clay loam.

Figure 12.—Electrometric titration curves of Gila sandy loam from the
New University Farm.

Although calcium carbonate doubtless plays an important rôle
in contributing to the buffer capacity of alkaline calcareous soils,
it must be borne in mind that the zeolites also exert a pronounced
effect (15). The curves obtained for the soils in the above figures
do not show the marked constancy of pH over the wide range of
acid additions as does calcium carbonate. Instead, the pH de-
creases gradually until the final inflection point is reached. This
result suggests that the zeolites, which greatly predominate over
the calcium carbonate in the soils studied, must have a relatively
weak buffer action. The titration curves for calcium and sodium
bentonites are shown in Figure 13. The extent of buffering power
of any salt of a weak acid or base depends upon the dissociation
constant of the acid or base from which it was formed. We know
practically nothing concerning the strength of the clay acids, as
measured by dissociation constants, but if the buffering power is
less, as indicated by the gradual drop in pH of these soils, the
alumino-silicic acids composing the zeolites must certainly be
stronger than carbonic acid. An investigation to determine the
numerical values of these important dissociation constants, which
will further elucidate the peculiar behavior of the zeolitic com-
plexes, is now in progress. If the above deductions are correct,
and calcium zeolite and calcium carbonate are present together
in a soil, the carbonate will, upon treatment with an acid, react
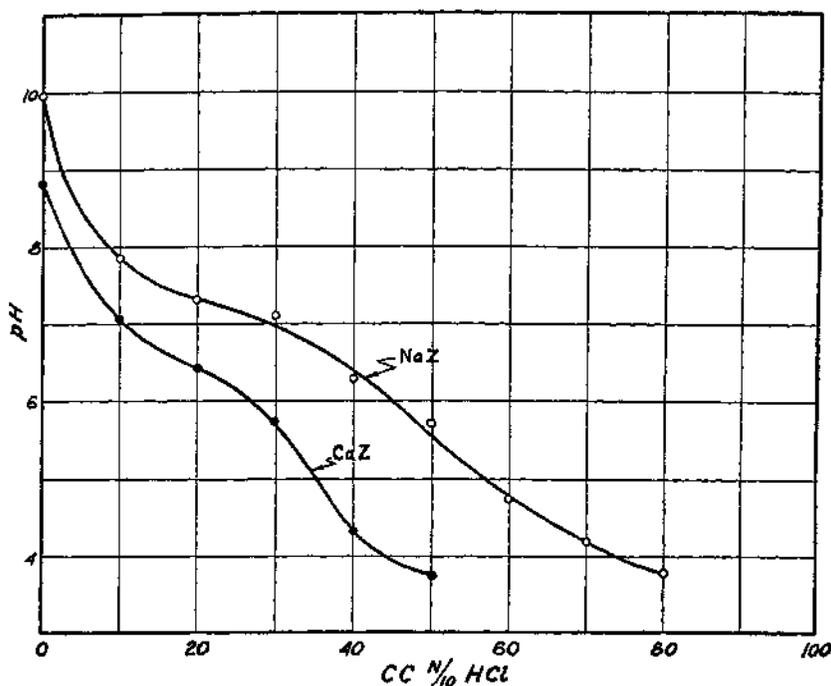first. This probably accounts for the ease with which calcium

Figure 13.—Electrometric titration curves of calcium and sodium bentonites.

carbonate disappears from neutral or slightly acid soils in which the base exchange complex is still highly saturated with bases.

A comparison of the curves for the leached and unleached soils shows that some of the alkalinity must result from hydrolysis of the clay fraction, since the pH is markedly lowered when the complex is saturated with calcium. Independent determinations of pH on a calcium saturated bentonite clay gave an average value of 8.67, while the pH of the corresponding sodium saturated clay was above 10.0.

From the data obtained in these electrometric titrations, the specific buffer capacities of the leached and unleached soils, sodium and calcium bentonite, and of calcium carbonate have been calculated after the method of Pierre (22). The data are given in Table 4.

The term "total buffer capacity" as here used is that of Pierre (22), being defined as the number of cc. of normal acid required to reduce the pH of 100 grams of the soil from its initial pH to a final pH of 4.8. The specific buffer capacity is defined as the total buffer capacity divided by the total change in pH.

The results in Table 4 show that the magnitude of the specific buffer capacity of alkaline calcareous soils is considerably higher than that of the partially unsaturated noncalcareous soils of humid

TABLE 4.—BUFFER CAPACITIES OF SOME ALKALINE
CALCAREOUS SOILS AND SOIL COMPONENTS.

Soil or compound	Initial pH	Total buffer cap. (cc. N acid)	Specific buffer capacity	Per cent CaCO₃	Spec. buffer capacity calc. from per cent CaCO₃
1. Sunrise clay					
Unleached	10.24	264	48.9	19.81	71.3
Leached	9.06	276	65.7		
2. Cajon f s.l.					
Unleached	9.28	60.8	13.5	4.67	17.0
Leached	8.88	39.0	9.0		
3. Mohave c.l.					
Unleached	9.21	94.5	21.5	7.00	25.5
Leached	8.88	108.5	25.2		
4. Gila sandy loam					
Unleached	9.33	26.0	5.8	4.07	14.8
Leached	8.95	23.0	5.2		
5. Ca-Bentonite	8.82	36.5	9.1	trace	......
6. Na-Bentonite	9.94	60.0	11.7	trace	.....
7. CaCO₃	9.40	168.0	365.0	100	365.0

regions. For comparison the following data from Pierre (22) may
be cited:

	pH	S.b.c.
Norfolk sand	5.65	0.35
Brown silt loam	6.15	1.19
Saginaw clay	6.60	3.11
Yolo silty clay loam	7.00	5.62

The difference is due to calcium carbonate content and high degree
of saturation of the arid calcareous soils.

If, as we have postulated, the high buffer capacity is due pri-
marily to the calcium carbonate present, and if the buffer mechan-
ism involves primarily the bicarbonate-carbonic acid buffer pair,
it should be possible to estimate the specific buffer capacity of
these soils from the percentage of calcium carbonate present and
the specific buffer capacity of the calcium carbonate itself, assum-
ing of course that the calcium carbonate is in the reactive form.
This was done by multiplying the specific buffer capacity of cal-
cium carbonate by the percentage of calcium carbonate present
in each of the four soils in Table 4. The results are given in the
last column of the foregoing table. The agreement between the
calculated values and those obtained from the electrometric titra-
tion curves is not very close, but it is significant that they are of
the same order of magnitude. In the case of the Sunrise clay
which is a heavy soil containing a high proportion of replaceable

sodium, the buffering power toward acids is doubtless due in part to the zeolite complex.

It will be seen, however, that the specific buffer capacities of sodium and calcium bentonites (expts. 5 and 6) are relatively low, being 11.7 and 9.1 respectively. The reason for this may be a relative irreversibility of the base exchange reaction. We are therefore inclined to believe that the buffer capacity is due principally to the calcium carbonate—that is, to the carbonate-bicarbonate-carbonic acid buffer system. It must be borne in mind that the calcium carbonate because of its low solubility serves mainly as a reservoir for carbonate and bicarbonate ions, and that the amount of free carbonate ions in a calcareous soil may be appreciable but generally very small. The bicarbonate-carbonic acid buffer pair is without doubt the principal factor in keeping the pH constant in spite of considerable addition of acid.

RELATION OF THE pH IN CaCO₃ TITRATIONS TO THE CARBONIC ACID-BICARBONATE EQUILIBRIUM

In order to determine whether or not the carbonic acid-bicarbonate buffer pair controls the equilibrium in a soil discussed in the foregoing, an experiment was carried out in which the soil samples were equilibrated with hydrochloric acid solution and the pH measured. The equilibrium solutions were then analyzed for carbonic acid and bicarbonate ion. From the data obtained, the pH was calculated from the first ionization constant of carbonic acid.

Samples of Mohave clay loam, each weighing 25 grams, were made up to 1:10 suspensions by addition of 250 cc. of carbon-dioxide-free water. Varying amounts of normal hydrochloric acid were then added, and after equilibration, the pH values determined. The mixtures were then allowed to settle as completely as possible, and aliquot volumes taken for titration. The free carbonic acid was determined by titration with N/100 sodium hydroxide solution, and the bicarbonate by titration with N/50 sulfuric acid. The results are shown in Table 5.

TABLE 5.—BUFFER EQUILIBRIUM IN A SOIL SUSPENSION TREATED WITH HYDROCHLORIC ACID SOLUTION.

Expt. no.	Cc. N HCl added	(H_2CO_3) mols /L.	(HCO_3^-) mols /L.	pH calc.	pH obs.
1	0.5	5×10^{-5}	2.76×10^{-3}	8.20	7.77
2	1.0	2.16×10^{-4}	2.84×10^{-3}	7.58	7.37
3	2.5	5.30×10^{-4}	3.64×10^{-3}	7.30	6.62
4	5.0	1.10×10^{-3}	4.08×10^{-3}	7.04	6.42
5	7.5	1.75×10^{-3}	4.14×10^{-3}	6.83	6.12
6	10.0	2.15×10^{-3}	3.74×10^{-3}	6.69	5.50

While the calculated and the observed pH values in Table 5 are not very closely concordant, the agreement is nevertheless striking in the respect that various other equilibria may be set up

in so complex a system as a soil. Unavoidable errors in the analytical technique may account for part of the discrepancy, although every possible precaution was taken in sampling and titration, especially to avoid loss of carbon dioxide. The consistency in trend and magnitude of the results suggests that the carbonic acid-bicarbonate buffer pair is in large measure responsible for the equilibrium pH of calcareous soils.

In view of the fact that the carbonic acid equilibrium involves two buffer pairs—namely, carbonate-bicarbonate and bicarbonate-carbonic acid, the foregoing calculation does not give the complete picture. It seemed of considerable interest to inquire into the mutual relationship of these two equilibria. The method chosen was to calculate from the respective ionization constants the pH of a calcium carbonate suspension, under three different assumptions, as follows:

1. *That the equilibrium is governed solely by carbonic acid and bicarbonate ion.* For this step,

$$K_1 = \frac{(H^+)\ (HCO_3^-)}{(H_2CO_3)} = 3.50 \times 10^{-7}.$$

From analytical data for bicarbonate and carbonic acid, as in the foregoing case, (H^+) is calculated and from it the pH value. The quantities in parentheses are concentrations expressed in mols per L.

2. *That the equilibrium is governed by the second ionization of carbonic acid only.* For the second step,

$$K_2 = \frac{(H^+)\ (CO_3^{--})}{(HCO_3^-)} = 3.73 \times 10^{-11}.$$

In this case the carbonate-ion concentration, since an excess of solid calcium carbonate is present in the equilibrium measurements, is assumed to be constant. For the present calculations, the value given by Seidell (28) for the solubility of calcium carbonate in distilled water at 25 degrees C.—namely 5.1 × 10⁻⁴ mol per L.—was used. The bicarbonate concentration was in all cases taken to be substantially identical with the number of mols of acid added, since the reaction occurs:

$$CaCO_3\ (s) + H^+\ (x\text{-}m) = Ca^{++}\ (xm) + HCO_3^-\ (xm)$$
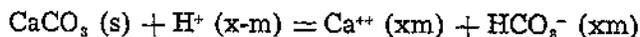
in which 1 mol of HCO_3^- is formed for every mol of H^+ added.

3. *That the equilibrium is governed by the two simultaneous step ionizations of carbonic acid.* In this case we assume that the carbonate ion from the dissolution and ionization of calcium carbonate goes directly to carbonic acid, and that the carbon dioxide formed practically saturates the equilibrium solution. This condition was actually observed in the experiments, and it is also an established fact that the carbon dioxide liberated in the soil is not all held in solution but passes out of the soil in large proportion

as soon as formed. This case involves the logical difficulty, however, that in order to be valid over the entire range of pH values from the highly alkaline to the highly acid condition, it must be possible to assume that carbonic acid can exist as such in the presence of free hydroxyl ions. This is obviously impossible, hence calculations made on the basis of the third assumption must be regarded as unreliable in solutions of high pH values. At any rate, on the basis of this assumption we obtain by multiplying the expression for K_1 by K_2 an equation as follows:

$$K_1 . K_2 = \frac{(H^+)^2 \ (CO_3^-)}{(H_2CO_3)}$$

in which the carbonate-ion concentration (CO_3^{--}) is considered to be represented with sufficient accuracy by the solubility of the calcium carbonate, which is present as a solid in excess, and the concentration of carbonic acid (H_2CO_3) is given substantially by the number of mols of acid added, assuming that all of the carbonic acid formed remains in solution.

The results are assembled in Table 6.

TABLE 6.—COMPARISON OF pH VALUES AT EQUILIBRIUM IN SUSPENSIONS OF CALCIUM CARBONATE TREATED WITH VARIOUS AMOUNTS OF ACID.*

Millimols HCl added	pH calculated			pH obs.
	Assumption No. 1	Assumption No. 2	Assumption No. 3	
0.5	8.20	......	......	7.77
1.0	7.58	10.14	8.30	7.37
5.0	7.02	9.14	8.05	....
10.0	6.69	8.85	7.80	5.50
20.0	6.00	8.60	7.65	5.45
50.0	5.40	8.43	7.45	5.35
100.0	4.55	8.14	7.30	5.30
150.0	4.30	8.00	7.24	5.35
175.0	3.84	7.90	7.19	4.45
200.00	3.00	7.84	7.15	......

*Wt. $CaCo_3$ = 10 gm. Initial pH = 9.40.

The foregoing results show that the closest agreement is obtained with the observed pH values on the basis of the first assumption—namely, the first ionization step of carbonic acid. The agreement holds surprisingly well even in the alkaline solutions. This finding substantiates the conclusion that when solid calcium carbonate reacts with an acid, the reaction takes place on the surface of the solid particles, forming carbonic acid directly, and since the carbonate ions go into solution slowly, the equilibrium in which bicarbonate is formed does not establish itself. Such is obviously not the case in readily soluble carbonates in which the concentration of carbonate ions is high and in which the step neutralization is very precisely realized by electrometric methods.

For the converse reason it is impossible in the case of calcium carbonate to realize the inflection point at which it is half neutralized.

In the electrometric titration for calcium carbonate shown in Figure 8, the first inflection point is not realized, but when the second one is closely examined, it is found that it does not occur at the stoichiometric end point. It will be recalled that a 10-gram sample of calcium carbonate was electrometrically titrated, which should have required, for complete conversion to carbonic acid, 0.2 mol of hydrochloric acid or in other words, 200 cc. of N acid. Reference to the graph will reveal that it actually required about 175 cc. N acid to dissolve completely the calcium carbonate initially present. Evidently the end point was premature, and a simple computation indicates that the reaction, at the point of inflection of the curve, had proceeded 75 per cent to form carbonic acid and 25 per cent to form bicarbonate ions. The constancy of pH at 5.4 is due to the carbonic acid-bicarbonate buffer pair. The inflection occurring at pH 4.5 represents the value for a saturated solution of carbon dioxide.

Some investigators, notably Wilson and Plice (35), endeavored to correlate the buffer capacity of soils with their initial pH values. Doubtless the soils they investigated contained only small amounts of calcium carbonate, and as a result the major portion of the buffer capacity was due to the clay fraction and organic matter in the soil. In the case of alkaline calcareous soils we have found no such correlation, for as the buffer curves for the soils show (figures 8, 9, 10, and 11), the soils studied all had very nearly the same pH in neutral water, yet their buffer capacities toward acid as shown by Table 3 are strikingly different. However, when we plot the specific buffer capacity of the unleached soils in question against the percentage of calcium carbonate they contain, we obtain approximately a straight line relationship, even though the soils differ markedly as to type, exchangeable bases, etc. This line of evidence is regarded as independent proof that calcium carbonate is essentially responsible for the buffering power of alkaline calcareous soils.

In connection with a discussion of the influence of calcium carbonate upon the buffer capacity of soils, it is of interest to mention its relation to the reduction of the pH of a highly calcareous soil in the field. Breazeale and McGeorge (4) have shown that plants manifest nutritional disorders in alkaline soils. It has been suggested by McGeorge (16) that to remedy this defective condition, it would not be necessary to reduce the pH of such a soil completely to neutrality; in fact, as the buffer curves show, it would require a considerable amount of acid to bring such a soil to neutrality, so that economically the practice would be prohibitive. However, if sufficient acid were added to reduce the pH of the first foot of soil to a point, say 7.8, at which the plant could absorb phosphates and nitrates efficiently, such an acid treatment might be economically desirable. In the soil buffer curves previously presented, it will be seen that the drop in pH after the initial additions of acid is

very abrupt; in such soils the acid treatment should be and has been found by McGeorge to be successful. It is quite possible, however, that such a reduction in pH may at best be only temporary in duration.

DISCUSSION

A discussion of the foregoing results in the light of our present knowledge necessitates keeping in mind the logical implications and limitations of physicochemical principles which govern the complicated problem of hydrolysis in mixtures and of such reactions at surfaces or interfaces. In the case of calcium carbonate we are dealing with a solid salt, slightly soluble, highly polar, capable of existing in several states and as double and basic salts, and in addition formed from a weak acid which is capable of undergoing ionization in two steps. The reaction with which we are concerned is as previously written:

$$CaCO_3 \text{ (s)} + H_2O \text{ (l)} = Ca^{++} \text{ (xm)} + HCO_2^- \text{ (xm)} + OH^- \text{ (xm)}.$$
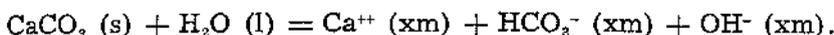
That this reaction involves a surface factor may be deduced from several lines of experimental evidence. In the first place the fact that the pH varies with dilution, that is, the $CaCO_3$-H_2O ratio, shows that a finite amount of material dissolves from the surface, which is essentially proportional to the amount of solid taken. In every dilution studied, there was present a considerable excess of calcium carbonate over that required to saturate the water taken. With a solubility of the order of 10^{-4} mol per L., or about 10 parts per million, it is evident that even in the highest dilution studied, namely 1:100, in which 1 gram of calcium carbonate was taken per 100 cc. of water, or 10 grams per liter, there should have been present a sufficient amount to saturate 10,000 liters of water. Elementary reasoning would lead to the conclusion that if the solutions were in all cases saturated with calcium carbonate, the concentration of the salt and hence the degree of hydrolysis would have been the same in all cases. Apparently this is true only after a limiting dilution, e.g., 1:10, is reached. At lower dilutions, 1:1, 1:2, or 1:5, the pH is considerably less than the maximum value.

It seems evident that either the surface of the particle is definitely changed when a layer of molecules is stripped off and put into solution, or the rate at which further molecules go into solution is extremely slow. This point of view is substantiated by the effect obtained on grinding the material. We have found that when calcite is ground in a ball mill for an extended period of time, its pH at a given dilution increases. McGeorge (16) found this to be true in the grinding of soils. It is also shown by the fact that precipitated calcium carbonate gives a considerably higher pH than the pulverized calcite. Hulett (10) found that grinding gypsum to a high degree of subdivision increased the solubility of the material by as much as 20 per cent.

In order to gain a little further insight into this phenomenon, an experiment was carried out with a soil in which the dilution was kept constant throughout at 1:10, but the absolute amounts of soil by weight were varied. The results were as follows:

TABLE 7.—EFFECT OF VARYING THE ABSOLUTE WEIGHTS OF SOIL AND WATER TAKEN UPON THE pH OF THE 1:10 SUSPENSION.

Wt. of soil (gm.)	Cc. neutral water	pH
3	30	8.20
4	40	8.56
5	50	8.61
8	80	8 84
10	100	9.02
15	150	9.02
20	200	9.11

These data show that the pH is influenced rather markedly by varying the absolute weight of soil taken, even though the ratio of soil to water be held constant. An increase in pH of nearly one unit is observed with a sevenfold increase in weight of sample. True it is that so complex a mixture as a soil may vary in composition from particle to particle and from sample to sample. However, in this experiment the material was mixed and sampled with unusual care. If the above data are plotted, it is found that the pH rises gradually as the size of sample increases, and the curve suggests that beyond 20 grams the pH would be substantially constant at constant soil-water ratio. In other words the phenomenon seems to involve the law of probability to the extent that in the smaller samples the distribution of calcium carbonate, sand, and clay particles may vary rather widely, and beyond a certain limiting number of particles the distribution may be relatively constant, hence also the pH of the suspension. If a method were available by which the percentage of calcium carbonate particles could be determined, it is quite probable that other things being equal the pH would be in proportion to the number present. This experiment serves to emphasize the fact that in making pH measurements on suspensions of granular solid materials, it is necessary not only to specify the ratio of weight of solid to that of water but also *the absolute weight of soil sample* to be taken. Unless this is done, the results of no two investigators working with the same soil can be correlated.

There is another factor, however, which comes into play in this effect of dilution upon the hydrolysis of a salt. It is well known that when a soluble salt, such as sodium acetate or carbonate, is continuously diluted, the degree of hydrolysis increases. Since the concentration of dissolved salt decreases with dilution, and since the concentration of free hydroxyl ions is the product of these two factors, it is conceivable that a concentration will ultimately be reached where the hydrolytic alkalinity will actually decrease toward the pH of pure water. In the case of slightly

soluble salts the time factor becomes important, since rate of dissolution is usually very slow.

Finally, one might attribute this dilution effect in part to the peptizing action of water, particularly in the absence or high dilution of electrolytes. In colloidal dispersion the degree of hydrolysis would doubtless be considerably increased.

CHEMICAL NATURE OF CALCIUM CARBONATE

It has been shown in the data of a previous section that calcium carbonate can exist in various forms in the soil. The two mineral forms, calcite and aragonite, and the conditions under which they transform into one another have been investigated in some detail by Vetter (31), Hatschek (9), Vaubel (30), and Johnston and Williamson (11). Investigators are not agreed as to the exact nature of the transformation. According to Vetter, the formation of aragonite and of hydrous calcium carbonate is not so much dependent upon the concentration of salt in the solution as on the presence of particular salts, notably those of magnesium. The hydrous phase would form in nature only under the most favorable conditions, such as low temperature, supersaturation, and the presence of organic substances. Tiny needles of aragonite were observed to build up into spherulites and these into spherical aggregates of calcite. Vaubel (30) states that aragonite contains a basic carbonate having an average of two OH groups in sixty-three molecules of $CaCO_3$. He assumes that in the aragonite unit molecule only one simple $CaCO_3$ molecule is present, whereas in calcite there is one double calcium carbonate molecule $(CaCO_3)_2$ for every eight molecules of $CaCO_3$. Artificial aragonite can be prepared only from dilute solutions and at temperatures higher than 30 degrees C. Hatschek (9) found that when concentrated calcium chloride and concentrated sodium or ammonium carbonate are mixed and heated to temperatures from 15 degrees C. to the boiling point, calcite is formed exclusively. Aragonite is the usual form precipitated in the stalactites of limestone caves (36).

While the foregoing findings do not appear to approximate soil conditions, it may be said that certain conditions exist in the soil which may favor such a transformation, namely the temperature, which may vary from below 30 degrees C. to some value above this limit. The ions which appear to catalyze the transformation of one form into the other are present in the soil solution. Certain it is that these two crystalline modifications have quite different properties. Aragonite is more soluble than calcite; pH measurements have also shown that it hydrolyzes to a greater extent than calcite; for example, in the 1:25 and 1:50 dilutions, the pH values of aragonite are 9.82 and 9.97 respectively. The corresponding values for calcite are 8.96 and 9.29.

In the laboratory preparation of calcium carbonate from different reagents, it was repeatedly observed that the products obtained had variable properties, not only in the manner in which they crystallized out but also in the extent to which they hydro-

lyzed. From the method of preparation it was possible to estimate qualitatively which of the crystal forms, calcite or aragonite, appeared to predominate in the final precipitate. The conditions of temperature and concentration, together with the length of time of contact of precipitate with solution, which might allow supersaturation to disappear slowly by the crystallization of calcium carbonate from the solution, were such as to favor the formation of one modification over the other. A photomicrographic study will be made of the materials obtained under these different conditions. Also solubility studies are contemplated to ascertain somewhat more closely the conditions under which the transformation occurs.

The nature of the reagents profoundly affects the character of the final product. In this connection an investigation is in progress to prove whether or not calcium carbonate might form either a basic carbonate analogous to that of magnesium and of the probable formula $CaCO_3.Ca(OH)_2.xH_2O$ or a double carbonate with sodium as suggested by Wegscheider (33), which has the formula $Na_2Ca(CO_3)_2$. The precipitations were made with calcium chloride solution and either ammonium carbonate or mixtures of sodium carbonate with varying amounts of sodium hydroxide. The precipitates obtained were washed with water or alcohol and dried.

It was found that only the precipitation with ammonium carbonate gave a product that had a percentage composition closely agreeing with that of calcium carbonate. The precipitates were granular and easy to wash free from excess of electrolyte. It was found also that precipitation from calcium hydroxide solution by means of carbon dioxide gas yielded a precipitate free from adsorbed impurities, but due to the fact that the solution had to be boiled in order to decompose the bicarbonate formed, it is not unlikely that the precipitate, though it had the true chemical composition, really consisted of a mixture of calcite and aragonite. In the remaining experiments in which the calcium carbonate was prepared by precipitation with sodium carbonate, either with or without added sodium hydroxide, the precipitates were extremely difficult to wash even with alcohol. Upon analysis they were found to contain sodium (gravimetrically determined as sodium uranyl zinc acetate) in amounts directly proportional to the concentration of sodium in which the precipitations were made. Whether these precipitates were double carbonates of calcium and sodium or solid solutions of one in the other, or whether the sodium carbonate was merely adsorbed on the surfaces of the calcium carbonate particles is difficult to establish on the basis of analysis alone, for the reason that the composition by weight is not greatly different from that of pure calcium carbonate.

However, the conditions under which the amorphous form of calcium carbonate is precipitated may obtain also, when a calcium-bicarbonate-bearing irrigation water is applied to an alkaline soil, and would seem to indicate a strong possibility of the existence of such a complex in the soil. Incidentally, when the pH of 1:10 suspensions of these synthetic carbonates were determined, it was

found that they were extraordinarily high, much higher than the pH of calcite or of the calcium carbonate precipitated by the use of ammonium carbonate. While these experiments have not yet been carried to completion and the results are still preliminary in nature, there seems to be definite evidence that such an amorphous and highly hydrated, colloidal form is precipitated in the soil and may be far more soluble and hydrolyzed than the mineral modifications described above. The nature of the calcium carbonate in caliche hardpans is of considerable interest in this connection.

There is finally the form of calcium carbonate which exists in the soil with a strongly adsorbed film or layer of colloidal material, either organic or inorganic in nature, and which is relatively inert so far as the hydrolytic action of water or the solvent action of carbon dioxide is concerned. We do not yet have extensive evidence on this point, and it is planned to make studies with the petrographic microscope on thin sections of soil material to establish this point. X-ray studies are also contemplated in this connection.

BUFFER ACTION IN SOILS

The nature of the buffer action in alkaline calcareous soils is an intriguing problem which has not yet been satisfactorily elucidated. Russell (25) in a discussion of the compounds in the soil which can exert buffer action enumerates the following: (1) organic matter, (2) clay, (3) phosphates. He does not include carbonates which as shown by the foregoing experiments may be most pronounced in their buffering power, particularly in arid soils.

Experimental evidence obtained in this investigation points rather definitely to the buffer rôle which calcium carbonate plays in arid soils. First, calcium carbonate is more reactive than the zeolites or organic matter. It is a simple inorganic salt, highly ionized, and does not depend upon oxidation or base exchange to exert its buffer action. Moreover, its buffer capacity has been shown to be considerably higher than that of sodium- or calcium-saturated bentonites. The pH of the soil as well as of calcium carbonate suspensions may be fairly closely calculated from the ionization constants of carbonic acid and of water. The interchanges between carbonic acid, bicarbonate ion, and carbonate ion are rapid and readily reversible. Hence its buffer action would very promptly manifest itself.

CONCLUSIONS

1. A study has been made of the conditions which affect the hydrolysis of calcium carbonate and the extent to which it contributes to the alkalinity of calcareous soils.

2. It was found that the hydrolytic properties of calcium carbonate depend upon the past history and method of preparation of the solid material.

3. Leaching calcium carbonate samples of different initial pH values with neutral water with intermittent measurement of pH showed that a constant pH is finally reached, which was numerically equal to 9.70.

4. The mean pH value of 9.50 as found for 1:10 calcium carbonate suspensions in neutral water is proposed as the standard pH value for pure calcium carbonate. This value is in close agreement with that of other investigators.

5. The pH of calcium carbonate varies with the dilution of the suspension, increasing markedly at the lower $CaCO_3$-H_2O ratios and remaining constant beyond a dilution of 1:25. This variation is believed to be due to a surface effect, as it depends upon the absolute amount of solid in contact with the solution.

6. Carbonates from different sources, such as the mineral calcite, aragonite, and precipitated calcium carbonate showed marked differences in their hydrolytic behavior, the pH at any given dilution being in the order named. The fact that the precipitated form gives the highest pH values is attributed principally to fineness of subdivision. The higher hydrolytic activity of aragonite in comparison with that of calcite is consistent with other physicochemical and crystal properties of these minerals. It is suggested that both forms may be present simultaneously in soils under certain conditions.

7. The effect of neutral salts was to reduce the hydrolysis of calcium carbonate, the order in which the chlorides of calcium, magnesium, potassium, and sodium affected it being approximately that of the lyotropic series.

8. Organic and inorganic colloidal materials are found to decrease the hydrolysis of calcium carbonate markedly. This effect is attributed to the adsorption of a film of the colloidal material, which inhibits the further hydrolysis of the calcium carbonate particles. The sol itself may also adsorb some of the free hydroxyl ions which are present in solution as a result of the hydrolysis. It is suggested that this may account for the fact that some soils containing considerable calcium carbonate may not be appreciably alkaline and even neutral.

9. When calcium carbonate is added to alkaline soils, there is no appreciable effect on the pH. In the case of acid soils the effect closely approximates an ordinary electrometric buffer curve for the soil, with a very pronounced increase in pH upon additions up to 10 per cent by weight of calcium carbonate, beyond which the pH slowly rises to that of pure calcium carbonate.

10. Buffer titration curves for calcium carbonate, sodium and calcium bentonites, and for four alkaline calcareous soils were obtained. It was found that the calcium carbonate gives only one inflection point corresponding to the total neutralization of the sample taken. The pH remains constant over an extended series of additions of acid, indicating high buffer capacity. The sodium and calcium bentonites on the other hand showed relatively slight buffer action.

11. A correlation of these results with similar curves for soils leads to the conclusion that the buffer capacity of these soils is due in large measure to the calcium carbonate present. This is also substantiated by the fact that the specific buffer capacity of calcareous soils is found to be approximately a linear function of the percentage of calcium carbonate present.

12. Calculations from the ionization constants for carbonic acid, made on the basis of three different assumptions, showed that the first ionization constant reproduces the observed pH values for the buffer titration of calcium carbonate most closely. It is concluded that this equilibrium is the predominant one in determining the pH of calcium carbonate and of soils.

13. Various evidences have been adduced to show that calcium carbonate controls the pH equilibrium in alkaline calcareous soils as follows:

a. Calcium carbonate is more reactive than the zeolites or soil organic matter.

b. Calcium carbonate has a higher buffer capacity than the calcium- and sodium-saturated bentonites.

c. Arid soils usually have a very low organic matter content and yet show a high specific buffer capacity.

d. The carbonate-bicarbonate-carbonic acid interchanges are more readily reversible than is the base exchange equilibrium in zeolites, which upon hydrolysis take up hydrogen ions into the base-exchange complex.

e. The pH of a soil may be estimated fairly closely from the ionization constants for carbonic acid, showing that the carbonic acid equilibria predominate.

14. Analysis of solutions resulting from the equilibration of a calcareous soil with various amounts of acid and calculation of the pH values from the concentrations of bicarbonate ions and free carbonic acid gave substantial agreement with observed pH values. This is regarded as evidence that the carbonic acid equilibrium determines the hydrolytic pH of a calcareous soil, provided the amount of soluble carbonates is not high.

15. Various considerations lead to the conclusion that calcium carbonate probably exists in calcareous soils in one or more of the following forms:

a. Calcite

b. Aragonite

c. Basic calcium carbonate: $CaCO_3.Ca(OH)_2.xH_2O$

d. A double sodium-calcium carbonate: $CaCO_3.Na_2CO_3$

e. A highly hydrated, amorphous form resulting from recent precipitation on or between soil particles.

f. $CaCO_3$ particles coated with an adsorbed film of a protective organic or inorganic colloid.

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