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## FACTORS CONTRIBUTING TO THE REACTION OF SOILS AND THEIR *pH* MEASUREMENT

By

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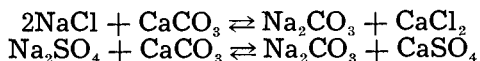
# FACTORS CONTRIBUTING TO THE REACTION OF SOILS AND THEIR pH MEASUREMENT

BY W. T. McGEORGE

## INTRODUCTION

Investigations pertaining to the factors responsible for the alkaline reaction of soils, notably black alkali types, have passed through two rather clearly defined periods. The first is that in which the Hilgard theory dominated, while the second began with the investigations of Gedroiz.

Hilgard attributed alkalinity largely to sodium carbonate and explained its presence in soils by chemical reactions between the soluble salts of sodium and calcium carbonate.



Since these reactions are reversible it is obvious that an excess of calcium salts will reduce the alkalinity of the soil but not completely neutralize it unless the products of the reaction, NaCl and Na<sub>2</sub>SO<sub>4</sub>, are removed by leaching.

During most of the period in which the Hilgard theory dominated quantitative methods were used for determining alkalinity, and the results were expressed as total alkalinity or titratable alkalinity.

Although the Hilgard theory contributed greatly to our understanding of alkali soils, and effective soil reclamation was usually accomplished by gypsum applications and leaching, and often by leaching alone, many important phases of the problem still remained unsolved during this period. The behavior of some alkali soils when subjected to reclamation could not be explained on the basis of the knowledge which had accumulated during this period. Evidence of this was shown by the fact that many alkali soils underwent serious structural deterioration after the alkali salts were removed by leaching, a condition usually referred to as a "freezing up" of the soil.

During the second period a number of these more baffling problems were clarified by the investigations of Gedroiz, Kelley, Hissink, and others. Their work showed an important deficiency in Hilgard's investigations—namely, that salts in the soil solution react chemically with organic and inorganic soil colloids. If the reactions are between sodium salts and inorganic colloids, sodium clay compounds are formed which possess both active and potential alkalinity. These compounds cannot be leached from the soil and will become more actively alkaline as the soluble salts are removed from the soil by leaching. The pH of the soil increases as the salt concentration of the soil solution is reduced because of an increase in the hydrolysis of the sodium clay com-

plex. Gedroiz believed that the hydrolysis of this complex was the principal source of sodium carbonate in black alkali soils.

Following these initial base-exchange studies, soil students throughout the world conducted experiments of a similar nature on soils of many types and pH values. The outcome of these investigations was a widespread confirmation of the original base-exchange work—namely, that replaceable hydrogen dominated the exchange complex in acid soils and replaceable sodium in alkaline soils. In general the work greatly clarified our knowledge of the properties of acid and alkaline soils, notably the procedure to be followed in reclaiming and neutralizing their acidity or alkalinity. The importance of this work to the cropping of alkali soils was of course much greater than for acid soils as the liming of acid soils had already become a well-developed practice. Also since acid soils rarely if ever possess an excess of soluble salts, their reclamation involves neutralization only, while alkali soils require both leaching and neutralization.

Equipped with the knowledge gained from these base-exchange studies, it is now definitely possible to reclaim any alkali soil if the soil can be made to take water.

With the development of colorometric and electrometric methods for determining the hydroxyl-ion and hydrogen-ion concentrations in soils, which followed closely on the heels of the early base-exchange studies, fertility problems on acid and alkaline soils were still further clarified. The soil student is now equipped with methods for determining both quantity and intensity of soil acidity or alkalinity—that is, titratable alkalinity and acidity as well as hydroxyl- or hydrogen-ion concentration.

Since the major soil problems connected with the husbandry of Arizona soils are related in some way to alkali, the research program in soils at the Arizona Experiment Station deals largely with the behavior of alkali soils and their properties. During the course of these investigations alkali soil reclamation, base exchange, and pH have been extensively studied. The pH studies have dealt largely with the relation of soil pH to plant growth and have also included methods for determining pH and interpreting pH values on a field basis. From these investigations we have obtained evidence that compounds other than sodium carbonate and sodium clay have an important influence on the high pH of semiarid soils. Since all the alkaline soils of the Southwest are calcareous our attention was directed toward calcium carbonate either in such forms as calcite, aragonite, dolomite, and limestone or the double carbonate of calcium and sodium ( $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$ ) mentioned by Cameron and Bell (7).

Thus far the investigations have shown (5) that the pH of chemically pure calcium carbonate lies between 9.3 and 9.7. The examination of a number of natural forms of calcium carbonate showed a wide variation in pH values. These were represented by extremes of a minimum of 8.2 for a sample of calcite to a maximum of 12.2 for a sample of limestone. It was also shown in this

work that the type of curve obtained by varying the  $\text{CaCO}_3$ -water ratio at which the pH is determined corresponds very closely with the curve obtained by varying the soil-water ratio for alkaline-calcareous soils. Buffer titration curves also showed that the buffer capacity of alkaline-calcareous soils is due in most part to calcium carbonate rather than clay.

The experiments presented in this bulletin were designed to increase our knowledge of the properties of compounds and soil conditions responsible for soil alkalinity. Base-exchange studies, soil titrations, and pH determinations were largely employed.

#### pH VALUE OF ALKALINE-CALCAREOUS SOILS

In spite of the fact that the pH determination of the soil has been a regular practice in all soil laboratories, there is no carefully standardized procedure regarding the type of instrument, the amount and ratio of soil in the soil-water mixture, the time allowed for the soil-water mixture to reach equilibrium, or other factors that influence the magnitude of the pH value. We recently adopted the practice of determining the pH value in a mixture of one part soil in ten parts of water (10 grams soil in 100 cc. of boiled, distilled water) because at this dilution the potentially alkaline compounds reach an approximately maximum hydrolysis (14). Either the hydrogen or glass electrode may be used but preferably the latter. The pH value thus obtained represents the maximum active alkalinity of the soil and a pH value which is rarely if ever reached by the soil under field conditions. It is therefore of limited value in the practical analysis of soil or crop behavior.

Recognizing a certain handicap from our inability to determine the pH of the soil at low moisture content, we devoted some time to a study of this phase of the alkali problem. It was anticipated that if this could be accomplished we should be better able to interpret the behavior of plants growing on alkali soils, and the ability to determine the pH of the soil at any desired moisture content should contribute to a clearer understanding of the nature of the soil alkalinity. Obviously high pH values are developed by the hydrolysis of potentially alkaline compounds of varying tendencies to dissociate, and an estimation of pH at any desired moisture content should certainly indicate the activity of the alkali salts responsible for the alkaline reaction.

The solution of this phase of the problem proved more simple than anticipated, for it was found that the spear type glass electrode was admirably adapted to our needs. By pressing this electrode with its companion calomel electrode into a moist soil, pH readings may be quickly and accurately made. Determinations may be made as low as the moisture equivalent. The method is limited only by the amount of water required to form a continuous liquid film connecting the glass and calomel electrodes. In one soil a pH reading was obtained at 6-per-cent moisture content. Semiarid soils containing little or no organic matter and often containing rather high percentages of sandy particles will require very little moisture to establish such a film. Soils

containing appreciable amounts of organic matter will require relatively large amounts of moisture to establish a connecting film. A preliminary study of the method indicated that there is not a great deal of difference in the pH values obtained at different moisture contents below the water-holding capacity of the soil. Thus extreme care in adjusting the moisture content preparatory to the determination is not necessary for routine soil analyses. This preliminary study (15), in which eleven soils were employed, showed that the pH values obtained at low moisture contents, approximately the moisture equivalent, were 0.9 to 1.5 pH lower than the values obtained at a 1:10 soil-water ratio.

For the purpose of further studying the reaction of soils at different soil-water ratios a group of sixty-five soils was selected varying in pH from 3.0 to 10.1 as determined at a 1:10 ratio. The pH values obtained from these soils at the moisture equivalent and at a 1:10 soil-water ratio are given in Figure 1.

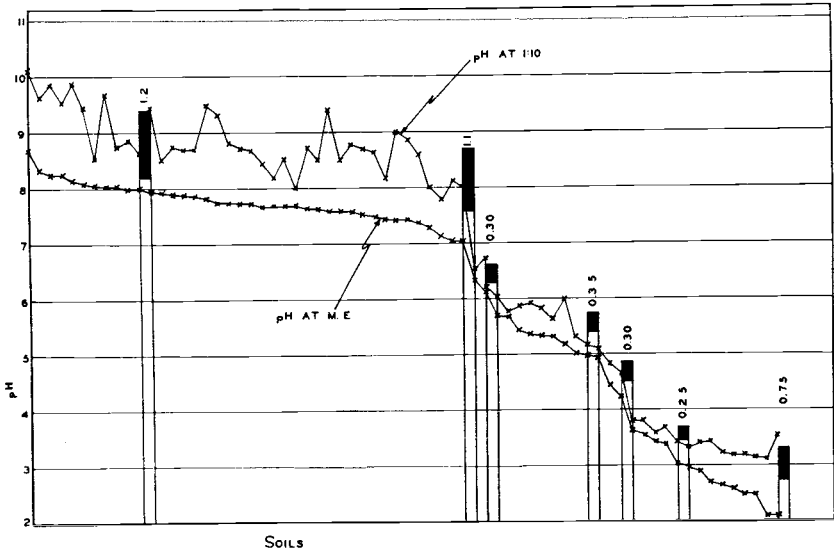


Figure 1.—Relations between soil pH values obtained at the moisture equivalent and at a soil-water ratio of 1:10.

It is clear from this figure that wide differences in pH are characteristic of the soils with pH values above 7.0. Below pH 7.0 the gap between the two curves is small and in some cases negligible until the curve reaches pH 3.0. Beyond this point the gap between the two curves widens. It is of special interest that the pH values obtained at the moisture equivalent are lower than for a 1:10 ratio regardless of the nature of the cations attached to the exchange complex or other alkaline or acid compounds present. Above pH 7.0 the hydroxyl-ion concentration is greater at a dilu-

tion of 1:10, while below pH 7.0 the hydrogen-ion concentration is greater at the moisture equivalent.

At each point on the moisture equivalent curve where it crosses the horizontal lines representing unit pH values a perpendicular line is drawn illustrating the average difference in pH between the soils at these two moisture contents. For example, the average of all the pH values at the moisture equivalent between pH 8 and 9 was subtracted from the average of all the pH values of the same soils at 1:10, and this value is represented by the black line. The same was repeated for each of the other pH units. The results obtained show a remarkable consistency. Between pH 8 and 9 the difference is 1.2, between pH 7 and 8 it is 1.1, between pH 6 and 7 it drops to 0.3, between pH 5 and 6 it is 0.35, between pH 4 and 5 it is 0.3, between pH 3 and 4 it is 0.25, and between pH 2 and 3 it is 0.75.

It is of interest to discuss these experimental data in the light of some postulations regarding colloidal behavior of soils, for this will clearly illustrate the potential value of a method for determining the pH of the soil at any desired moisture content. The data and the theories involved especially illustrate the wide difference in the soil-reaction problems as applied to acid and alkaline soils.

The colloidal material of soil is composed of acidoid silica groups and basoid ferric- and aluminum-oxide groups. When these colloid particles are wet or suspended in water, their behavior is governed in large part by an inner shell of anionic character and an outer shell of cations. The ionized bases in this outer shell represent the exchangeable bases of the complex, for the exchange reactions are surface reactions. The anionic group is fixed and insoluble while the cations arrange themselves in a distribution which is governed by their ionic activity and degree of hydration.

The influence of hydration of the ions has been discussed by Baver (2). The sodium ion, with its high hydration, is loosely bound to the colloid particle and therefore is capable of greater dissociation at the surface of the particle than any of the other ions commonly present in soils and which are less hydrated than sodium. The dissociation tendency of the four bases commonly present in soils increases with hydration—for example,  $\text{Ca} < \text{Mg} < \text{K} < \text{Na}$ . On the basis then of the hydration of the ions we should expect a wide variation in the pH of the alkaline soils at various soil-water ratios and, since sodium ions are capable of straying farthest from the colloid surface, we should expect the greatest variation in pH values for the soils in which the complex is in most part combined with sodium. A ratio between the pH of the soil and degree of sodium or other base saturation should also exist.

The theory of colloidal behavior as explained by Michaelis is also of interest in connection with the behavior of these soils. Insoluble substances having a tendency to dissociate at the surface as large insoluble ions which remain at the surface are surrounded by smaller soluble ions of opposite charge held in a layer



near the insoluble surface by electrostatic attraction. The tendency of these soluble ions to diffuse depends upon the tendency of the colloid to ionize. The decreasing tendency is  $\text{Na} > \text{K} > \text{Ca} > \text{Mg} > \text{H}$ , sodium being the most highly hydrated and the most highly ionized. Here again we find that our experimental results are in accord with theory.

We must not overlook the fact however that in addition to the alkali compounds of colloidal nature, there are also alkali salts present in the soil, both cations and anions of which are soluble and contribute to the pH of the soil. These salts are principally sodium and calcium carbonates, although the carbonates of potassium and magnesium may also be present. While Hilgard is often quoted as having said, "calcium carbonate is a standing characteristic of all alkali soils," its contribution to the pH of alkali soils has received practically no consideration. Our investigations have led us to conclude that calcium carbonate is often responsible for excessively high pH values in southwestern soils and that its importance has been dimmed by the more potential and more familiar alkaline properties of sodium carbonate and sodium hydroxide.

It is true that calcium-carbonate alkalinity is not so serious a problem as sodium alkalinity and that it lacks many of the injurious characters of the latter. Also it is not so easily identified because it lacks the solvent power for organic matter, and therefore the black color of the typical black alkali soil is absent. Then again there is a wide difference in the solubilities of the hydroxides and carbonates of these two bases. Obviously then calcium-carbonate alkalinity should be more easily reclaimed. It is our experience that high pH values from calcium carbonate exist largely in soil and subsoil horizons where aeration is restricted. As already mentioned the pH of chemically pure calcium carbonate varies from 9.3 to 9.7 and is influenced by the amount of water mixed with the solid. Obviously, then, both calcium carbonate and sodium carbonate contribute to the wide gap between the curves in Figure 1.

Below pH 7.0 the gap between the two curves is greatly reduced, for the hydrolytic basic ions are fewer and the hydrogen ions largely dominate the system. As in the case of the basic ions there are also two or more sources of hydrogen ions. That is, some are attached to the insoluble colloidal anion and some exist as free acids in the soil solution. Those attached to the insoluble colloidal anion cannot stray far from the colloid, and this property has led Weigner to designate the two types as "free hydrogen-ions" in true solution and "swarm hydrogen-ions," which are on the surface of the colloidal particle, moving and sedimenting with them. Since the "swarm ions" usually dominate the system in acid soils, it follows that the pH value should show the greater hydrogen-ion concentration at the moisture equivalent. The data in Figure 1 show that this is true, and therefore the closer the plant root approaches the soil particles, the greater hydrogen-ion concentration it will meet. On the other hand, the closer the root

approaches the soil particle in an alkali soil, the lower the hydroxyl-ion concentration it will meet. On this basis we should expect notable differences in the behavior of roots toward the soil particles in acid and alkaline soils. Bradfield (3) showed that on placing an acid bentonite in a collodion bag and immersing it in water the pH of the colloidal suspension in the bag was 2.8 at the end of twenty-four hours, while the pH of the water outside the bag was 5.4.

In drawing the curves of Figure 1 it was necessary to select one or the other set of values in a descending order, and this of course makes the other curve jagged. The cause of this jagged trend is explained in part by the discussion of the hydration and ionic activity of the colloids and other alkaline or acid salts. In addition to these there are other factors which contribute to the irregularity of the second curve. For example, there is the effect of the soluble salts present in the soil. It has been shown that the presence of sodium sulphate in solution has little or no effect on the pH of calcium carbonate, while the pH is materially reduced by the presence of sodium chloride (5). Then again it may be related to the presence or absence of nonzeolitic colloids which have a marked effect on pH (5). We must also recognize the influences due to soils of different buffer capacities, degree of fineness or particle size, and the fact that the stronger acids and bases always hold their ions more loosely than the weaker compounds.

The trend which the curves follow below pH 3.0 is of special interest. The group of acid soils selected for this experiment represent a wide variety of types. It includes a number of peat and muck types, a laterite, and a number of soils which were saturated with hydrogen in the laboratory so as to have soils of pH values lower than usually found in nature. It was anticipated that in the latter a pH would be reached where free hydrogen ions would dominate the system and possibly change the relation between the two curves. That is, an excess of free hydrogen ions should show a higher hydrogen-ion concentration, lower pH, at 1:10 ratio than at the moisture equivalent. Instead of creating such a condition the hydrogen-ion concentration of the soil at the moisture equivalent continued to be greater than that at a soil-water ratio of 1:10.

The pH value is now extensively employed in evaluating the fertility of the soil as well as its productivity. It is therefore evident that if CO<sub>2</sub>-free distilled water, at dilutions much above the moisture equivalent, yields values which are never reached in the field this fact minimizes its application to physiological and agronomic problems. Recognition of this prompted the experiment shown graphically in Figure 1 in which the distilled-water error is shown and is reduced to a minimum by using the moisture content represented by the moisture equivalent of the soil.

In a previous publication (14) it was shown that tap water may be advantageously used in many cases for the pH determination if one desires a value most closely representing field conditions. Further evidence of this is given in Table 1 in which a comparison

is shown between the pH values of the soil in tap water and distilled water.

TABLE 1.—THE pH VALUES OF SOILS IN DISTILLED AND TAP WATER AT DILUTIONS OF 1:1, 1:5, 1:10, 1:20 AND AT ONE HOUR AND 24 HOURS.

Dilution	Distilled water				Tap water			
	A	B	C	D	A	B	C	D
One hour								
1:1	8.2	8.1	8.1	8.7	8.0	8.0	8.0	8.6
1:5	8.7	8.6	8.8	9.6	8.2	8.1	8.0	9.1
1:10	8.9	8.8	9.1	9.9	8.2	8.1	8.0	9.1
1:20	9.2	9.1	9.2	10.1	8.2	8.1	8.0	8.8
Twenty-four hours								
1:1	8.2	7.8	8.0	8.5	8.1	7.8	7.9	8.4
1:5	8.5	8.3	8.4	9.4	8.2	8.0	8.0	8.9
1:10	8.5	8.4	8.4	9.7	8.2	7.9	7.8	8.9
1:20	8.7	8.6	8.7	9.9	8.1	8.0	8.0	8.7

The data given in this table show practically no change in pH on dilution with tap water, and likewise the pH values obtained at one hour and twenty-four hours agree quite closely. On the other hand, all four soils increase in pH on dilution with distilled water and give different values at one hour than at twenty-four hours. This is probably due to equilibrium changes in the soil-water mixture. There appears to be little to favor the use of boiled distilled water as a medium for soil pH determinations when used at high dilutions, especially if one desires data of practical value. Even rain water, which most closely resembles distilled water, carries carbon dioxide into the soil, and the reaction of alkali soils depends in large part upon equilibria between CO<sub>2</sub> gas, CO<sub>2</sub> dissolved, CO<sub>3</sub> ion, and HCO<sub>3</sub> ion. This is well illustrated by the rapid change in pH of tap water when exposed to the air. Water fresh from the tap in our laboratory has a pH value of 7.3. On standing in a beaker for one half hour it increases to 7.6, in three hours to 7.9, and in five hours to 8.2. Therefore in using tap water for pH determinations on soils, it should not be exposed to the air if uniformly reproducible results are desired. We have often observed similar conditions in the field. The slower the irrigation water penetrates the soil, especially waters pumped from under ground, the higher the pH becomes, and there is a corresponding reduction in the value of the water, for the dissolved CO<sub>2</sub>, notably improves the soil structure. The author has tested irrigation water in the field, where soils were tight and water penetration restricted, and often found it showing phenolphthalein alkalinity which is about pH 8.5. Obviously the water after it reaches a pH of 8.5 is of less value to the soil than if it had penetrated at once with a pH of 7.3 and carrying an equivalent amount of dissolved CO<sub>2</sub>.

These experiments show that the value of a pH determination for interpreting the properties of the soil, as influenced by the presence of hydroxyl ions or the behavior of plants growing thereon, is governed by the analytical procedure followed. For plant behavior the pH value at the moisture equivalent or tap water at any soil-water ratio gives best results. For investigations of a research nature or for studying soil behavior pH values both at the moisture equivalent and a dilution of 1:10 with boiled distilled water should be employed. The factors which govern pH are: completeness with which the complex is saturated with base, character of base, tendency to ionize, and extent of hydrolysis. The degree of buffering is also a factor, for soils may be quite alkaline and yet have a low pH if well buffered. On the other hand, they may be weakly alkaline and have a high pH if lightly buffered.

#### RELATION OF SOME SOIL PROPERTIES TO pH VALUE

For the next experiment forty-three soils were selected representing a wide variation in alkaline-calcareous types and quite thoroughly representative of Arizona irrigated lands. These soils were examined for a number of physical constants and some chemical determinations, which are usually more or less associated with soil reaction. The pH values were determined at the moisture equivalent, the water-holding capacity, and at a ratio of one part soil to ten parts distilled water. Other determinations made on these soils were per cent clay; moisture equivalent; water-holding capacity; total soluble salts including chloride, sulphate, sodium and calcium separately; replaceable sodium, potassium, calcium, magnesium, and total replacement capacity; and finally the solubility of calcium in ammonium acetate. These data are given in Table 2.

All pH determinations were made with the glass electrode (Beckman pH meter), using air-dry soil and making all moisture additions with boiled distilled water.

Replaceable bases were determined by leaching 10 grams of soil with 250 cc. of neutral normal ammonium acetate solution. Sodium, potassium, and magnesium were determined in the leachate. Total replacement capacity was determined by total absorption of ammonium by the soil from neutral ammonium acetate. Replaceable calcium was calculated by difference—that is, by subtracting the sum of the replaceable sodium, potassium, and magnesium from the replacement capacity. The solubility of calcium carbonate is so great in all the solutions used for base replacement that calcium cannot be determined directly in the leachate.

With a view toward gaining some information on the activity of the calcium in these soils, the amount of calcium extracted by leaching the soils with neutral ammonium acetate was determined. Total soluble salt, which usually affects the pH determination, was calculated from the conductivity of a 1:5 soil-water extract.

Chloride, sulphate, sodium, and calcium were also determined in the 1.5 water extract of the soil and calculated to dry-soil basis. Moisture equivalent and moisture-holding capacity were determined by the regular method.

The soils were all alkaline-calcareous types and include a group of soils from the University farms at Mesa and Tucson, two groups from the Casa Grande Valley, and the rest from scattered sections of the state. There were also two soils from Tulare Lake bed in California and one from Sinaloa, Mexico. In three cases the soils were saturated with calcium or sodium in the laboratory in order to have several soils which were known to be saturated with these bases.

In the first three columns of Table 2 the pH values which were determined at moisture contents represented by the moisture equivalent, the water-holding capacity, and at 1:10 ratio are given. As should be expected all the pH values at 1:10 are much higher than at the moisture equivalent or the water-holding capacity, while there is little difference between the latter two values. The average difference between the pH at the moisture equivalent and 1:10 ratio is 1.02, which is in close agreement with the data presented as Figure 1. If one recognizes the degree of buffering in alkaline-calcareous soils, he can readily appreciate that 1.02 pH may play an important part in the physiological behavior of crops being grown on such soils. The group of Casa Grande soils, numbers 7 to 17 inclusive, in which *a* samples represent surface soils (1 ft.) and *b* samples represent subsoils (1-2 ft.), is of interest. The subsoils show a greater increase in pH on dilution with water than the surface soils, indicating a greater potential alkalinity in the former. This does not bear any apparent relation to the replacement capacity or the amount of replaceable sodium present. In fact the replaceable sodium is higher in the surface soils. This indicates that active forms of calcium carbonate may be involved in this pH behavior. It should be stated at this point that our soil investigations show that in the cropping of irrigated lands in Arizona the pH of the subsoil is a greater growth-limiting factor than that of the surface soil, for the former invariably has a higher pH. Furthermore the pH of the subsoil increases from overirrigation or waterlogging.

Referring to the three soils which were saturated with calcium and sodium by leaching with the respective chlorides, it will be noted that the sodium-saturated soils show the greatest increase in pH with dilution. In the Mission soil, which was also leached free of calcium carbonate before saturating with bases, the increase in pH on dilution is much less than in the sodium-saturated soils containing calcium carbonate. This is further evidence of the important part that calcium carbonate plays in the pH of alkaline-calcareous soils.

In Figure 2 some relations between replaceable sodium and pH are shown graphically. The lower part of the figure shows the relation between the pH of the soil as determined at the moisture equivalent and in a 1:10 soil-water ratio and the milliequivalents

TABLE 2.—RELATION OF SOME PHYSICAL AND CHEMICAL CONSTANTS TO pH VALUE IN FORTY-THREE SOILS.

Soil sample	pH moist. equiv.	pH W.H.C.	pH 1:10	M.E.* rep. cap.	M.E.* rep. Na	M.E.* rep. K	M.E.* rep. Mg	M.E.* rep. Ca	M.E.* acetate sol. Ca	Moist. equiv.	W.H.C.	Ppm† total salts	Ppm† Cl (chloride)	Ppm† SO <sub>4</sub> (sulphate)	Ppm† Na (sodium)	Ppm† Ca (calcium)	Per cent clay
1 Univ. Farm, Mesa	7.75	8.10	8.70	15.7	2.6	1.7	3.2	8.2	11.2	24.6	60.6	430	.....	.....	.....	.....	25.4
2 Univ. Farm, Mesa	7.75	8.00	8.80	13.1	1.5	0.9	2.3	8.4	18.4	11.0	39.9	500	.....	.....	.....	.....	28.7
3 Univ. Farm, Mesa	8.05	8.30	8.75	8.4	1.5	1.0	1.9	4.0	18.6	11.9	41.6	460	.....	.....	.....	.....	10.2
4 Univ. Farm, Mesa	8.00	8.25	8.65	17.9	3.8	2.1	3.8	8.2	22.5	27.4	65.3	350	.....	.....	.....	.....	34.2
5 Univ. Farm, Mesa	7.75	8.00	8.20	8.6	1.1	1.1	1.8	4.6	18.2	15.9	48.0	500	.....	.....	.....	.....	9.2
6 Univ. Farm, Mesa	7.75	7.80	8.50	6.3	1.0	0.7	1.6	3.0	18.8	15.4	37.6	450	.....	.....	.....	.....	7.6
7a Casa Grande, Gilbert	8.15	.....	8.35	24.3	2.8	1.0	3.0	17.5	13.9	20.4	51.8	1,925	110	313	220	18	36.8
8b Casa Grande, Gilbert	7.60	7.75	8.80	24.1	2.7	1.1	2.4	17.9	14.5	20.9	52.0	2,375	480	745	281	105	37.8
9a Casa Grande, Gilbert	7.55	7.85	8.70	22.0	5.6	1.0	2.6	12.8	22.0	20.7	49.3	4,875	1,120	646	814	43	38.4
10b Casa Grande, Gilbert	7.85	8.25	9.55	22.8	5.0	1.0	2.2	14.6	19.2	21.4	53.6	1,440	86	tr	388	37	36.8
11 Casa Grande, Gilbert	7.75	8.00	9.35	21.7	3.8	0.9	3.7	13.3	22.5	19.6	50.5	1,530	170	335	357	37	35.8
12a Casa Grande, Gilbert	7.50	7.75	8.60	25.7	3.1	1.0	2.4	19.2	13.1	22.3	57.5	1,495	256	436	254	26	39.3
13b Casa Grande, Gilbert	7.45	7.85	8.90	25.3	2.7	0.9	2.7	19.0	12.4	23.3	63.3	1,045	118	tr	219	56	41.3
14a Casa Grande, Gilbert	7.10	7.75	8.25	31.3	13.6	1.1	0.7	15.9	20.2	25.7	61.2	28,000	10,120	1,582	1,797	1,455	44.3
15b Casa Grande, Gilbert	7.60	8.20	9.40	31.8	7.7	1.2	1.9	21.0	21.2	31.0	76.9	1,150	186	292	177	48	52.8
16a Casa Grande, Gilbert	7.90	.....	8.70	25.0	1.6	1.3	2.4	18.7	12.5	22.2	49.2	775	156	tr	393	tr	39.3
17b Casa Grande, Gilbert	7.45	7.85	9.05	21.8	2.1	1.5	2.1	16.1	12.7	21.3	55.5	565	30	tr	184	56	33.8
18 Old Univ. Farm, Tucson	8.70	9.15	10.10	9.8	7.4	1.3	0.9	0.2	15.1	17.4	41.6	7,750	680	2,165	743	105	12.9
19 Mesa, Smith	7.65	7.60	8.50	11.6	2.3	1.2	2.6	5.5	22.7	18.2	46.0	1,790	140	346	138	161	24.4
20 Peoria, Davis	7.60	7.65	8.50	16.0	1.8	1.2	2.5	10.5	13.5	14.9	42.4	1,565	180	140	119	56	16.2
21 Univ. Farm, Mesa	7.95	7.90	8.50	10.6	1.9	0.8	1.9	6.0	48.6	16.9	52.8	845	42	tr	76	78	18.5
22 Calif., Tulare	7.65	7.70	8.75	24.8	5.5	1.4	7.1	10.8	56.9	50.7	88.8	2,100	240	416	1,125	41	62.4
23 Calif., Tulare	7.50	7.50	8.40	24.6	9.0	1.2	8.40	6.6	51.9	49.0	100.4	5,250	920	1,884	588	446	62.8
24 Casa Grande	8.15	8.25	9.95	7.5	4.6	0.4	1.2	1.3	8.7	10.0	29.1	1,150	148	tr	386	tr	8.4
25 Casa Grande	8.05	8.25	9.75	7.7	4.6	0.5	1.2	1.4	22.7	11.7	31.1	4,375	430	1,087	884	11	12.8
26 Casa Grande	8.10	8.40	9.45	43.4	29.4	2.2	2.2	9.6	39.5	63.5	76.0	2,410	220	263	734	67	72.4
27 Casa Grande	8.25	8.35	9.85	47.6	41.2	1.9	1.6	2.9	35.5	49.7	64.0	3,760	406	852	1,105	18	60.8
28 Casa Grande	8.25	8.70	9.55	44.4	29.7	2.2	2.6	9.7	49.8	49.1	82.1	3,760	886	502	888	18	77.2
29 Univ. Farm, Tucson	7.75	7.75	8.65	12.5	2.7	1.4	2.4	6.0	42.5	13.4	35.8	1,150	96	tr	331	18	21.2
30 Univ. Farm, Tucson Ca sat.	7.75	7.95	8.65	12.2	0.2	1.3	1.5	9.2	45.2	.....	.....	725	10	tr	64	131	18.0
31 Univ. Farm, Tucson Na sat.	7.95	7.95	9.50	12.8	9.2	1.1	1.5	1.0	37.2	.....	.....	325	15	tr	32	63	21.0
32 Yuma	7.45	7.60	8.15	21.8	3.9	1.1	5.0	11.8	45.5	29.3	64.1	3,030	335	905	518	198	53.8
33 Yuma Na sat.	8.35	8.50	9.70	24.3	20.7	0.6	1.7	1.3	37.0	29.3	64.1	705	15	181	35	281	53.8
34 Yuma Ca sat.	7.90	8.05	8.75	22.2	1.0	0.9	1.6	18.7	48.4	29.3	64.1	785	35	tr	56	93	43.0
35 Pinal silt loam	7.90	7.80	8.65	6.8	0.2	0.6	1.3	4.7	27.4	11.4	35.8	500	10	tr	15	75	9.2
36 Palo Verde loam	7.30	7.15	8.00	5.2	0.6	0.3	1.5	2.8	7.5	16.3	31.5	1,980	270	498	263	93	11.2
37 Tubac clay loam	7.70	7.20	8.00	7.8	1.1	0.8	1.8	4.1	7.1	13.1	39.5	675	25	tr	25	56	13.2
38 Mohave	7.70	7.60	8.55	11.3	1.0	1.1	0.8	8.4	40.4	19.3	58.4	1,225	225	214	97	56	25.2
39 Tucson	8.00	7.80	8.85	7.8	0.8	1.1	1.5	4.4	35.9	17.5	48.0	730	10	313	127	56	12.2
40 Sinaloa, Mex.	8.10	7.90	8.55	20.3	5.1	3.4	2.8	9.0	21.2	23.2	72.4	2,025	238	424	227	93	17.2
41 Mission, Ca sat.	6.65	6.65	7.20	44.4	1.0	0.7	1.5	41.2	40.0	37.5	82.9	.....	.....	.....	.....	.....	50.0
42 Mission, Ca sat.	6.55	6.50	7.00	44.2	2.0	0.8	1.1	40.3	40.0	38.7	76.7	.....	.....	.....	.....	.....	48.0
43 Mission, Na sat.	7.10	7.10	7.85	47.2	32.2	1.3	1.2	12.4	12.0	51.4	97.0	.....	.....	.....	.....	.....	66.0

\* Milliequivalents per 100 grams soil.

† Parts per million dry soil.

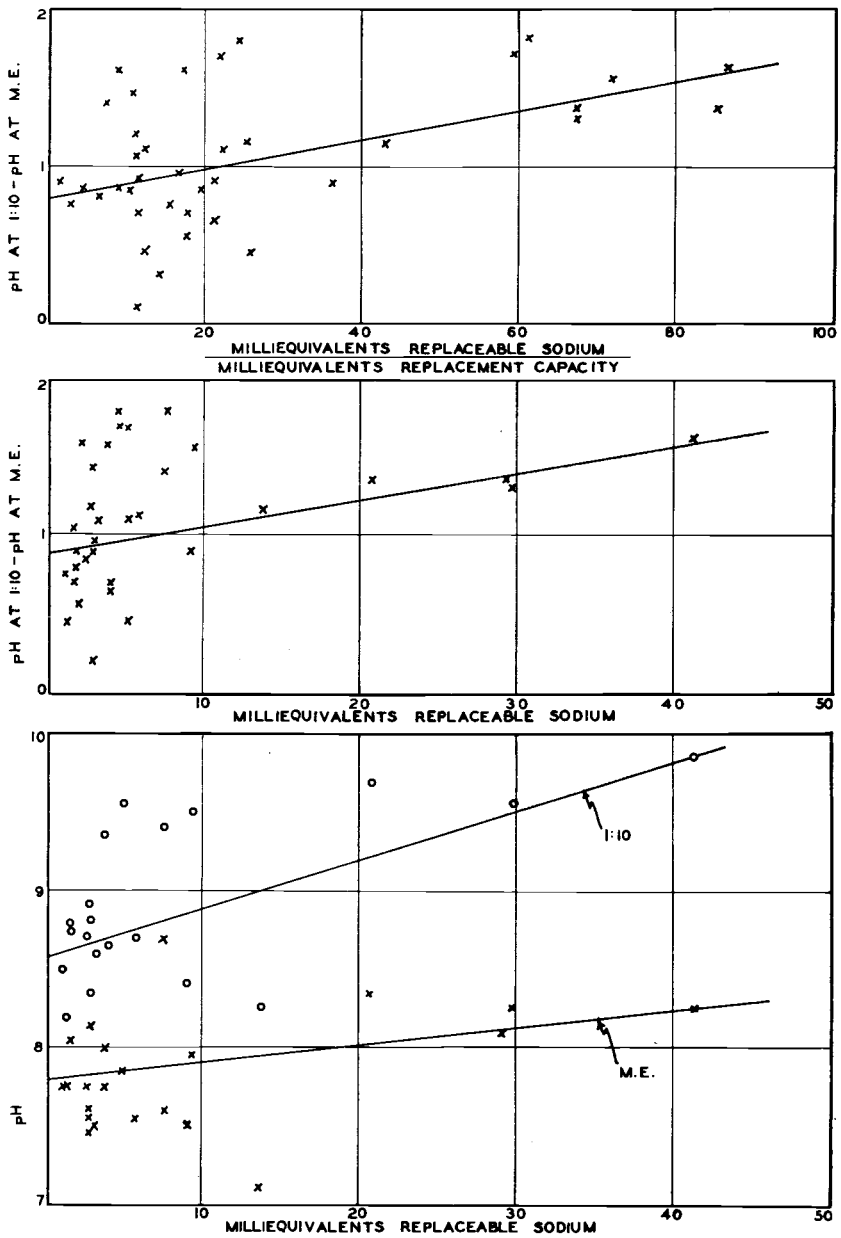


Figure 2.—Relation between the replaceable sodium in the soil and pH value.

replaceable sodium present in the soil. Directly above this the difference between the two pH values is plotted against the milliequivalents replaceable sodium. At the top of the figure the ratio of replaceable sodium to total exchange capacity is plotted against the difference between the two pH values.

It is evident in all cases that there is a tendency toward a straight-line relationship for all the soils containing a high replaceable sodium content and where the exchange capacity is in large part satisfied with sodium. A comparison of pH at 1:10 ratio and at the moisture equivalent shows that the former values stray farther from the straight line than the latter. It is significant that the straight-line relationship applies only to the soils containing more than 10 milliequivalents of replaceable sodium. In all the soils containing less than this amount the points are in utter confusion in spite of the fact that some of these soils possess rather high pH values. It is the group thus represented that has led us to investigate soil alkalinity beyond the sphere of sodium carbonate and sodium zeolite.

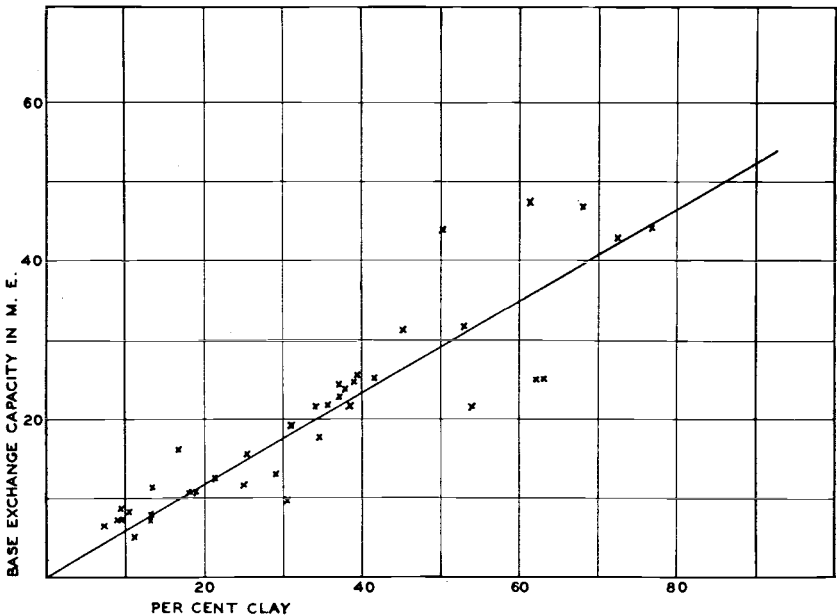


Figure 3.—Relation between the per cent clay in soils and their replacement capacity.

In Figure 3 the relation between the per cent clay in the soils and the replacement capacity is shown as a straight line, but no relation between clay content and pH could be developed from the data.



Moisture equivalent and water-holding capacity are two constants which are extensively employed in studying the properties of semiarid soils. However they show no relation to pH values, which is of interest.

It was expected that some definite relation would be shown between the soluble salts and the pH value of the soils, but apparently no such relation exists in this group. This is probably because there is a wide variation in the character of the salts present in the different soils. For example, soil number 18 with a total replacement capacity of 9.8 milliequivalents, of which 7.8 is sodium, and a soluble-salt content of 7,750 ppm has pH values of 8.7 and 10.1 at the moisture equivalent and at 1:10 ratio respectively. On the other hand, soil number 27 has a replacement capacity of 47.6 milliequivalents, of which 41.2 is sodium, and a salt content of 3,760 ppm, less than half that of soil number 18, yet has pH values of only 8.25 at the moisture equivalent and 9.85 at 1:10 ratio.

One observation which may have some bearing on the alkaline properties of these soils was made during the accumulation of the data given in Table 2. In soils number 18, 24, 25, 31, and 34 all black-alkali types high in replaceable sodium, the sum of the replaceable sodium, magnesium, and potassium added up to an amount greater than the replacement capacity as measured by the amount of ammonium absorbed by the exchange complex on leaching with neutral ammonium acetate. In fact the replaceable sodium alone was higher than the replacement capacity in some cases. The procedure followed in making these determinations was to give the soil a preliminary leaching, once with water and five times with 80-per-cent ethyl alcohol, in order to remove the soluble salts before leaching with ammonium acetate.

In order to determine whether the error was in the determination of the replacement capacity or in that of the replaceable sodium, the replacement capacity was determined by several different methods. These tests showed that the neutral replacement-capacity determination was correct and that the apparent error was in the determination of replaceable sodium.

Some experiments were then conducted in which the preliminary leaching of the soil was varied. Comparisons between water and different dilutions of alcohol were made. The results obtained are given in Table 3.

TABLE 3.—EFFECT OF PRELIMINARY LEACHING ON THE DETERMINATION OF REPLACEABLE SODIUM.

Nature of leaching	Milliequivalents sodium
Leached with water.....	7.4
Leached with 25% alcohol.....	9.2
Leached with 50% alcohol.....	10.9
Leached with 80% alcohol.....	12.5
Leached with 95% alcohol.....	15.9

This experiment shows that leaching with alcohol of 50-per-cent strength or higher will not reduce the absorbed sodium to a point equivalent to that represented by the neutral replacement capacity and that it is doubtful if this can be accomplished with 25-per-cent alcohol. In view of the fact that the neutral replacement capacity of this soil is 9.8 the data indicate that solutions of less than 25-per-cent alcohol should be used to remove sodium salts from the soil preparatory to determining the replaceable sodium. It must be admitted from these data that the determination of replaceable sodium in black-alkali calcareous soils is only approximate at best.

All evidence indicates that this sodium, which is removed with such difficulty by preliminary leaching, is present in an absorbed form in which calcium carbonate or the high pH of the soil may have a part. Reference is made to the results obtained in the analysis of soil 43 as compared with the sodium-saturated soils. This soil was leached with dilute HCl until free from calcium carbonate and then leached with NaCl solution until nearly saturated with sodium. The analysis shows that the soil contained 12 milliequivalents of calcium and 32 milliequivalents of sodium. The pH of the soil was 7.85 when mixed with water at the ratio of 1:10. It appears that this low pH or the absence of calcium carbonate eliminated the error associated with the determination of replaceable sodium, as no difficulty was experienced with this soil. This is another example of a lower pH for a soil containing a high percentage of replaceable sodium but no calcium carbonate. The sodium formed by the hydrolysis of sodium clay produces a higher pH in the presence of calcium carbonate due to the formation of sodium carbonate and a greater diffusion of the sodium carbonate throughout the soil solution as compared with the lesser diffusion of the "swarm ions" of the sodium clay.

On the other hand, the absorbed sodium in excess of that indicated by the determination of replaceable sodium with neutral solutions of replacing bases is much more responsible for low soil productivity than that hydrolyzing to only pH 7.0. The cations which have the greatest replacing power are least hydrated. Those which have the least replacing power and produce the most gelatinous complexes are those which are most highly hydrated. The highly hydrated ions can develop a much less intimate association with the soil colloids than the ions which are less encumbered by attached water molecules. Why then should absorption at high pH values be greater than at low pH values?

Tiulin (17) found that soils absorb more base from alkaline salt solutions and that this base is exchangeable. Mattson (12) says that free sesquioxides form adsorption compounds with bases in alkaline solutions. Bradfield (4) has also noted greater absorption of base from alkaline solutions:

Lemberg in 1870 working on silicate minerals found an equivalent exchange of bases between minerals and solutions of neutral salts. With alkaline solutions the free base was absorbed without any appreciable exchange of bases. A few years later in 1877 Van Bemmelen made his classic studies on absorption by colloidal gels. Like Lemberg, he found

that solutions having an alkaline reaction, either the free hydrate or the alkaline salts of weak acids such as  $\text{H}_2\text{CO}_3$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_3\text{B}_3\text{O}_6$ , were absorbed more strongly by soils and by silica gel than the neutral salts of the same metals. With the alkaline solutions there was no appreciable exchange of bases. . . . Thirty years later, Sullivan studied the effect of a large number of salts upon a variety of silicates. In most cases some exchange of bases occurred, but it was quantitative only in case a neutral mineral was treated with a neutral salt.

Mattson and Hester (13) suggest that total combining capacity of soil should be defined in terms of pH, for the capacity to absorb bases varies with the pH of the colloid.

The above references are cited to show an agreement between the data obtained in our experiment and the experiences of others. Additional confirmation has appeared recently in a publication of Puri and Asghar (16).

Apparently the exchange capacity of the soil is a function of  $\bar{p}\text{H}$  and the nature of the base as well as the combining capacity of the clay complex. In titrating hydrogen-saturated clays Baver (2) and Puri and Asghar (16) have shown that while the shape of the titration curves is the same for all bases, the amount of alkali required to produce a particular pH differs. This is related to the ionic activity and hydration as well as the distance which the bases can stray from the nucleus.

Our experiments show that the base-exchange capacity as determined with neutral salt solutions and especially as it concerns the highly absorbed sodium may have less significance in the behavior of alkali soils than is usually considered to be true. The terms "base-exchange capacity" and "saturation capacity" are predicated on the basis of pH 7.0 as the saturation point. The error of this assumption in soils other than black-alkali types, sodium-saturated soils, is probably negligible but may introduce a serious error in the analysis of alkali soils. As already mentioned the absorption of cations, especially sodium, by the exchange complex is in large part a function of pH or hydroxyl-ion concentration. Bradfield (4) and Mattson and Hester (13) have shown that the capacity to absorb sodium, lithium, or potassium is greater in alkaline solutions than in neutral solutions. In consideration of the function of pH in absorption capacity, Bradfield suggests pH 8.5 as the neutral point in the titration of an acid soil with NaOH solution and 7.5 as the neutral point when titrating with  $\text{Ca}(\text{OH})_2$  solution. On the other hand, Puri and Asghar (16) go further and state, "it [pH] has no theoretical significance even if it refers to an arbitrarily fixed uniform pH value." On the basis of our experiments we are inclined to agree with them, for it is shown that there is a wide variation in the activity of the absorbed sodium in different soils. For an example the reader is again referred to the data on soils number 18 and 27 in which the soil with lower exchange capacity shows the higher pH value.

Puri and Asghar are inclined to place greater significance on the pK value where the highly hydrolytic bases are concerned. As shown by Bradfield (3) the pK value may be obtained from the

mass law equation

$$pK = pH + \log \text{ salt/acid}$$

According to Britton (6) when a weak acid is titrated with a strong base the salt equals the acid when the acid becomes half neutralized and therefore at this point  $pK = pH$ . The fundamental importance of this point in the titration of weak acids, such as acid clay, is so great that Puri and Asghar have strongly emphasized its value in studies on soil reaction and exchange capacity. In simple terms the  $pK$  value is the  $pH$  prevailing when a weak acid, or the  $pOH$  when a weak base, has been half neutralized. In dibasic and polybasic acids there will be step  $pK$  values as illustrated in Table 4.

TABLE 4.— $pK$  VALUES FOR SOME OF THE WEAK ACIDS.

	$pK$ step one	$pK$ step two	$pK$ step three
Acetic acid.....	4.73	.....	.....
Carbonic acid.....	6.52	10.35	.....
Phosphoric acid.....	2.1	7.13	12.3
Boric acid.....	9.22	.....	.....

In other words carbonic acid is completely neutralized at  $pH$  10.35 and phosphoric acid at 12.3.

In view of the fact that clay acidoids are weak acids and resemble the above acids when an attempt is made to saturate them with bases, it is clearly evident that the saturation of the exchange complex in soils must be an intricate process. In all cases it should be above  $pH$  7.0 and in many cases above  $pH$  8.5. With this in mind Puri and Asghar (16), largely on the basis of the work of Harris (9) suggest that the  $pK$  value of soils be assumed as 4  $pH$  units higher than the  $pH$  of the hydrogen-saturated soil. In a group of sixty-five soils they obtained  $pK$  values varying from a minimum of 4.75 to a maximum of 9.75.

As a further study of the relation of  $pH$  to the absorbing capacity of the soil the following experiment was conducted. Five-gram portions of soil were weighed into filters and leached with normal ammonium-acetate solutions adjusted to  $pH$  7.0, 8.5, and 9.4. Another series of the same soil was leached with normal sodium-acetate solutions adjusted to  $pH$  7.0, 9.1, and 11.0. Each 5-gram portion was leached with 250 cc. of the respective solution so as to assure complete saturation with sodium ion or ammonium ion. The soils were then washed once with distilled water and five times with 70-per-cent ethyl alcohol to remove the excess of salt. The soils that had been leached with ammonium acetate were then analyzed for fixed ammonium by distillation with alkali. The sodium-saturated soils were leached with 250 cc. of normal ammonium acetate and sodium determined in the leachate by the zinc-uranyl-acetate method. The results obtained from these analyses are given in Table 5.

TABLE 5.—ABSORPTION OF AMMONIUM AND SODIUM FROM SOLUTIONS OF DIFFERENT pH VALUES.

pH of replacing solution	M.E. base absorbed
Ammonium acetate pH 7.0.....	25.5
Ammonium acetate pH 8.5.....	25.6
Ammonium acetate pH 9.4.....	24.8
Sodium acetate pH 7.0.....	25.2
Sodium acetate pH 9.1.....	26.9
Sodium acetate pH 11.0.....	27.4

It is evident from this experiment that the absorption of ammonium ion is in no way affected by the pH. On the other hand, there is a definite increase in absorption of sodium ion with increase in pH. It is not so great as one would anticipate from our study of the absorbed sodium in natural black-alkali soils. This phase of the problem will be studied more thoroughly as our alkali-soil research is continued because there is much evidence that black alkali soils artificially prepared in the laboratory differ greatly from those formed naturally in the field. It is possible that the aging of the colloid at high pH values in the presence of the highly hydrolytic sodium ion may influence the absorption. The problem of absorption, at least as it concerns sodium, is by no means one of simple proportions, as our investigations have previously shown that the exchange capacity of black-alkali soils can be increased by alternately wetting and drying.

#### pH OF CALCIUM-SATURATED SOILS

The next experiment was designed to study the pH values of alkaline-calcareous soils when the exchange complex is saturated with calcium, and the moisture content is at the moisture equivalent and a 1:10 ratio. Thirteen of the soils given in Table 2 were leached with calcium-acetate solution until saturated with calcium and the excess of calcium removed by leaching with water.

TABLE 6.—pH OF CALCIUM-SATURATED SOILS.

Soil no.	M.E. rep. cap.	pH at moist. equiv.		pH at 1:10 ratio	
		Orig. soil	Ca sat.	Orig. soil	Ca sat.
21	10.6	7.95	7.95	8.50	8.50
22-3	24.7	7.60	7.80	8.60	8.20
18	9.8	8.70	8.25	10.10	8.65
19	11.6	7.65	7.85	8.50	8.30
20p	16.0	7.60	7.75	8.50	8.35
20g	13.8	7.60	7.65	8.50	8.45
32	21.8	7.45	7.45	8.15	8.50
24-8	12.1	8.20	7.70	9.70	8.55
29	12.5	7.75	7.85	8.65	8.40
29a	19.5	7.75	7.75	8.65	8.30
37	7.8	7.70	7.20	8.00	8.15
39	7.8	8.00	7.80	8.85	8.70
36	5.2	7.30	7.65	8.00	8.10

The pH values were determined with the spear-type glass electrode as previously described. These data are given in Table 6.

These data show that calcium-saturated soils have a more or less constant pH value of 7.45 to 8.25 at the moisture equivalent and 8.1 to 8.7 when diluted to a 1:10 soil-water ratio. The greatest change in pH on saturation with calcium occurred of course in the black-alkali soils 18 and 24-8. There appears to be no relation between the replacement capacity and the pH of the soil when saturated with calcium.

#### pH OF HYDROGEN-SATURATED SOILS

In the next experiment practically the same group of soils was leached with 0.1N HCl until free from calcium carbonate and bases to form so-called unsaturated soils. After complete saturation with hydrogen the soils were washed by filtration through clay. This left a soil at practically the moisture equivalent. The pH values were determined on the soils at this moisture content and then diluted to a ratio of one part soil to ten parts water and the pH again determined. These data are given in Table 7 and show pH values varying from 2.1 to 3.35 at the moisture equivalent and 3.30 to 4.75 at a 1:10 ratio.

TABLE 7.—pH OF HYDROGEN-SATURATED SOILS.

Soil no.	M.E. rep. cap.	pH moist. equiv.	pH 1:10 ratio
21	10.6	2.70	3.35
7-17	23.8	2.50	3.30
22-3	24.7	2.60	4.75
18	9.8	2.10	3.60
19	11.6	3.05	3.75
20p	16.0	3.00	3.65
20g	13.8	3.00	3.65
32	21.8	2.50	3.40
24-8	12.1	2.10	3.40
29	12.5	2.65	3.60
29a	19.5	2.60	3.50
37	7.8	2.65	3.60
39	7.8	3.10	3.75
36	5.2	3.35	3.65

The average difference between the pH values determined at the moisture equivalent and at 1:10 ratio is 0.93 which compares favorably with the value 0.75 obtained for the group of soils below pH 3.0 shown in Figure 1. Also there appears to be no relation between the replacement capacity of this group of soils and their pH value at either moisture content. Joffe and McLean (10) also observed no correlation between pH and total replaceable hydrogen. Anderson and Byers (1) found that pH values of hydrogen-saturated soils vary with the difference in chemical composition of the colloids and different degrees of dispersion.

## TITRATION OF HYDROGEN-SATURATED SOILS

The acidic or alkaline character of soil colloids is often manifested by the titration of the hydrogen- or base-saturated soils or their colloids and by the comparison of the type of curve obtained from these titrations with those of known colloids and other basic or acid salts. For a study of the titration curves of hydrogen-saturated southwestern soils the thirteen soils previously saturated with hydrogen (Table 7) were titrated with standard alkali, seven of them with  $\text{Ca}(\text{OH})_2$  solution and six with standard  $\text{NaOH}$  solution.

The following method was employed: 25 grams of soil were placed in a 250 cc. wide-mouth bottle and 100 cc. of distilled water added. Titration was then conducted by adding successive increments of quantitatively measured volumes of the standard alkali to the soil-water mixture. The bottles were placed in an end-over-end shaking machine after each addition of alkali and shaken for two hours. They were then allowed to stand twenty-four hours, to reach equilibrium, at the end of which time they were shaken by hand and the pH determined with the glass electrode. This operation was repeated daily until the pH of the mixture was well above 7.0.

The data obtained are given in Figures 4, 5, 6, and 7 and are grouped according to the replacement capacity of the soil in milliequivalents. For example, in Figure 4 the replacement capacity varies from 5.2 to 8.9, in Figure 5 from 9.4 to 10.6, in Figure 6

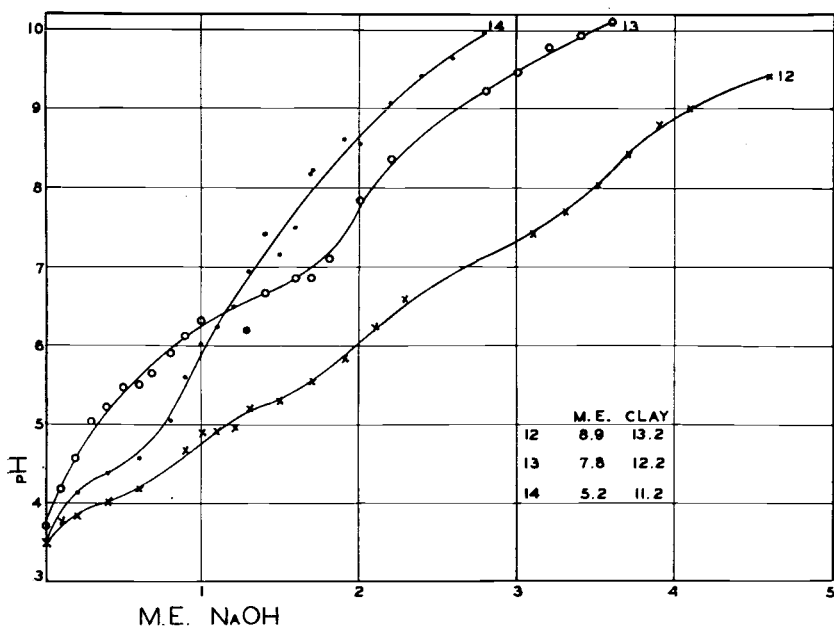


Figure 4.—Titration curves for soils of low replacement capacity.

from 12.1 to 14.2, and in Figure 7 from 16.7 to 23.8. As an aid to studying these curves the replacement capacity in milliequivalents and the per cent clay in the soils are inserted in the figure. In all cases the soils with even numbers were titrated with  $\text{Ca}(\text{OH})_2$  solution and those with odd numbers were titrated with  $\text{NaOH}$  solution. The curves represent the relation between the milliequivalents base and pH of soil.

The first set of curves, Figure 4, represents the soils of lowest exchange capacity. Inflections are on the whole very slight except for soil number 13. The points at which the curves cross the horizontal line representing pH 7.0 agree very closely with the saturation capacity as measured by absorption of ammonium from ammonium acetate. Also the low degree of buffering is in agreement with the low exchange capacity, the low clay content, and therefore their weakly acidic character. The curve for soil number 14 tends slightly toward the lateritic or halloysitic type of curve. This soil belongs to the Palo Verde series and being non-calcareous indicates a maturely developed soil. The inflection point, if any, exists at a point between pH 4 and 5. Soil number 12 belongs to the Tubac series and soil 13 to the Tucson series. All three of these soils are from upland maturely developed fan areas. The Tucson soil possesses a decided inflection point while the Tubac soil shows only slight inflection.

The second set of curves, Figure 5, brings together the soils with replacement capacities between 9.4 and 10.6 milliequivalents. The

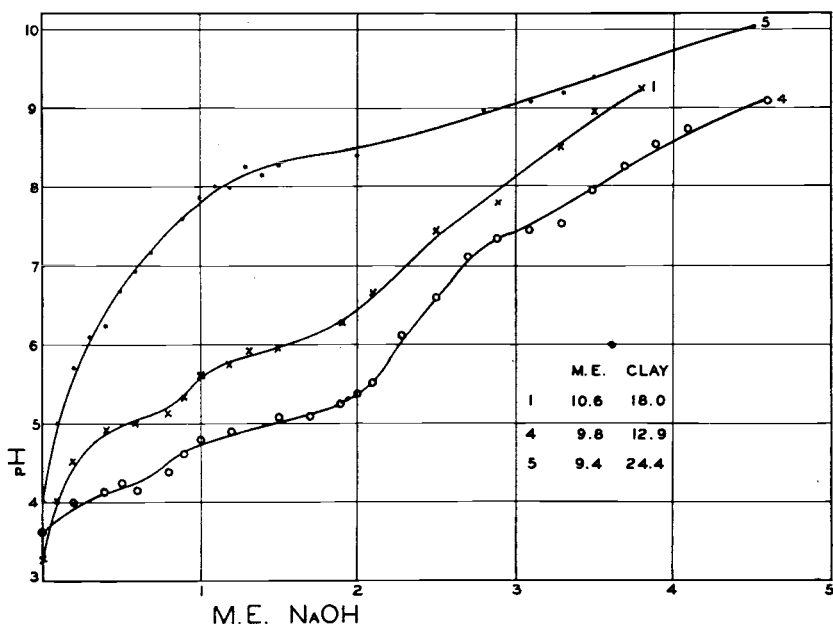


Figure 5.—Titration curves for soils of 9.4 to 10.6 milliequivalents replacement capacity.



curve for soil number 5 is notably different from the rest and closely resembles the lateritic or halloysitic type, at least much more so than soil 14 in Figure 4. It is also of interest that this curve crosses the pH 7.0 line far below the point representing the base saturation capacity. This soil was titrated with NaOH solution, and it is quite evident that the colloid is of an extremely hydrolytic character. This soil is a reddish brown type, series unknown, but apparently a well-matured type. Soil number 1 is a Laveen clay loam and shows two rather distinct inflection points between pH 5 and 7. Soil number 4 is a Gila clay loam from the Santa Cruz River Valley and shows two distinct inflection points between pH 5-6 and pH 7-8.

The third set of curves, Figure 6, represents the soils with exchange capacities of 12.1 to 14.2 milliequivalents. All the curves are very similar, bentonitic types, and all except soil number 9 cross the horizontal pH 7 line at points agreeing quite closely with the replacement capacity. The soils in this group are strongly buffered below pH 6.0. Soil number 7 belongs to the McClellan series and was taken near Peoria, Arizona. It possesses one decided inflection point near which the soil is well buffered. Soil number 9 is also of the McClellan series and like number 7 possesses one distinct inflection point and is similarly buffered. Soil number 11 belongs to the Gila series, has two inflection points, and is likewise well buffered.

The fourth set of soils brings together those of highest exchange

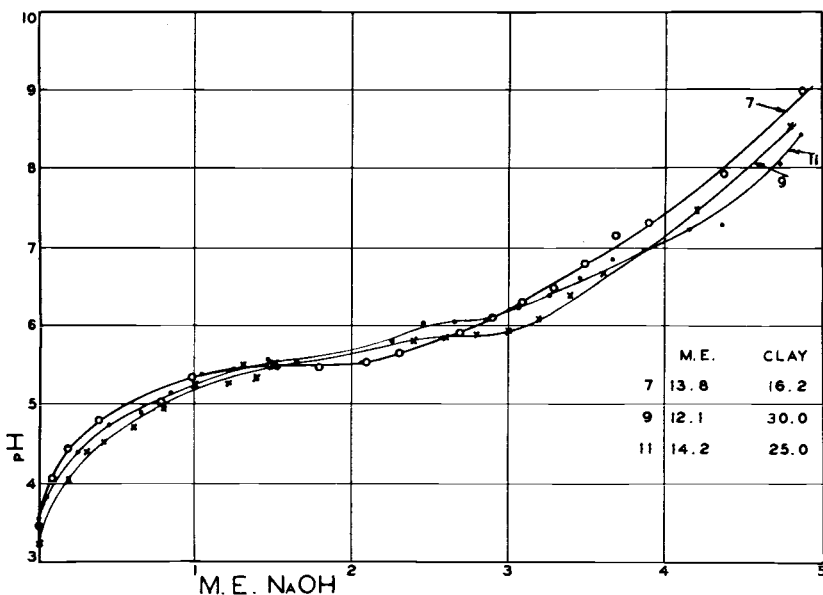


Figure 6.—Titration curves for soils of 12.1 to 14.2 milliequivalents replacement capacity.

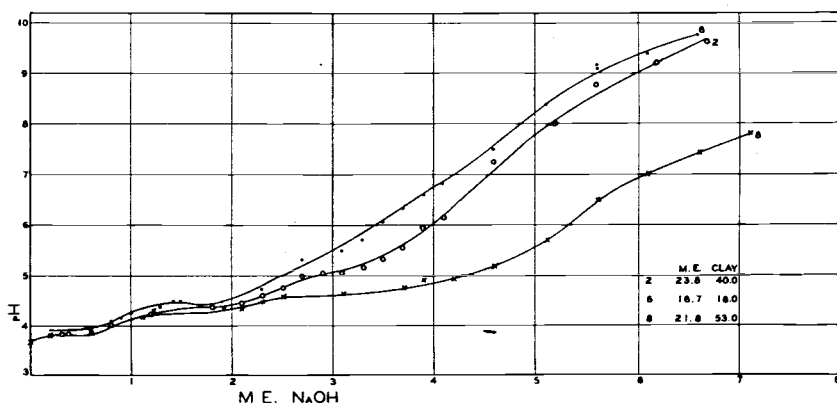


Figure 7.—Titration curves for soils of high replacement capacity.

capacity—namely, 16.7 to 23.8 milliequivalents. Their highly buffered nature is in agreement with the high exchange capacity and the high clay content. All are very strongly acidic and strongly buffered between pH 4 and 6. Soils number 2 and 6 are both of the McClellan series. The inflection points are not clearly defined due probably to the highly buffered state of these soils, but there appears to be only one. Soil number 8 is a Gila clay from the Yuma Valley, and here again the curve is strongly buffered but two inflection points appear.

In classifying the nature of these curves comparisons have been made with the curves of Anderson and Byers and presented in *Technical Bulletin 542*, U.S. Department of Agriculture. All the curves presented in these four figures resemble bentonitic types with the possible exception of soils 5 and 14. It is of interest that the soils of highest and lowest exchange capacity show the least distinct inflection points. The greatest inflection is noted in the curves representing the soils of replacement capacity between 9.4 and 14.2. The data indicate that the soils of the McClellan series possess one and those of the Gila and Laveen series two inflection points. The curves also show weakly acidic characters for the Tucson and Palo Verde soils and strongly acidic characters for the Gila and McClellan series.

#### TITRATION OF SOILS AT THE MOISTURE EQUIVALENT

Titration curves for soils are usually determined in dilutions of one part soil in five parts water or greater. In view of the results obtained in our study of pH determination at the moisture equivalent, and since it appeared to be a simple procedure to conduct soil titrations while maintaining the moisture content at this point, such an experiment was conducted with three soils.

The technique employed was as follows: 20 grams of soil were placed in each of a series of 50 cc. beakers. Standard solutions of HCl having been prepared of 0.1, 0.5, 1.0, 4.0, and 10.0 normality,

increasing amounts of HCl were added to the series, and the moisture was maintained at the moisture equivalent by employing increasing concentrations of the standard HCl solutions. After the addition of acid the soils were thoroughly and frequently stirred with a glass rod for a period of twenty-four hours. During this period the beakers were kept in a moist chamber to prevent loss of moisture. pH determinations were made with a glass electrode as described below, and the data are given in Figure 8. All HCl additions are calculated to cubic centimeters of 0.1N HCl for convenience in plotting the data.

*Soil No. 4.*—This is a black alkali soil for the titration of which four sets of pH values were obtained as given in the lower part of Figure 8. Curve number 1 represents the pH values obtained at the moisture equivalent and curve number 2 the values obtained at 1:10 soil-water ratio. Following these determinations the 1:10 soil-water mixtures were filtered through clay filters. The soils were washed once with water. In this manner the salts originally present in the soil were removed as was also the salt formed during the titration with HCl. pH determinations were then made on these salt-free soils at the moisture equivalent and at 1:10 ratio. These data are given in curves 3 and 4 respectively in the lower part of Figure 8.

*Soil No. 8.*—This soil is a highly buffered type containing 8.5 per cent calcium carbonate and 53.8 per cent clay. The same procedure described above was followed in the titration of this soil. These data are also given in Figure 8. Curve number 1 represents the HCl titration at the moisture equivalent, curve number 2 the titration values at 1:10 ratio, curve number 3 is the same as 1 except that the salts have been washed out of the soil, and 4 the same salt-free soil at 1:10 soil-water ratio.

*Soil No. 13.*—This soil is a lightly buffered type containing 3.57 per cent calcium carbonate and only 12.2 per cent clay. Only two series of titration values were obtained for this soil—namely, moisture equivalent and 1:10 ratio after the salts had been removed by filtration and washing.

There are several important observations presented in these data. All the curves obtained in the several titrations for each individual soil agree very closely. It is thus evident that a soil titration will yield the same type of curve regardless of the amount of salt present in the soil solution or the soil-water ratio at which the pH determinations are made. It is of special interest to note the wide variation in degree of buffering exhibited under the several conditions studied. This is important in consideration of the exchange capacity of the soil by titration methods. For example in soil number 4 it only required 25 cc. of 0.1N HCl to reduce the pH to 7.0 at the moisture equivalent, while a volume of 100 cc. was required for the 1:10 ratio. Likewise after washing out the soluble salt from the soil, 140 cc. was required to reduce the pH to 7.0 at the moisture equivalent and 180 cc. at 1:10 ratio. These differences are greatest in the highly buffered soil number 8 and least for the lightly buffered soil number 13.

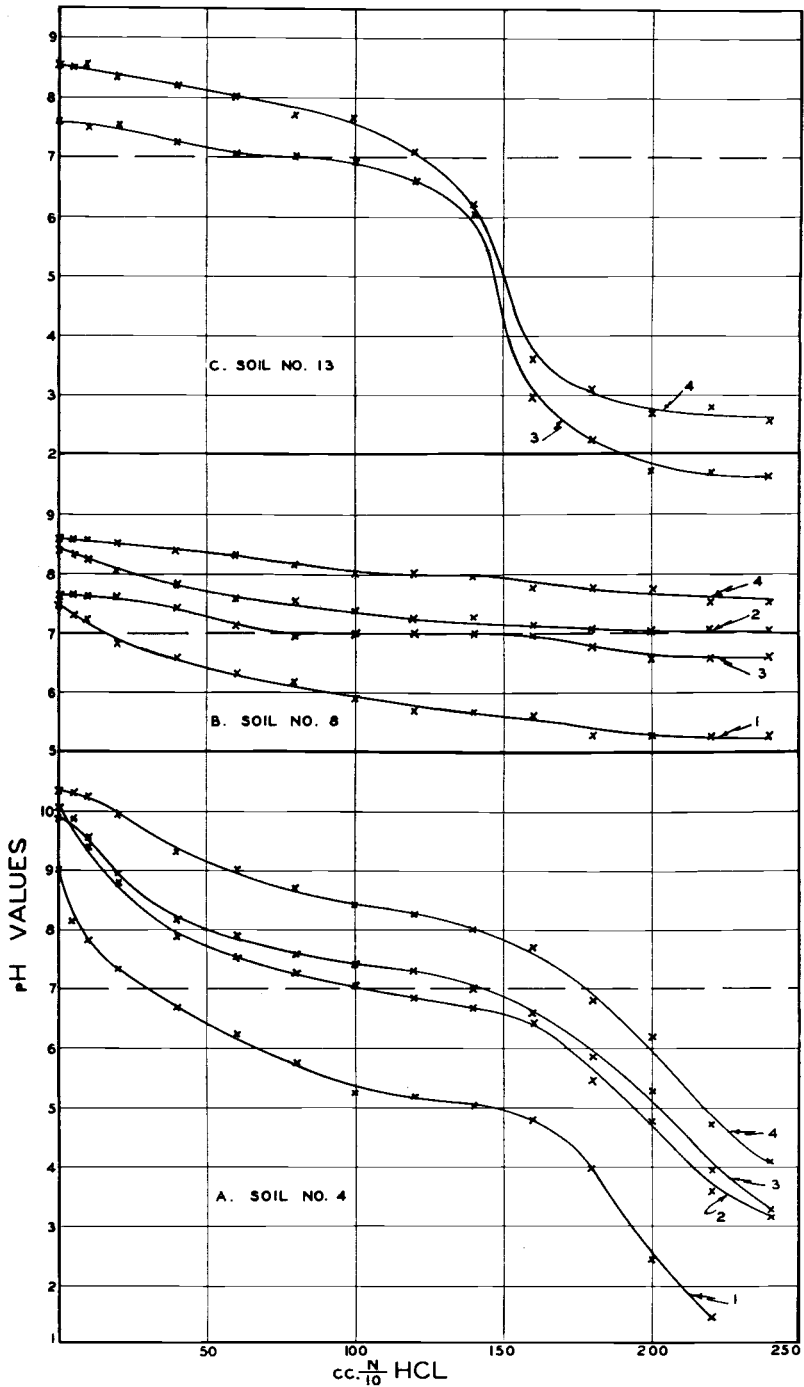


Figure 8.—Titration curves for soils at the moisture equivalent as compared with 1:10 soil-water ratio: 1, moisture equivalent; 2, 1:10 ratio; 3 and 4, moisture equivalent and 1:10 ratio, respectively, after washing the excess of salt from the soil.

These data have considerable practical bearing on the reclamation of alkali lands. There is no intent in such reclamation to reduce the pH of the soil below 7.0. We are therefore interested largely in the amount of acidifying materials required to reduce the pH to near neutrality. The experiments show that the amount required will be best indicated by titrating the soil at the moisture equivalent, as this more closely represents the moisture content of the soil in the field.

#### RELATION OF $\text{CaCO}_3$ TO THE pH OF THE SOIL

As previously mentioned, when the exchange complex is saturated with sodium the pH value of the soil is always higher when the soil is calcareous than when no calcium carbonate is present. This together with our observation that natural forms of calcium carbonate may vary in pH from 8.2 to 12.2 (5) illustrates the importance of this compound in the reaction of alkali soils. It has been proved many times that calcium carbonate promotes the formation of sodium carbonate in arid and semiarid soils, for it is quite soluble in solutions of sodium chloride or sulphate.

Cummins and Kelley (8) have shown the role of calcium carbonate in titratable alkalinity of soils. They found that appreciable amounts of titratable alkalinity were produced only when calcium carbonate was present. On leaching sodium-saturated soils containing calcium carbonate and others free from calcium carbonate, the leachings at first showed no sodium carbonate when it was absent. On continued leaching with water the alkalinity of the leachings was about the same from both soils due to the hydrolysis of the sodium clay.

The influence of calcium carbonate on the pH of the soil is illustrated by the next experiment. Three soils were selected and separated into two portions each. One portion of each soil was leached with 0.1N HCl until free from calcium carbonate. The other portion was untreated. These calcareous and noncalcareous soils were leached with solutions of sodium chloride and calcium chloride to the point of neutral base saturation with the respective bases, and the excess salt was removed by washing. This procedure supplied the following materials for the experiment: A, a calcareous soil saturated with calcium; B, a calcareous soil saturated with sodium; C, a noncalcareous soil saturated with calcium; D, a noncalcareous soil saturated with sodium. The pH values of these soils were determined at the moisture equivalent, at a ratio of 1:1, and at a ratio of 1:10 using both boiled distilled water and tap water. The data obtained in this experiment are given in Figure 9.

It is evident that the calcium-saturated soils show very little change in pH as the soil-water ratio is increased. In every case the noncalcareous soil exhibits the higher pH. It should be mentioned in this connection that all the calcium carbonate had been removed from one by leaching with HCl, and the activity of the calcium carbonate was unquestionably modified by leaching with

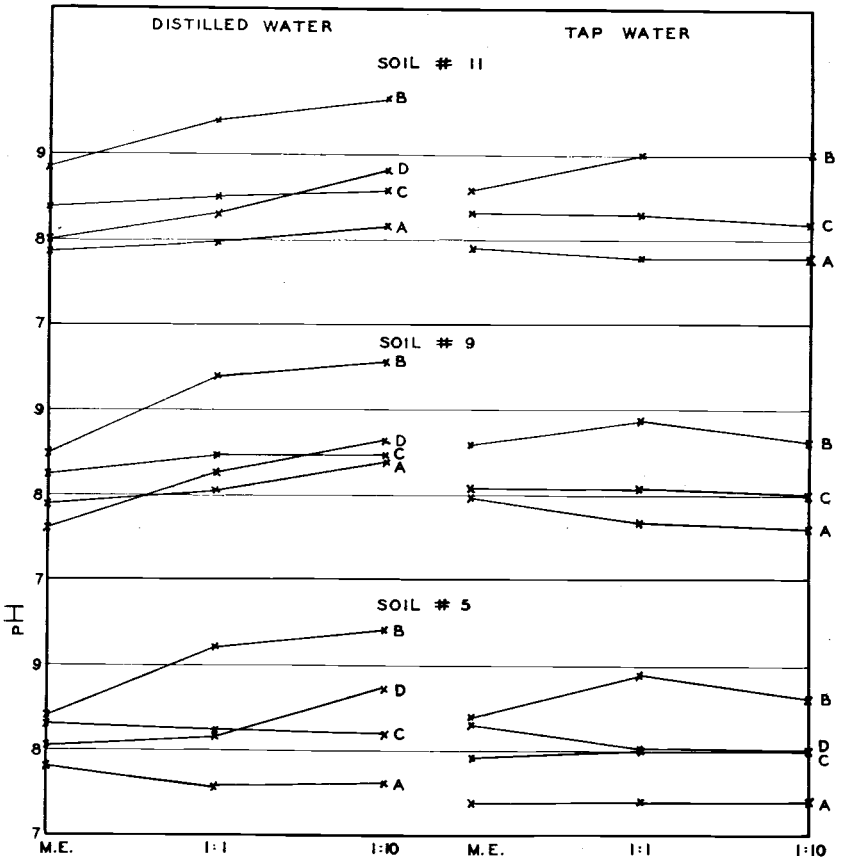


Figure 9.— pH values of calcareous and noncalcareous soils saturated with Ca and Na: A, calcareous soils saturated with Ca; B, calcareous soils saturated with Na; C, noncalcareous soils saturated with Ca; D, noncalcareous soils saturated with Na.

the solutions of calcium and sodium chloride. That the activity of the calcium carbonate was reduced is evident from a comparison of these data with the observations of Buehrer and Williams (5) showing a considerable increase in pH with increase in ratio of  $\text{CaCO}_3$  to water. This is another case which suggests a radical difference in the behavior of artificially prepared soils and similar soils as they occur in nature.

The sodium-saturated soils exhibit a notable increase in pH on dilution, and this increase is of much greater magnitude in the calcareous than the noncalcareous soils. This explains why the presence of sodium salts is much more detrimental to crops on western soils than in soils of other sections of the country which

are noncalcareous. It probably also explains why sodium nitrate can be continuously used in humid and semihumid lands which are noncalcareous without any apparent injury.

When tap water was used in preparing the soils for the pH determination, only the sodium-saturated calcareous soils showed any increase in pH with increase in soil-water ratio. Even this was practically negligible as it was only pH 0.5 in the highest—namely, soil number 5. These data, obtained by the use of tap water, again emphasize the value of tap water for determining pH values of soils when the data are to be used in interpreting field conditions. They also show the magnitude of the error and the limitations attached to pH values determined by dilution with boiled distilled water which creates a condition never met in the field.

In order to further illustrate the behavior of calcareous and noncalcareous soils, the same three soils were titrated with standard acid. Both the pH values and buffer capacities obtained from these titrations are given in Figure 10. These soils were titrated with 0.1*N* HCl by starting with 10 grams of soil in 50 cc. of water. Increments of acid were added daily from a burette, the soils shaken in an end-over-end shaking machine for two hours and let stand twenty-four hours before making the pH reading.

It is evident from these curves that the buffer capacity of these soils is largely a property of calcium carbonate. The relative amount of acid required to saturate the exchange complex in the noncalcareous soils is very small indeed compared to that required by the calcareous soils. The amount of acid required to reduce the pH of the calcareous soils to 7.0 is small in all soils, but the rate is greatly reduced at this point depending upon the amount of calcium carbonate in the soil. Soil number 9 contains 1.5 per cent, soil number 11 contains 5.36 per cent, and soil number 5 contains 8.5 per cent calcium carbonate. It is of interest that the amount of acid required to reduce the pH to 7.0 is quite similar especially for the calcium-saturated calcareous soils and for the sodium-saturated calcareous soils. The former shows the least alkalinity or buffering capacity during the early additions of acid. Later, as the addition of acid is continued the curves for the two soils follow each other very closely. It is recognized in interpreting these data that as the addition of acid is continued the soluble salt formed increases the buffer effect.

While these three soils cover a wide range of buffer capacity the buffer effect is not manifested until practical neutrality is reached. Thus, so far as any influence of alkalinity on the physiological behavior of crops is concerned, the buffer capacity does not warrant a great deal of consideration. The principal significance of these curves is that all the soils, regardless of the buffer capacity or nature of the base saturating the complex, are reduced quite rapidly to near neutrality on addition of acid—the calcareous only slightly less rapid than the noncalcareous soils.

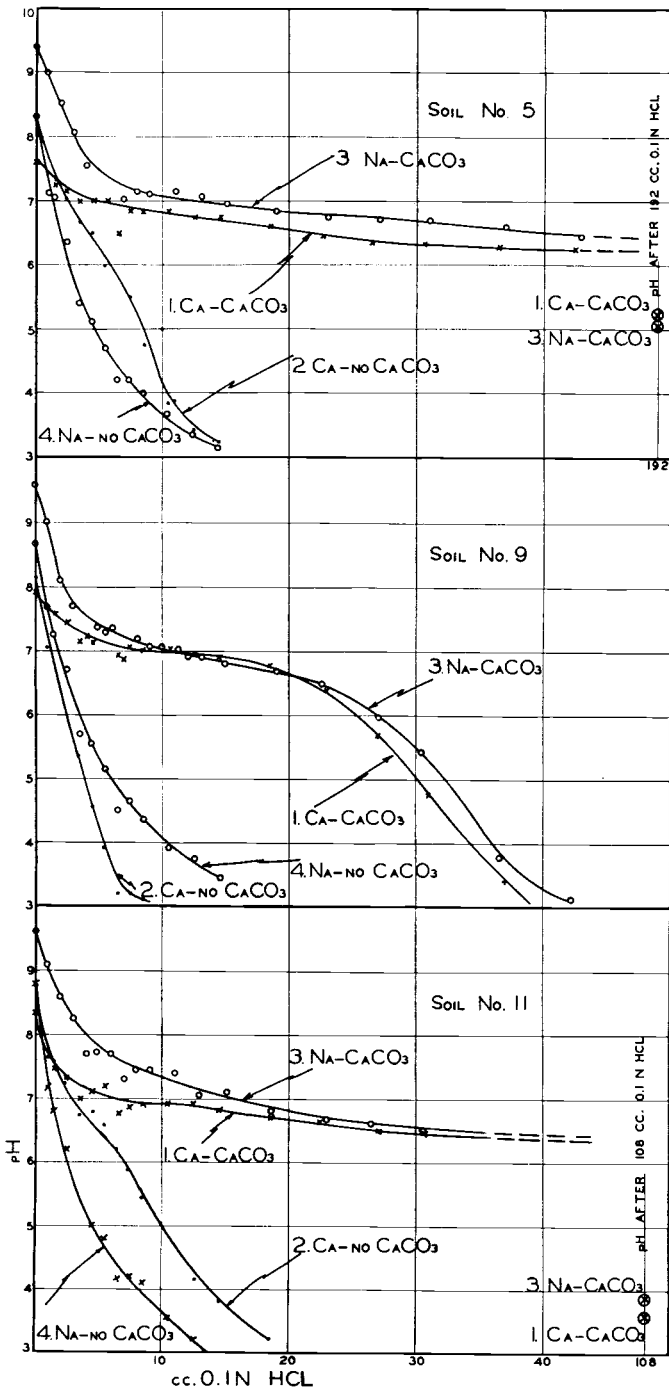


Figure 10.—Comparative buffer capacities of calcareous and noncalcareous soils saturated with Na and Ca.



## SUMMARY AND CONCLUSIONS

1. The structural and physiological factors involved in the husbandry of alkali soils are governed largely by the concentration, character, and activity of the hydrolytic bases present in the soil and the soil solution. Of these bases the only one heretofore considered as most adversely affecting soil structure and the physiological behavior of crops is sodium as sodium carbonate or sodium clay. Early work on alkali soils was largely confined to quantitative studies on sodium carbonate. Later quantitative studies were extended to include the sodium absorbed by the exchange complex. With the inauguration of studies in hydroxylion concentration alkali-soil studies have been further extended to include the intensity factor.

2. Investigations at the Arizona station show that while sodium is the most active hydrolytic base present in semiarid soils the activity of calcium as calcium carbonate has been largely overlooked. Calcium carbonate has always been considered a minor or indirect contributing factor, although the reactions between soluble sodium salts and calcium carbonate are recognized as of major importance. Also it has been shown that a sodium-saturated clay will exhibit a higher pH when calcium carbonate is present than when it is absent. Our investigations lead us to attribute increasing significance to calcium carbonate and show that of itself it can undergo sufficient active hydrolysis to seriously affect plant growth and soil properties, especially in heavy, poorly aerated soils.

3. For many years the pH value of the soil has been determined by methods which yield results that cannot be translated into field conditions—that is, the technique employed permits a degree of hydrolysis never attained in the field. The magnitude of this error for both alkali and acid soils is shown in this bulletin, and a method is proposed which eliminates this error and permits a determination of pH at a moisture content equal to that in the field. While, as shown, this error is small in acid soils where the “swarm hydrogen ions” dominate the system, it often amounts to more than 1 pH value in soils of pH values above 7.0 in which one or more hydrolytic bases dominate the system.

4. It is further suggested by our investigations that since tap water closely approaches the average irrigation water in composition and is buffered similarly, pH values of much practical value may be obtained by using this water as a medium for the pH determination. Even black alkali soils show little change in pH with variation in the soil-water ratio when tap water is used.

5. A study of the factors or soil conditions influencing the pH value of the soil yielded data of considerable importance. First, the replacement capacity of the soil is a straight-line function of the clay content for all the soils studied. A study of the relation between the replaceable bases and pH of the soil showed that in all cases soils containing in excess of 10 milliequivalents of replaceable sodium there is a straight-line relation between the pH and

replaceable sodium. Furthermore this straight-line relationship applies only when more than 20 per cent of the exchange capacity is satisfied by sodium. pH is therefore a function of replaceable sodium in soils of high exchange capacity when sodium is present in sufficient amounts to dominate the system. In soils with exchange capacity below 10 milliequivalents we were unable to identify any single dominating factor. There is probably a conflict in such soils between calcium carbonate, sodium carbonate, replaceable sodium, and the soluble salts.

6. Much to our surprise there was no apparent relation between the soluble salts (white alkali) and the pH values in this group of soils. This is undoubtedly due to the wide variation in the character of the salts present, for when a salt effect is studied on individual soils and individual salts there is a definite relation to pH.

7. There is evidence in these investigations that a determination of the pK value of black alkali soils may be of considerable value. The pK value of soils as mentioned by Bradfield (3) and proposed by Puri and Asghar (16) appears timely. In our base-exchange studies on black-alkali soils we were unable to obtain agreement between the exchange capacity as determined with neutral ammonium acetate and the sum of the replaceable bases present in the soil. In all cases the sum of the bases determined individually was greater than the exchange capacity. On extending our investigations it was found that the apparent error was one of high replaceable sodium values. From our own studies as well as those of others we know that the absorbing capacity of the soil is increased by the presence of hydroxyl ions. We are therefore inclined to question the value of a determination of the replaceable sodium in black-alkali soils when neutral salt solutions are employed. The growth of crops in alkali soils is much more seriously affected by the absorbed sodium in excess of that hydrolyzing above pH 7.0 than that hydrolyzing to only pH 7.0 or less. It appears, therefore, that the quantitative determination of replaceable sodium in black-alkali soils should be designed to include absorbed sodium in its entirety. In view of the fact that the pK value when the acidoid or hydrogen-saturated clay is half neutralized is equal to the pH value at this point, the pK value should have considerable significance in interpreting the alkaline properties of black-alkali soils.

8. A study of the pH of soils saturated with calcium and hydrogen did not disclose any relation between the pH and the exchange capacity or milliequivalent amounts of these cations present in the complex.

9. As a further means of studying the pH of alkali soils a number of buffer titration experiments were conducted on alkaline-calcareous types. These included hydrogen-saturated soils and calcareous and noncalcareous soils saturated with sodium and calcium. The extent of buffering obtained by the titration of the hydrogen-saturated soils shows a close relation to the exchange capacity and the clay content of the soil. There is also some in-

dication that the curves for the soils belonging to the McClellan series possess one inflection point and those belonging to the Gila series two inflection points. By comparing the titration curves of the calcareous and noncalcareous base-saturated soils the important contribution of calcium carbonate to the buffer capacity of southwestern soils is manifested. The buffer capacity is closely related to the calcium-carbonate content and is so much greater than that of the clay fraction that the latter is shaded into insignificance. Therefore, while the clay content contributes most to the high pH of black-alkali soils, the buffer capacity is largely a function of calcium carbonate.

10. Buffer titration curves of soils and soil colloids have, in the past like the pH determinations, usually been made in very dilute mixtures of soil and water. In view of this titrations were conducted with the soils at the moisture content represented by the moisture equivalent as well as at a ratio of 1:10 both in the presence of salts and after the removal of the salts originally present and those formed during the titration. It was found that the nature of the curves was the same in all cases. However, the effect of the dilution and the salt content is shown in the buffer capacity of the soils. The degree of buffering, like the pH value, increases with dilution, and both are greater after the salts are removed from the soil by filtration. It is significant that the experiments show that far less acid is required to reduce the pH of an alkali soil to pH 7 at field-moisture content than at 1:10 dilution. This proves that the reduction of pH in alkali soils is a much simpler operation than previous soil studies have indicated.

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