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AGRICULTURAL EXPERIMENT STATION

THE DETERMINATION AND INTERPRETATION OF SOIL PH VALUES

By

W. T. McGEORGE

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THE DETERMINATION AND INTERPRETATION OF SOIL PH VALUES

By W. T. McGEORGE

INTRODUCTION

Hydrogen-ion concentration is a contributing factor in most biological systems, particularly as regards plant growth and the micropopulation of the soil. It is also a controlling factor in the soil mineral system as regards both the chemical and the physical properties of the soil. With the development of accurate methods of measuring acidity and alkalinity in soils and of interpreting pH values, a greater interest in soil reaction in relation to soil properties and the economic production of crops has arisen. While it is known that soils of extreme acidity or alkalinity are non-productive for most crops, a lack of precise methods, as well as the selection of an analytical technic, has prevented any precision in the establishment of safe or preference ranges. In the Southwest, practically all the problem soils are on the alkaline side of neutrality primarily because they contain CaCO_3 , but often because they contain an excess of replaceable sodium which is sometimes accompanied by Na_2CO_3 . That is, they possess both active and potential alkalinity in greater or lesser amounts. In view of this, soil-reaction studies have been major projects in the Agricultural Chemistry and Soils Department. These investigations have included such subjects as base exchange, effect of H-ion and OH-ion concentration on ion absorption by plants, effect of alkalinity on the availability of plant food elements in the soil, methods of aiding plant nutrition in an alkaline environment, methods of determining pH values of soils, and factors affecting the pH determination and its interpretation. In spite of the large amount of work that has been done on the technic of pH determination and its interpretation, the manner in which inherent soil properties contribute to minimize or maximize the pH values of alkaline-calcareous soils is still more or less obscure.

This bulletin presents a continuation of studies on the nature of soil alkalinity and the factors affecting the OH-ion concentration and the pH determination in semiarid soils. The complexity of the alkali problem has frequently been manifest during soil investigations in this laboratory. As one example, it was noted that the soil solution of alkaline soils contains sodium silicate and sodium aluminate and that with alternate wetting and drying, hydrates and silicates are formed, thus increasing the exchange capacity and therefore the potential alkalinity (8). In another experiment, "breakdown" and "build-up" in the exchange com-

plex were noted, the former by treating the soils with acid and the latter by treating them with alkali (7). Also it has been observed that black alkali soils contain more adsorbed sodium than the capacity represented by the NH_4 adsorbed by the soil during replacement of the bases (23), a condition which has been noted by Kelley and Brown (16) on both alkaline and saline soils.

The mineral fraction of the soil is composed of the products of rock weathering and the organic fraction of the soil by the products of the weathering of plant and animal debris. These residual materials, which in general are the soil mass, are largely humus, alkaline earth carbonates, the hydrated silicates and oxides of iron and aluminum in which the alkaline and alkaline earth bases may be combined; and in semiarid soils the soluble salts deposited in the soil by excessive evaporation must be included. In these soils calcium carbonate, sodium carbonate, and the group of minerals which comprise the exchange complex represent the major alkaline compounds. The carbonates are simple compounds with quite definitely defined properties. On the other hand the adsorption and exchange complex may be composed of one or several minerals, not necessarily silicates, the structure, composition, and properties of which are extremely variable. The alumino-silicate compounds and the sesquihydrates that display the sharply manifested capacity for cation exchange and adsorption, when coming in contact with electrolytes, exert an influence on soil pH depending in large part upon the nature of the cations attached. When the soil comes in contact with water the soil colloids, with the attached cations, hydrolyze and ionize and the bases appear in solution as hydroxides. The early investigations indicated that the exchange capacity of the soil is a constant value, but later work has proved that these early conclusions are in error.

Briefly, then, the exchange complex, the calcium carbonate, and the soluble salts are the major factors contributing to the alkalinity of semiarid calcareous soils which we express as pH. In these soils the part which the exchange complex plays in soil reaction is complicated by the presence of salts, for salines repress hydrolysis. Since the pH of the soil is a complex of many factors, it is obvious that the ideal method for determining the pH value, in which the farmer is most interested, is one which permits the same magnitude of ionization and hydrolysis as occurs under field conditions. In previous publications from this laboratory the belief has been expressed that the pH of a soil paste, approximately the moisture equivalent, approaches this ideal most closely; but there are still contributing factors which need clarification in order the better to interpret this pH value. Important among these are: the influence of total salinity; the influence of individual cations and anions; the influence of sodium carbonate and bicarbonate; the influence of the hydrolytic properties of the

exchange complex; the influence of the proportion of different-sized particles in the soil; and the relation of pH of the soil paste to the so-called isohydric pH, the pH of exchange neutrality, and the equi-ionic pH.

SALINITY-PH RELATIONSHIPS

In order to illustrate the variety of conditions and the difficulties involved in the determination and interpretation of the pH values of alkaline-calcareous soils, some pertinent soil analyses are submitted in Tables 1 and 2. The soils presented in Table 1 are from widely scattered sections of the state and represent a wide variety of types and a set of conditions in which no relation between pH and general methods of soil analysis seems apparent. The soils in Table 2 represent a single type—that is, a group of sixteen separate samples from sixteen separate but adjoining borders in a single field.

Briefly, the methods used in the analyses of these soils were as follows. Replaceable bases were determined by leaching 20 grams of soil with 50 per cent methanol until free of neutral salts, then with 250 ml. of neutral normal ammonium acetate solution. Sodium, potassium, and magnesium were determined in aliquots of this leachate. Total exchange capacity was determined by washing the soil on the filter until it was free from ammonium acetate, and by distilling the ammonia into standard acid, using MgO to alkalize the soil suspension in a Kjeldahl flask. Replaceable calcium was determined by subtracting the sum of the sodium, potassium, and magnesium from the total.

Calcium carbonate was determined by the A.O.A.C. method of absorbing the total CO_2 liberated on treating the soil with HCl, in NaOH solution, precipitating the CO_2 with BaCl_2 , and titrating the excess hydroxide.

Mechanical analyses were made by the hydrometer method.

Soluble salts were determined by conductivity, using the L. and N. soil conductivity bridge and a suspension of one part soil in five parts distilled water which had been shaken for one half hour or by totaling the anions and cations. The separate ions were determined in this water extract after the soil suspension had been filtered.

The soils given in Table 1 vary in replacement capacity from 3.7 milliequivalents per 100 grams to 23.6, from noncalcareous soils to 10.18 per cent CaCO_3 , from 310 to 8,020 parts per million soluble salts, and mechanically from sand to clay. These soils may be identified from the following classification and numbers.¹

1. Superstition sand from the Yuma Mesa.
2. Clay loam soil from the Casa Grande Valley.

¹Wherever these numbers appear in this bulletin, they refer to the soils listed here.

3. Laveen sandy loam, University Farm, Mesa.
4. Gila clay loam.
5. Pima clay loam, Safford Valley.
6. Palos Verdes sandy loam, noncalcareous surface layer.
7. Gila clay loam, black alkali soil.
8. Casa Grande clay, brown silted phase.
- 9B. Sandy black alkali soil.
- 10B. Sandy black alkali soil.

TABLE 1.—CHEMICAL AND MECHANICAL ANALYSES OF SOILS IN GROUP 1

Soil no.	pH values				Replaceable bases, m.e. per 100 gm.				
	Original soil		Na sat. soil		Na	K	Mg	Ca	Total
	Paste	1:10	Paste	1:10					
6	7.20	8.15	9.80	10.20	1.0	0.6	1.8	1.3	4.7
4	7.20	8.45	9.40	10.30	1.1	1.4	2.3	2.6	7.4
5	7.70	8.35	8.85	10.15	2.4	3.8	5.6	11.8	23.6
3	7.75	8.85	9.05	10.25	1.2	1.8	4.7	1.5	9.2
2	7.95	9.10	9.00	10.15	2.2	2.4	5.4	4.0	14.0
8	8.00	9.40	9.20	10.20	10.9	2.0	3.8	3.6	20.3
1	8.40	9.35	9.70	10.00	0.3	0.4	1.0	2.0	3.7
10B	8.50	9.60	9.75	10.25	1.0	2.0	4.1
9B	8.55	10.00	9.80	10.30	1.9	1.3	5.8
7	9.55	10.40	9.70	10.40	7.4	0.2	1.4	0.2	9.2

Soluble salts—p.p.m. soil

	CO ₃	HCO ₃	Cl	SO ₄	Ca	Mg	Na	Total salts
6	0	230	40	tr.	tr.	20	80	370
4	0	245	110	225	1,200	tr.	695	3,582
5	0	875	630	400	200	tr.	695	2,800
3	0	730	210	160	225	tr.	230	1,555
2	0	230	160	375	170	10	160	1,105
8	tr.	575	190	125	95	10	235	1,230
1	0	180	20	tr.	75	tr.	35	310
10B	25	220	210	1,200	100	tr.	700	2,455
9B	35	375	75	100	35	tr.	220	840
7	935	180	940	2,400	150	tr.	3,415	8,020

Per cent

	CaCO ₃	Mech. anal.		
		Sand	Silt	Clay
6	0.00	72	17	11
4	5.45	44	27	29
5	2.20	34	37	29
3	10.18	50	34	16
2	4.88	42	29	29
8	1.33	40	18	42
1	1.93	91	6	3
10B	84	10	6
9B	83	8	9
7	4.60	38	37	25

While this is a smaller group of soils than was used in previous pH-salinity studies (23), the data are in agreement in that there is no apparent correlation between pH values and concentration of soluble salts, nor between pH and the concentration of separate anions and cations. It seems quite clear that in a group composed of many or even several soil types, the variation in values between individuals of a group will obscure relationships which can be shown to exist in individual soils themselves. The data suggest that the study of pH values as affected by salinity can best be conducted with single soil types or with each soil separately.

It is the general assumption, and correctly so, that neutral salt solutions do repress the pH values of semiarid soils and that these soils do usually contain more or less salinity and alkalinity. In view of this, it appears puzzling at first that attempts to correlate pH with salinity in large groups of soils have failed to confirm this. That is, in spite of the fact that we know salts repress pH values in soils, there is no apparent uniformity about the pH-salinity relationship; therefore no correction value can be used to approximate it. The degree of hydrolysis of salts increases with dilution, and it has been shown experimentally in this laboratory (4, 21), working with individual soils and salt solutions, that neutral salts repress pH values in alkaline-calcareous soils and that the repression is of appreciable magnitude. It is of particular interest, in this connection, that calcium salts produce a greater repression than sodium salts. Since the analytical data for the second group of soils are pertinent to a discussion of the data in Table 1, they are presented at this point.

This second set of soil samples was selected to represent a limited area, sixteen borders adjoining one another in a single field, and they all represent a single soil type, Imperial Silty clay, which varies widely in alkalinity and salinity and has equally variable anion and cation ratios. These samples were selected to have a wide variation in alkalinity but to avoid variables which might arise from soil mineral or soil-type differences. The analytical data for this group are given in Table 2.

The analytical data in Table 1 show no correlation between soluble salts and pH except that the pH of the soils containing free carbonate are higher than those containing little or no soluble carbonate. Salinity in the second group varies from 6,260 to 75,190 parts per million soil and pH values (as determined on the soil paste) from 7.55 to 8.95. It is clear from these data that when employing a single soil type certain relations will be found between salinity and pH. The following salinity-pH relations for the pH of the soil paste, the 1:10 soil:water ratio, and the increase in pH from paste to 1:10 ratio were obtained for this group of soils. Correlation statistics were calculated according to Snedecor (29).²

²Calculations by W. P. Martin.

TABLE 2.—CHEMICAL ANALYSES AND MECHANICAL ANALYSES OF SOILS IN GROUP 2

Soil no.	M e. per 100 gms.		pH values		Mechanical analyses (%)		
	Ads. cap.	Ads. Na	Paste	1:10	Sand	Silt	Clay
11	33.9	12.5	7.87	8.57	38	27	35
12	33.9	8.7	7.85	8.40	28	28	44
13	33.3	7.7	8.02	9.15	29	25	46
14	35.0	4.8	7.95	8.55	32	33	35
15	30.4	11.7	7.55	8.15	36	36	28
16	29.0	12.3	7.95	8.45	37	33	30
17	25.0	9.3	8.05	8.65	31	33	36
18	24.0	6.0	8.20	8.60	27	37	36
19	24.0	11.3	8.35	9.40	23	30	47
20	28.0	23.4	8.35	9.40	20	32	48
21	26.0	16.4	8.15	9.00	22	34	44
22	29.0	13.0	8.45	9.75	21	25	54
23	29.0	22.1	8.45	9.65	22	28	50
24	31.0	26.5	8.95	9.85	22	26	52
25	27.0	14.5	8.55	9.55	20	28	52
26	28.0	5.9	8.32	9.32	22	29	49

Chemical analyses, ions as p.p.m. in 1:10 water extract, total salts as p.p.m. in soil

	CO ₂	HCO ₃	Cl	SO ₄	Ca	Mg	Na	Total salts
11	0	190	676	1,240	90	11	715	29,220
12	0	102	528	1,060	106	45	520	23,610
13	5	149	72	450	22	2	368	10,680
14	0	117	84	840	135	7	291	14,740
15	0	80	2,056	1,680	750	82	2,588	72,360
16	0	90	1,556	2,720	620	56	2,296	73,380
17	5	68	500	2,000	367	7	1,104	40,510
18	5	73	160	1,100	390	5	498	22,310
19	34	102	1,848	1,000	26	tr.	2,912	59,220
20	34	107	2,788	1,200	26	tr.	3,364	75,190
21	10	78	1,228	1,400	206	2	2,137	50,610
22	48	204	152	180	37	tr.	423	10,440
23	48	156	536	700	22	tr.	1,141	26,030
24	38	136	248	1,160	52	2	1,599	32,350
25	38	156	320	360	30	4	675	15,830
26	10	107	36	200	11	2	260	6,260

Carbonate. PH increases with increase in concentrations of CO₂ (Fig. 1). The correlation between CO₂ and pH is significant both for the soil paste and at 1:10 soil:water ratio, and the increase in pH on dilution from paste to 1:10 ratio.

Bicarbonate. PH increases with increase in concentration of HCO₃ (Fig. 2). Correlation between HCO₃ and pH is significant at 1:10 soil:water ratio and for the increase in pH on dilution from paste to 1:10, but it loses its significance for the pH of the soil paste.

Chloride. While it is known that chlorides repress pH values, the statistical analysis of the data does not show any significant correlation between pH and Cl (Fig. 3).

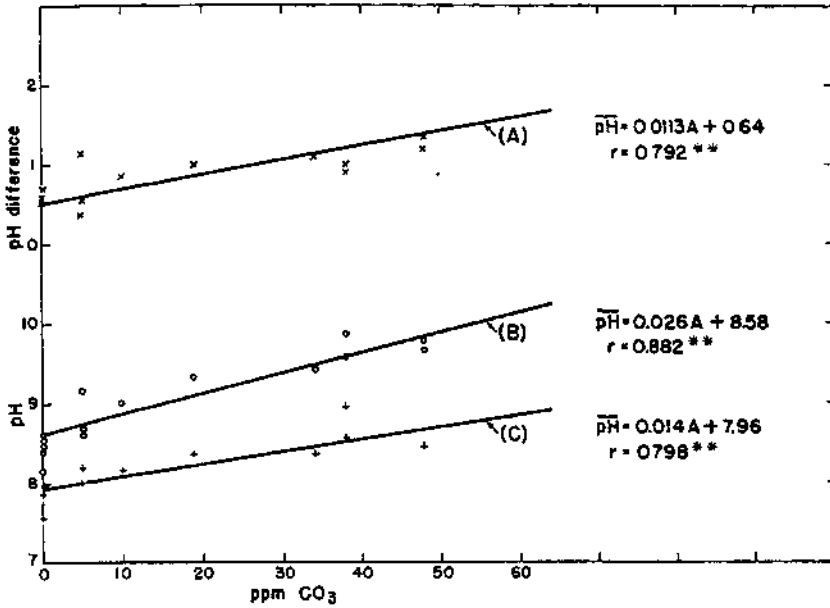


Figure 1.—Correlation between pH and p.p.m. CO_3 in soils: A, difference between pH at 1:10 and soil paste; B, pH at 1:10 soil:water ratio; C, pH of soil paste.

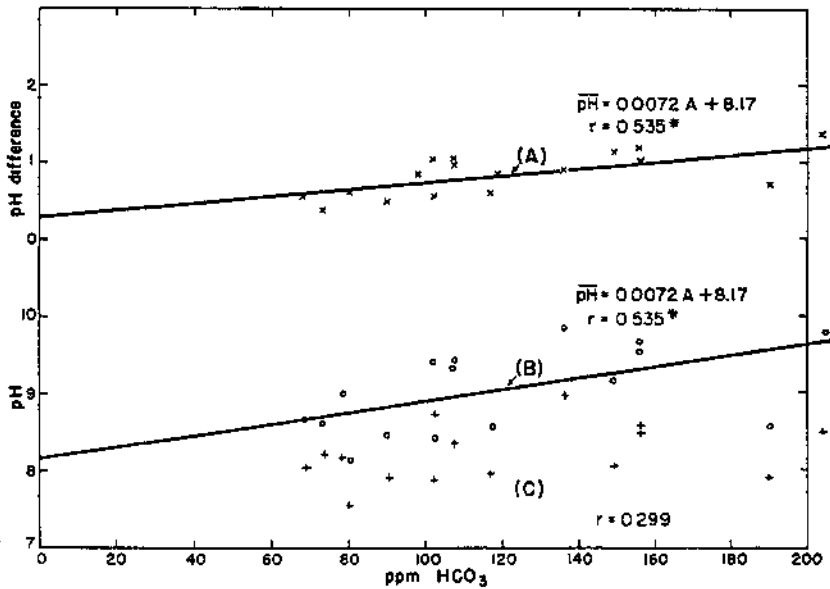


Figure 2.—Correlation between pH and p.p.m. HCO_3 in soils: A, difference between pH at 1:10 and soil paste; B, pH at 1:10 soil:water ratio; C, pH of soil paste.

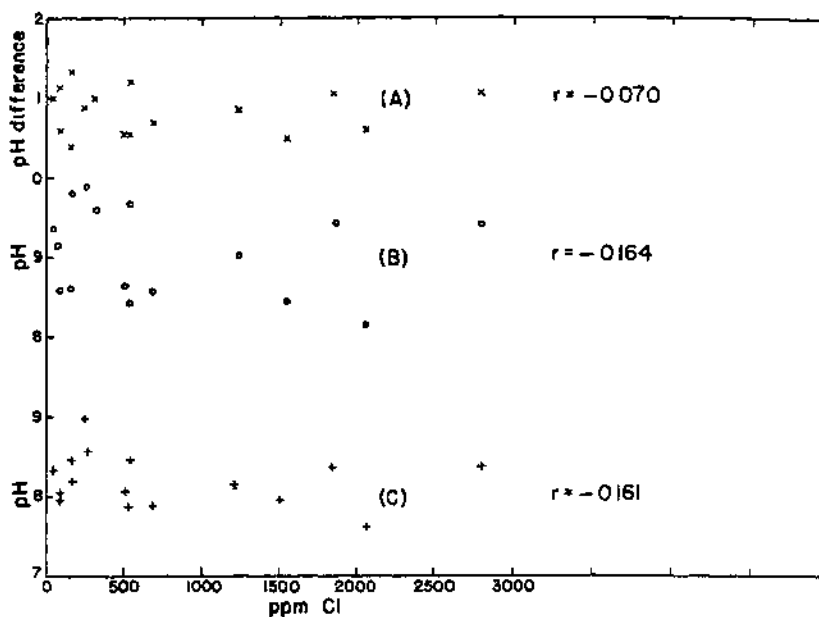


Figure 3.—Correlation between pH and p.p.m. Cl not significant.

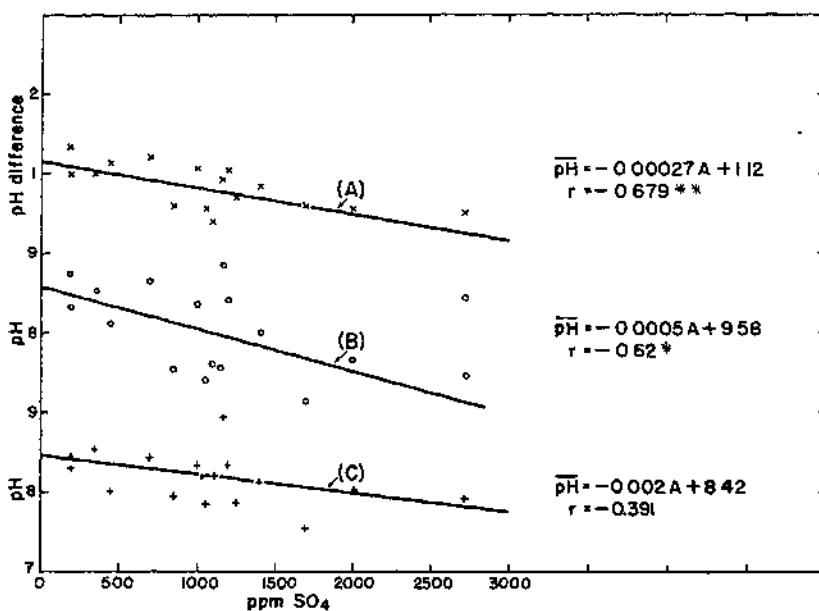


Figure 4.—Correlation between pH and p.p.m. SO_4 in soils: A, difference between pH at 1:10 and soil paste; B, pH at 1:10 soil:water ratio; C, pH of soil paste.

Sulphates. PH decreases with increase in concentration of sulphate (Fig. 4). At 1:10 soil:water ratio the correlation is significant and is highly significant for the increase in pH on dilution from paste to 1:10; but like the HCO_3 , it loses its significance for the soil paste.

Calcium. PH decreases with increase in concentration of Ca (Fig. 5). The correlation between pH and Ca is significant for the soil paste, and highly significant for the 1:10 soil:water ratio and for the increase in pH with dilution.

Sodium. There is no significant correlation between pH and Na (Fig. 6).

Total salts. There is no significant correlation between pH and p.p.m. total soluble salts (Fig. 7).

Alkaline earth bases. There is definitely less Mg and Ca in the soil extracts of the soils containing soluble carbonates.

An examination of the data in Tables 1 and 2 shows several definitely defined characteristics of the salines and the hydrolytic clay complex which throw some light on the pH problem, particularly with regard to the effect of dilution on pH and the pH-salinity relationship which is not in evidence when a comparison is made between pH and total salinity of a group of soils. The only significant data in Table 1 are the pH values which show the dilution effect; namely, the difference between the pH at 1:10 and pH of the soil paste, both in the original soils and after saturating the exchange complex with sodium. The soils in their original state of course contain the original salinity, while the sodium-saturated soils are free from neutral salts. The salt-free sodium-saturated soils show an increase in pH with increase in soil:water ratio, just as they did when the original salines were present. In other words, the increase in pH with increase in soil:water ratio is a property of the potentially alkaline clay complex and will function independently of the presence or absence of salts. It is of interest that the dilution effect noted for these salt-free soils is not in accord with results obtained by Puri and Asghar (26), who found that in the absence of salts the pH of the soil is not affected by variation in the soil:water ratio. Since ionization is confined to the surface, they believe that mere dilution in the absence of salts may have no marked effect on the pH value of the soil suspension as a whole. Buehrer and Williams (5) in a study of the effect of soil:water ratio on the pH of eight different aluminosilicate minerals commonly present in soils, found that only bentonite increased in pH with increase in dilution. All others showed a decrease in pH. However, Buehrer and Williams (4) have shown an increase in pH for CaCO_3 with increase in ratio of CaCO_3 to water. Since CaCO_3 is a constituent of most of the soils of the irrigated areas of Arizona, it is clear that the two most important potentially alkaline compounds in these soils exhibit a dilution-pH relation even when there are no salts present to repress hydrolysis. Since the pH of the soil is a function of sur-

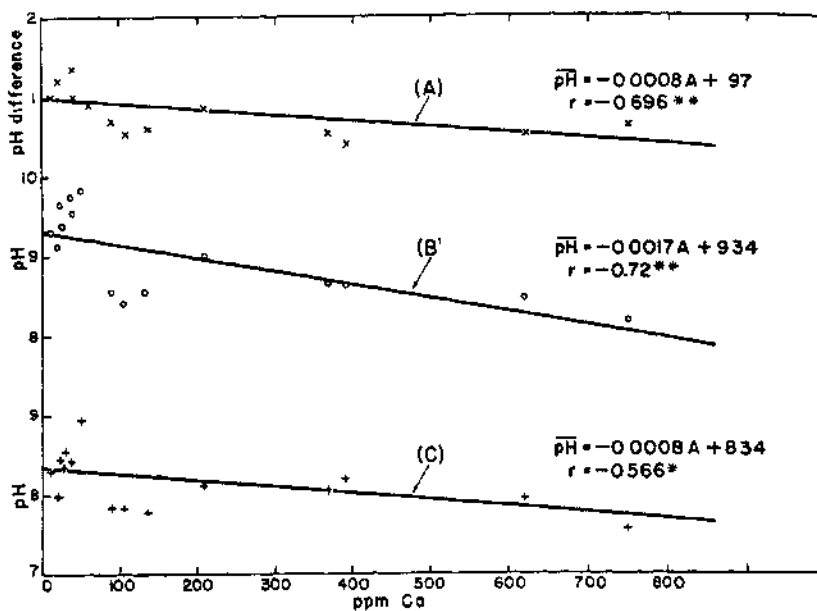


Figure 5.—Correlation between p.p.m. soluble Ca and pH in soils: A, difference between pH at 1:10 and soil paste; B, pH at 1:10 soil: water ratio; C, pH of soil paste.

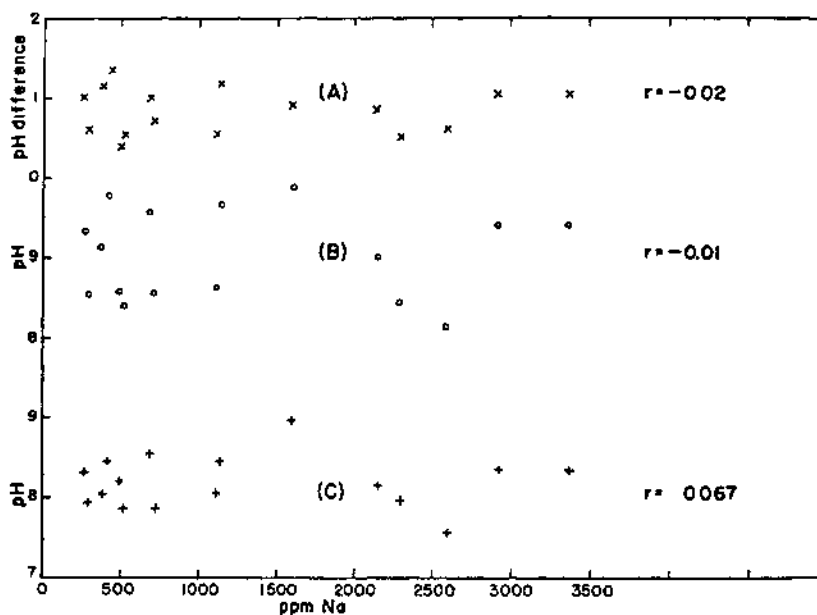


Figure 6.—Correlation between pH and p.p.m. Na in soils not significant.

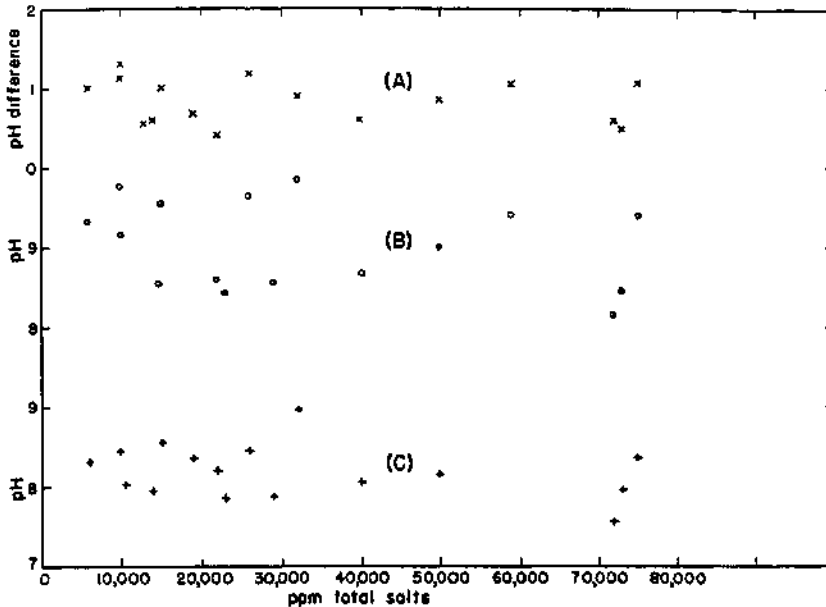


Figure 7—Correlation between pH and p.p.m. total soluble salts in soils not significant.

face ionization, the hydrolysis of soil minerals and carbonates, and the several colligative properties of the soluble salts, it is evident that the dominance of one of these factors might affect the influence of the others in a comparison of analytical data from a large group of miscellaneous soil samples.

That this is true for the salines is brought out very clearly by the data in Table 2 and already briefly summarized. These analytical data show definite cation and anion concentration correlations with pH values, and they are in agreement with some of the properties exhibited in laboratory experiments with single soils and single salt solutions. In most part the salts present in these soils are sodium salts; namely, the chloride, sulphate, bicarbonate, and carbonate. The pH of the soil increases with increase in concentration of carbonate and bicarbonate ions (Figs. 1 and 2) and decreases with increase in concentration of sulphate and chloride³ ions (Figs. 3 and 4). This is a further explanation for the absence of any correlation between sodium, total soluble salts, and pH values. The data show that in a confusion of ions such as exists in a group of different soil types, no correlation should be expected between pH values and the concentration of

³In this set of soils the pH-Cl relationship is not significant. However it can be shown experimentally that chlorides do repress pH values in saline soils.

sodium or total salts. In other words, the opposite effects of the different anions on pH tend to oppose or balance one another and thus may or may not obscure the pH-salinity relations that can be demonstrated under controlled conditions.

Since most of the irrigated soils of Arizona are calcareous, the pH-CaCO₃ relationship is important. The data in Table 1 show a relation between the presence of CaCO₃ and pH, but it is not quantitatively related to the percentage of CaCO₃ in the soil. That is, the noncalcareous soil shows the lowest pH value at both 1:10 soil:water ratio and on the soil paste. This is true for the sodium-saturated soils as well as for the soils in their original state. While CaCO₃ is not usually classified as one of the soluble salts, in salinity studies on semiarid soils its solubility is of sufficient magnitude to warrant some recognition in pH and base exchange studies. Apparently, because of its low solubility, the mere presence is sufficient to impart the CaCO₃ effect on pH, and this may be a reaction between CaCO₃ and sodium salts. Buehrer and Williams (4) have previously shown the absence of any correlation between percentage of CaCO₃ in soils and their pH values.

USE OF CENTRIFUGE FOR DEMONSTRATING THE SALINITY-PH RELATIONSHIP

The preceding experiments show definite cation and anion relationships between concentration and pH value of the soil, but they fail to show any relation between pH and total salinity, probably because of the confusion and opposite effects of the different ions. In order to conduct a further study of the pH-salinity problem, an experiment of a slightly different approach was designed, using an Ivan Sorvell centrifuge. Fifty grams of soil and 50 ml. of boiled distilled water, making a 1:1 ratio, were placed in an 80 ml. cellulose nitrate tube, stoppered, thoroughly shaken by hand, and centrifuged for ten minutes at 5,000 r.p.m. This operation was repeated ten times, decanting the supernatant solution and adding a new portion of distilled water. PH determinations were made each time on the soil-water mixture before centrifuging and separately on the supernatant water and the soil paste compacted in the bottom of the tube, after centrifuging. Conductivity of each water extract was determined with an L. and N. soil conductivity bridge, and chemical analyses were made of some of the water extracts. These data are given in part in Table 3, and the following is a discussion of the results.

Soils number 2, 3, 4, 5, and 8 represent irrigated soils which are saline but contain no black alkali. That is, they contain CaCO₃ and some replaceable sodium, but the latter is not present in sufficient amounts to impart the characteristic black alkali properties. The data for these soils show that when the centrifuge is used to separate the soil and water extract, a definite pH-salinity relation-

ship can be demonstrated for all saline soils. The pH values for the soil paste, the soil-water suspension, and the water centrifugal separate all increase with successive extractions, and the conductivity determinations show successive reductions in salinity. It is significant that the greatest increase in pH from successive extraction of salines was obtained for soils 4 and 5, and these soils were highest in soluble calcium. This is in agreement with our experiments (21) which showed that calcium salts repress pH values of soils more than do sodium salts. These centrifuge studies prove that the best way to determine a pH-salinity relation in soils is by analyzing the soils before and after removal of the salines rather than to attempt to establish a correlation between pH and the total salinity determinations.

For the black alkali soils, 7 and K, both the conductivity and the pH behave differently with successive extractions of the soluble salts; that is, there is a decrease in the pH of the soil paste as compared with the increase found for the soils which do not have any black alkali present. For the soil-water suspension and the water extracts the pH increases as in the case of the saline soils, but this increase is much smaller and almost within experimental error. It should be mentioned that both soils, 7 and K, contained some Na_2CO_3 , and the exchange complex was nearly saturated with sodium. As already mentioned, we have found that black alkali soils usually contain more adsorbed sodium than the equivalent of the total exchange capacity of the soil as determined with neutral normal ammonium acetate solution. We have postulated that this indicates a surface adsorption of NaOH , or Na_2CO_3 in excess of the sodium chemically combined with the exchange minerals, or that in black alkali soils some of the replaceable sodium is more loosely held. The decrease in pH of the soil paste as the successive water extracts increase in pH indicates that by the removal of this loosely held alkalinity the clay complex, at the moisture content represented by the soil paste, undergoes a reduction in hydrolytic capacity. Kelley and Cummins (17), in a study of the effect of salts on soils, found notable differences in the reaction between soils and solutions of neutral and alkaline sodium salts. On treating the soils with the neutral and alkaline solutions, sodium was removed from the solution in increasing amounts in passing from the less to the more alkaline solutions. There may also be some relation between the difference in behavior noted for the black alkali soils and the observations of Kelley and Brown (16) that neutral soils absorb substantial amounts of $\text{Ca}(\text{OH})_2$ without exchange of cations and that this absorbed $\text{Ca}(\text{OH})_2$ appears to be loosely held. On leaching such soils they report that the leachate continued alkaline after prolonged leaching. Jarusov (15) has noted what he refers to as "dissimilar mobility" for replaceable H ions; namely, H ions which are characterized by a high degree of mobility, and hydrolytic H ions as of a lower degree of mobility.

Soil no. 6

1	7.80	7.65	7.50	0	91	22	37	886
2	7.75	7.85	7.55					2,110
3	8.25	8.20	7.60					4,080
10	8.30	8.30	7.90					8,000

Soil no. 7

1	9.90	9.90	9.80	180	1,525	900	49	2,130	53
2	10.20	9.95	9.70	216	732	290	71	1,115	97
3	10.20	10.05	9.70	216	216	120	71	1,365	157
10	10.25	10.05	9.45						511

Soil no. 8

1	8.60	8.35	8.05	0	141	60	22	168	450
2	9.00	8.80	8.25	tr.	139	28	8	139	865
3	9.05	8.90	8.30	tr.	139	14	7	133	1,180
10	9.25	9.35	8.35						2,180

Soil K

1	10.10	9.95	9.85						49
2	10.25	10.10	9.80						120
3	10.30	10.20	9.85						328
10	10.15	10.00	9.35						1,019

Soil R.I.

1	4.30	4.60	4.40						
2	4.45	4.60	4.50						
3	4.50	4.60	4.55						
10	4.60	4.70	4.70						

Referring to the pH values of the first and tenth soil-water suspensions, the change in pH from the first to the tenth is least for the black alkali soils. Since these soils are saline as well as alkaline, the data indicate less pH repression from salinity in black alkali soils than in the saline soils where sodium carbonate is absent and replaceable sodium is not present in sufficient amount to impart the black alkali properties. The black alkali soils are highest in CO_3 and HCO_3 ions which tend to increase the pH of the soil suspension and oppose the decrease in pH produced by Cl and SO_4 ions. When such soils are subjected to successive extractions with water, the ratio of $\text{HCO}_3 + \text{CO}_3 / \text{Cl} + \text{SO}_4$ increases, and this alkalinity tends to maintain a higher pH at the tenth water extraction, desalinization. The degree of hydrolysis of the exchange complex of the saline soils is not nearly so great as in the soils where the exchange complex is nearly saturated with sodium and free Na_2CO_3 is present.

It is of interest to study the data in Table 3 from another angle. The effect of dilution on the pH, obtained by subtracting the pH of the soil paste from the pH at 1:1 soil:water ratio, is greatest in every case at the tenth extraction. Since the soluble salts are largely washed out of the soils at this point, this is additional evidence of pH repression by salinity and that the increase in pH of the soil with increase in soil:water ratio is definitely a property of the soil colloids and their ion atmosphere, independently of the salinity effect on pH and the fact that salts do influence their hydrolysis.

The relation between the pH and the conductivity of the tenth water extract is also of interest (Fig. 8). Excepting the noncalcareous soil and the Superstition sand, both distinctly different from average semiarid soils, the values obtained by subtracting the pH of the soil paste from the pH of the 1:1 soil-water suspension, the dilution effect, varies only between the minimum of 0.6 and the maximum of 0.9 while the resistance (L. and N. soil conductivity bridge) varies from 511 to 3,580 ohms. This again indicates a source of error arising from attempts to correlate the pH of soils with total salts if they are calculated from conductivity, for it is clearly evident that the soil colloids in a soil suspension, as well as the soluble salts, contribute to the total conductivity of the soil suspension. Figure 8 shows that there is a wide variation in the conductivity of these soil suspensions which have been washed ten times and are therefore essentially free of soluble salts. The conductivity is highest for the two black alkali soils and least for the Palos Verdes and Superstition soils, which are lowest in clay content. Figure 9 shows how the pH of the soil suspension decreases with the increase in conductivity.

Soil number 1, Superstition sand, is an unusual type of soil containing more than 90 per cent sand and only 3 per cent clay; but in spite of this it has a relatively high pH value. The salinity is very low. In this soil the changes in pH with successive extrac-

tions were only minor, as was also the difference in pH between the water extract and the soil. This is evidence that the silt and clay fractions exhibit the major influence on pH changes of this nature.

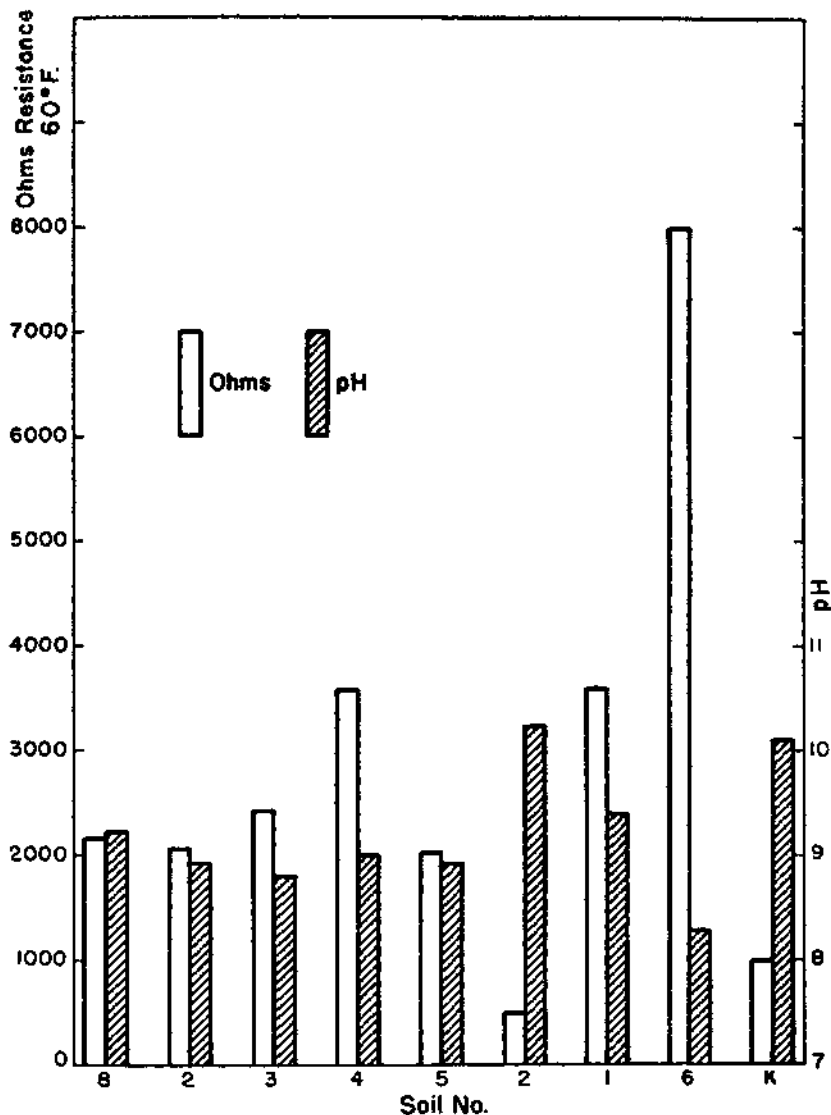


Figure 8.—Correlation between pH and conductivity of tenth water extract, Table 3.

The Palos Verdes soil, number 6, is a noncalcareous soil low in salinity. It is an upland soil from which the CaCO_3 has been leached out of the surface soil into the lower soil horizons. It shows only a very small increase in pH with successive extractions.

For the purpose of comparison, an acid soil from Rhode Island (R.I.) was included in the experiment. In this soil both salinity and CaCO_3 effects are entirely absent, and replaceable H is the dominant cation. It is of interest that the pH increases with successive extractions in both the soil-water suspension and in the soil and water separates, but at each extraction all three determinations are in rather close agreement.

The centrifugal method shows that several significant factors are involved in the pH changes in soils with change in soil: water ratio. Arid saline soils, calcareous and noncalcareous, increase in pH value with successive extractions with distilled water and reduction in conductivity, but there is no relation between the magnitude of the initial or final pH and the initial or final conductivity. The black alkali soils continue to decrease in pH (soil paste) with successive extractions up to the end of the ten extractions made in this experiment. In practically all cases the pH of the soil-water suspension is greater than either the water separate or the soil paste. It is of further interest that for every soil there was an increase in pH of the soil-water suspension with increase in number of extractions. This applies to the calcareous and noncalcareous soils, to those containing Na_2CO_3 , and where it was not present, and to those both high and low in salinity, and it shows the prolonged hydrolytic property of the exchange complex.

The analytical data presented in Tables 1 and 2 were obtained by analytical methods commonly employed in the examination of semiarid soils and illustrate how several factors may affect the pH values and the changes in pH values with variation in soil: water ratios. Both the calcareous and noncalcareous soils will exhibit hydrolysis as an inherent property of the mineral soil fraction, but in the presence of neutral or alkaline salts this will be in proportion to the concentration and ratio of ions. Among the ways in which salinity functions to repress pH values there are reduction in activity of water, coagulation of colloids, reduced surface, repression of hydrolysis, and chemical reaction with the exchange complex and thus a change in hydrolytic equilibria.

THE HEHNER METHOD

Many years ago the Hehner method (28) was quite widely used in water analysis to determine the Na_2CO_3 and the method was applied to a limited extent in the analysis of alkali soils. The following is the method as applied to soils. Twenty-five grams of soil are weighed into a 500 ml. volumetric flask, 400 ml. of boiled distilled water added, and the whole digested on the steam bath

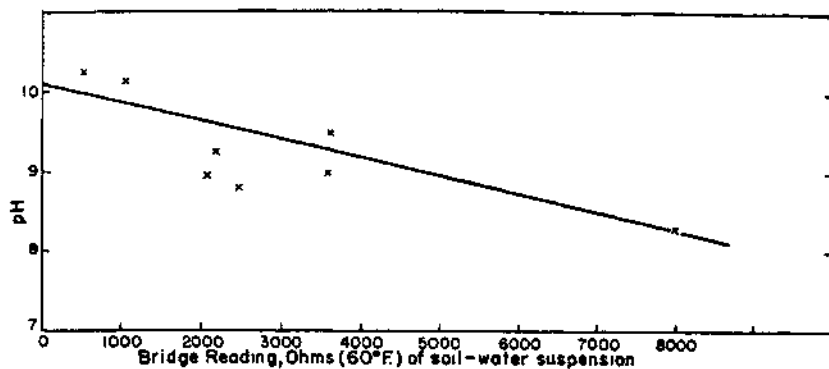


Figure 9.—Relation between conductivity and pH of soil which has been extracted ten times with distilled water.

TABLE 4.—COMPARISON OF HEHNER AND PH VALUES

Soil no.	P.p.m. total sol. salts	Per cent Na_2CO_3 Hehner value	PH soil paste	PH 1:10	PH 1:10-paste
Alkaline soils					
1	310	.0424	8.40	9.35	0.95
2	1,105	.0636	7.95	9.10	1.15
5	2,800	.0212	7.70	8.35	0.65
7	8,020	.2544	9.55	10.40	0.85
8	12,302	.1164	8.00	9.40	1.40
X	24,000	.3284	8.95	9.85	0.90
B	6,480	.1060	9.30	9.98	0.68
13	10,680	.1692	8.02	9.15	1.13
19	59,220	.1484	8.35	9.40	1.05
20	75,190	.1692	8.45	9.40	0.95
22	10,440	.2548	8.45	9.75	1.30
23	26,030	.2648	8.45	9.65	1.20
24	32,350	.2120	9.85	9.85	0.90
25	15,830	.1164	8.55	9.55	1.00
K	5,320	.2964	9.65	10.35	0.70
C	-----	.1904	8.85	10.00	1.15
92	840	.0952	8.55	10.00	1.45
94	1,775	.0212	8.50	9.60	1.10
Saline soils					
4	3,582	-----	7.20	8.45	1.25
11	29,220	-----	7.87	8.57	0.70
12	23,610	-----	7.85	8.40	0.55
14	10,470	-----	7.95	8.55	0.60
15	72,360	-----	7.55	8.15	0.60
16	73,380	-----	7.95	8.45	0.50
17	40,510	-----	8.05	8.65	0.60
18	22,310	-----	8.20	8.64	0.44
21	50,610	-----	8.15	9.00	0.85

for ten hours. It is then cooled, made to volume, shaken, and filtered. Fifty ml. of the filtrate is evaporated to dryness on the steam

bath in a platinum dish, with 25 ml. of N/25 Na_2CO_3 . This residue is rubbed up in the dish with an agate pestle by using boiled distilled water for complete transfer to a 100 ml. vol. flask, made to volume, shaken, and let stand over night. Fifty ml. of this is drawn off with a pipette, transferred to a glass bottle, 5 ml. of CHCl_3 , and 5 ml. of a 0.1 gram per liter solution of erythrosin are added. This is titrated with N/20 H_2SO_4 until it becomes colorless.

If less acid is required than is necessary to balance the Na_2CO_3 which was added, then some of the carbonate has reacted with calcium and magnesium salts, and no Na_2CO_3 is present in the soil extract. If more acid is required for the titration than that equivalent to the Na_2CO_3 added, then black alkali is present in the soil extract. Obviously the method measures both NaHCO_3 and Na_2CO_3 .

The Hehner method was selected for a further study of the relation between NaHCO_3 and Na_2CO_3 and the pH values of the soil as determined at the 1:10 soil:water ratio and on the soil paste. Twenty-seven soils were selected for this study, of which eighteen showed alkalinity by the Hehner method and nine did not. These data are given in Table 4, while the soils showing alkalinity are shown in relation to pH in Figure 10.

In interpreting these data an undetermined salinity effect on pH must be recognized. With due consideration to this salinity effect—namely, the wide variation in the saline concentration of the soil solution of this group of soils—it is believed that the correlation between the Hehner values and pH is quite definite for the values at 1:10 soil:water ratio and for the soil paste. On subtracting the pH of the soil paste from the pH at 1:10, in order to get the dilution effect on pH, a mean value of 1.04 is obtained for the black alkali soils and of 0.63 for the nine saline soils, showing greater hydrolysis in the former.

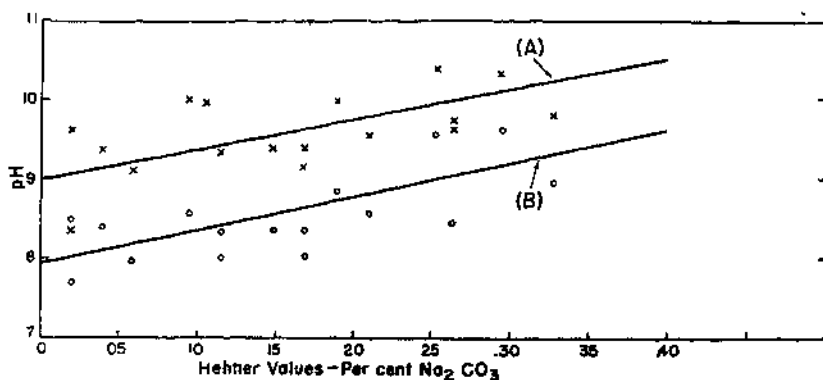


Figure 10.—Correlation between Hehner values and pH of soil: A, 1:10 soil:water ratio; B, soil paste.

The Hehner method, in agreement with the salinity studies, shows a definite correlation between the Na_2CO_3 , plus NaHCO_3 , in the soil and the pH value.

BASE EXCHANGE—PH RELATIONSHIPS

While base fixation and exchange had been recognized (beginning with the experiments of Way) as an important soil property, full appreciation of its value began with the researches of Gedroiz, Kelley, Hissink, and others sixty years or more thereafter. This new emphasis on the adsorptive property of the soil arose from the discovery that the clay fraction of the soil possesses definite chemical properties, that the exchange of bases between the soil minerals and the electrolytes of the soil solution takes place in chemically equivalent proportions, and that the nature of the cations attached to the exchange complex greatly influences soil properties. A new field of investigation was opened by these discoveries because soils in which the exchange complex is saturated or near saturated with sodium possess high pH values and exhibit many other properties which up to this time had been attributed only to Na_2CO_3 in black alkali soils. That certain soil properties might in turn have an influence on the adsorptive capacity of the soil for cations was not at first recognized. It has now been quite conclusively shown that the constancy of the exchange capacity value depends upon the pH of the salt solution used to determine the exchange capacity of the soil. That is, for complete saturation of the soil with bases, salt solutions of high pH values must be used instead of neutral salt solutions.

Kelley and Brown (16) obtained an increase in exchange capacity on treating soils with $\text{Ca}(\text{OH})_2$. Using mixtures of KCl and KOH, Bradfield (2) found an adsorption of K by the soil which increased with increase in pH, and the soil did not reach saturation until pH 10.0. Tiulin (30) and Bystrova have shown that replaceable H ions are not completely replaced by neutral salt solutions. Treatment of the soil with $\text{Ca}(\text{OH})_2$ gave a higher exchange capacity than neutral salt solutions, and this was more characteristic of podsolis than chernozems. They offered the explanation that neutral salt solutions do not completely replace H ions and that the sesquioxides and hydrates in acid soils, which have exchange properties as electronegative colloids, function only after treatment with an alkaline solution. Mattson (19) and his associates have had similar experiences with $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ ampholytes. After determining the isoelectric points of these hydrogels, they leached them with salt solutions of pH values equal to the isoelectric point and found that they exhibited no exchange properties. When they were leached with salt solutions with pH values higher than the isoelectric point they exhibited

cation exchange properties. Mattson says that total exchange capacity is a meaningless term and that the exchange capacity at pH 7.0 bears no simple relationship to total combining power. In expressing the exchange capacity of a soil he believes it is necessary to state the pH at which the determination was made. Puri (25) also concluded that the base exchange capacity of the soil is a meaningless term unless it is taken to pH 10.0 or the point at which the soil takes up a maximum of bases. He recommends exposing the soil to a normal solution of NH_4OH in a desiccator for complete saturation with NH_4 . He says the logical way of expressing base exchange capacity is by means of a titration curve from which the saturation capacity for any pH can be calculated.

Most of the work of the above nature has been done on acid soils. Alkaline-calcareous soils have pH values which are above the isoelectric points of the sesquioxides and hydrates, so it is hardly conceivable that there could be an increase in the exchange capacity from this source by treating these soils with salt solutions of high pH values. There is, however, some evidence that the exchange capacity of semiarid soils is increased by contact with salt solutions of high pH values. Reference is made to our own experiences, as well as to those of Kelley and Brown (16) and Kelley and Cummins (17), that on determining the replaceable bases and exchange capacity of black alkali soils, soils of high pH, the exchange capacity of the soil as measured by the adsorption of NH_4 from a neutral solution of ammonium acetate or ammonium chloride is less than the total replaceable bases set free in the leachate and often is less than replaceable sodium alone. This investigation is concerned with exchange capacity of the soil only in so far as it is related to the pH value of the soil. If the pH value of the salt solution in contact with the soil influences the exchange capacity, might one find a similar effect on the pH of the soil? The experiments immediately following were designed to study this phase of the pH problem.

Hydrolytic pH is, in most soils, a function of the silt and clay fractions because of the part these soil fractions play in cation adsorption. It is of interest to compare the data in Table 1 on this basis. In Figure 11 the sum of the percentage of clay and silt in the soil is plotted against the effect of dilution on the pH of the soil. It is shown that the increase in pH with dilution of the soil correlates with an increase in silt and clay.

Among the data in Tables 1 and 2 there are several soil samples which are high in replaceable sodium. The ratio of sodium to total replaceable bases was calculated, and the relation of this ratio to pH is shown in Figure 12. These ratios are plotted against two pH values; namely, the pH at 1:10 soil:water ratio and the pH of the soil paste. The data show a significant increase in pH with increase in Na/total rep. cap. Since eleven of these soils contain some sodium carbonate, it is possible that this may have some influence on the location of the points on the chart. Williams

(31) studied the relation between the Ca:Na ratio and pH in bentonite and found a linear relation between this ratio and pH, the line beginning at pH 10.2 for bentonite containing 44.27 m.e. Na and 22.7 m.e. Ca and ending at pH 9.6 for bentonite with 90.0 m.e. Ca and 2.42 m.e. Na. He made these pH measurements in 1:10 water suspensions.

For the group of soils given in Table 1 an experiment was conducted in which each soil was saturated with sodium in order to study the pH values of sodium-saturated soils. The experiment was also designed to determine whether the pH values of the sodium-saturated soils increase with the capacity for adsorption and the absolute amount of replaceable sodium. The data obtained are extremely illuminating. Sodium saturation was accomplished by leaching the soils with a normal solution of NaCl in which the pH was adjusted to pH 9.5 and washing the soils once with water and then with 60 per cent methanol to remove the excess of NaCl. The pH values obtained with these sodium-saturated soils are presented in Figure 13. They show that regardless of the adsorption capacity of the soil the pH values for all these soils at 1:10 soil:water ratio are approximately the same. This means that all soils, when saturated with sodium, will exhibit closely the same pH at 1:10, when neutral salts are absent, regardless of the absolute amount (as milliequivalents per 100 grams) of replaceable sodium present. The pH of Superstition sand with 3 per cent clay and 3.7 m.e. replacement capacity per 100 grams is just as high as the Casa Grande loam with 45 per cent clay and 23.7 m.e. replacement capacity. The "constant" pH value for these sodium-saturated soils appears to be approximately 10.2 at 1:10 soil:water ratio.

When the pH values of the sodium-saturated soils are determined on the soil paste, there is a highly significant decrease with increase in exchange capacity or m.e. replaceable sodium per 100

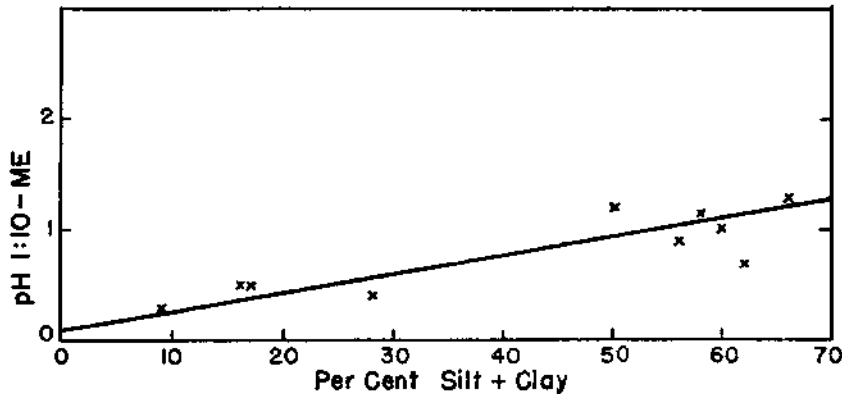


Figure 11.—Correlation between per cent silt plus clay in soil and difference between pH at 1:10 and soil paste, dilution effect.

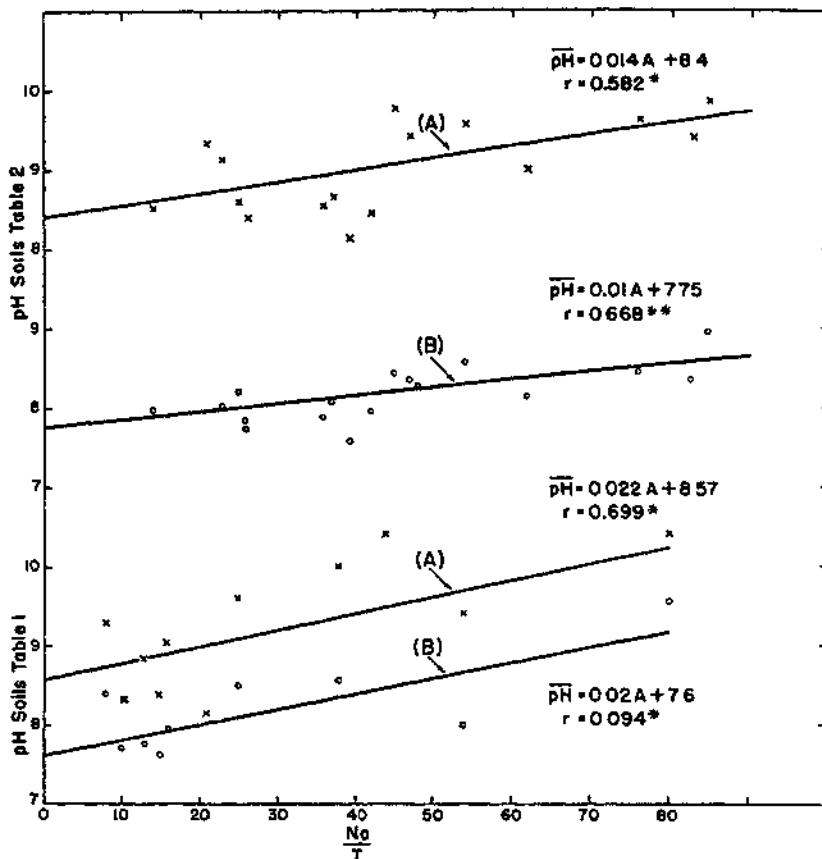


Figure 12.—Correlation between ratio of replaceable sodium to total replacement capacity and pH at (A) 1:10 soil:water ratio and (B) soil paste.

grams. That is, the pH is lowest for the soils containing the most replaceable sodium. It should be mentioned in this connection that the soils lowest in exchange capacity are also the lowest in clay content. One cannot help but attach considerable significance to the results of this experiment, and several things are suggested by it.

1. The soils containing the most replaceable sodium, the most silt and clay, when saturated with this cation, are more strongly buffered by the greater colloid content and therefore at field moisture content have a lower pH value than the soils of lesser colloid content which are less buffered.

2. Clay soils, when saturated with sodium, are higher in potential alkalinity and exhibit a greater degree of hydrolysis. Thus the difference between the pH of the soil at 1:10 soil:water ratio and the pH of the soil paste is greater than for the sandy soils.

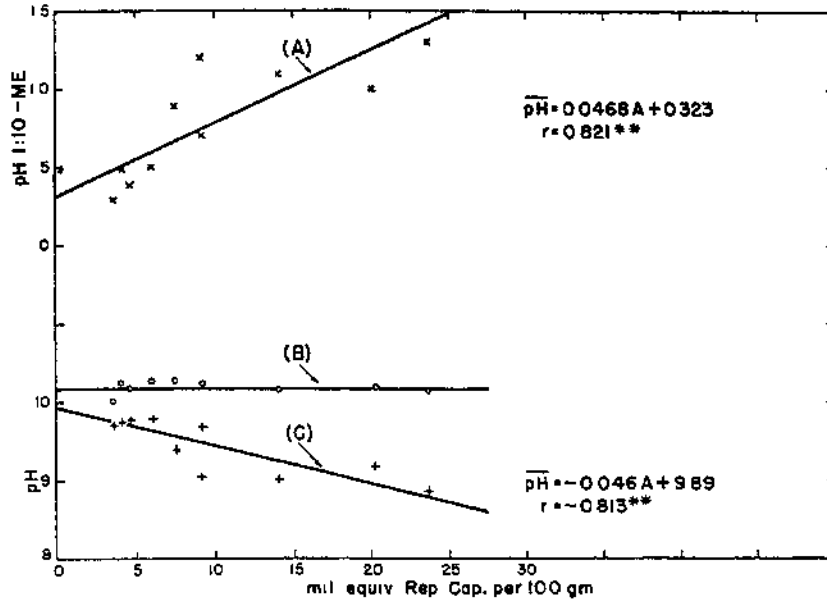


Figure 13.—Correlation between m.e. replaceable Na per 100 grams soil and pH at (B) 1:10 soil:water ratio, (C) soil paste, and (A) difference between 1:10 and paste.

3. The atmosphere of cations, at field moisture content, is more compact in the clay soils and therefore, even though the potential alkalinity is greater, the actual OH-ion concentration is less than in the sandy soils.

4. The hydrolyzing compounds in soils exist largely in the solid state and thus the surface exposed by the particles will in large part determine the extent of hydrolysis and the magnitude of the pH value. Hence the greater hydrolytic pH in the clay soils.

5. The exposed surface increases with dispersion and decreases with flocculation. Since there are fewer of the silt and clay fractions in the sandy soils to flocculate, there is less decrease in exposed surface on flocculation and therefore less reduction in pH in passing from the 1:10 soil:water ratio to the moisture content represented by the moisture equivalent in the sandy soils.

6. From the standpoint of the crop, it is believed that the data show that crops can better withstand alkalinity in sandy than in clay soils because of the lesser potential alkalinity and the lower buffer capacity in the former, even though the pH value may be the same in both types. The lower buffer capacity will offer less resistance to the reduction in pH of the soil-root contact film which is known to accompany root respiration.

The exchange complex of the soil is constituted of a number of different minerals. The mobility as well as the activity of the cations attached to the colloidal fraction of these minerals is

obviously quite variable. The dissimilar structure of the atmosphere of cations, according to Jarusov (15), greatly influences cation mobility; and he associates high mobility under conditions of a loose structure and low mobility where the ions exist in a compact cation atmosphere. It seems reasonable to assume that the differences noted for the pH values of sandy and clay soils may be associated with the nature of the cation atmosphere in soils of different mechanical texture.

The pH of most alkaline-calcareous soils is 8.0 or higher when the pH determination is made on a 1:10 soil:water ratio. Since this is above the isoelectric point of the sesquioxides and hydrates, this fraction of the exchange complex should be in possession of its full exchange properties when a salt solution is used to determine the exchange capacity of such soils. This is confirmed in the following experiment.

Six soils varying in exchange capacity from 3.7 to 23.6 m.e. per 100 grams, as determined with a solution of neutral normal ammonium acetate, were alternately leached several times with normal sodium acetate solution and normal ammonium acetate solution, both of which had been adjusted to pH 8.5. After each leaching to the saturation point, the excess reagent was washed out with 60 per cent methanol; thus it was possible to determine the displaced sodium in the ammonium acetate leachate and the displaced ammonium in the sodium acetate leachate. The data thus obtained are given in Table 5 and show a very close agreement between the replacement capacity as determined with a neutral salt solution and one which has been adjusted to pH 8.5. It is clearly evident from these data that the sesquihydrates in these soils are in full possession of their exchange property.

Following this experiment, soil number 8 was selected for a study of the effect of raising the pH of the leaching solution to 10.2. Each of 10-gram portions of soil was leached with 250 ml. of normal sodium acetate solution in which the pH had been adjusted to pH 10.2, the soil then thoroughly washed with 60 per cent methanol, then with normal ammonium acetate solution, and the sodium determined in the leachate. Eight replications were used in this experiment, and the eight separate determinations of

TABLE 5.—EXCHANGE CAPACITIES OF SOILS LEACHED WITH SOLUTIONS OF SODIUM ACETATE AND AMMONIUM ACETATE SOLUTIONS OF PH 8.5 AS COMPARED TO AMMONIUM ACETATE SOLUTION PH 7.0

Soil no.	Am. ac. 7.0	Sod. ac. 8.5	Am. ac. 8.5	Sod. ac. 8.5	Am. ac. 8.5	Sod. ac. 8.5
1	3.7	3.2	3.5	3.9	3.0	3.0
4	7.4	6.7	9.1	7.7
5	23.6	24.1	25.6	23.7
6	4.7	3.9	4.8	3.8	5.2
7	9.2	9.3	10.4	9.1
8	20.3	19.8	20.6	19.9	20.9	19.4

adsorption capacity checked within 1.4 m.e. per 100 grams of soil. That is a variation of 21.6 to 23.0 m.e. per 100 grams of soil. A comparison of these data with the exchange capacity given for this soil in Table 5 shows an increase of approximately 2 m.e. per 100 grams soil at pH 10.2, as compared to the value obtained at pH 7.0.

In the next experiment, six soils were leached with normal NaCl solution adjusted to pH 11.1. Five-gram portions of soil were leached with 250 ml. of this solution, then with 60 per cent methanol, and again with 250 ml. of normal ammonium acetate solution. Sodium was determined in the leachate, and the NH_4 fixed by the soil was determined by distillation into standard acid after the excess of ammonium acetate was washed out with 60 per cent methanol. The data obtained are given in Table 6, together with the replacement capacity of the soils as determined at pH 7.0.

This experiment and that preceding it show that the cation adsorbing capacity of alkaline-calcareous soils is increased by leaching with salt solutions adjusted to high pH values. Since this investigation is concerned primarily with pH studies, what effect does this higher replacement capacity have on the pH value of the soil? The next experiment was designed to study this phase of the pH-exchange complex problem.

Six soils were selected for a study of the pH values of soils which have been saturated with sodium at different pH values

TABLE 6.—COMPARING REPLACEMENT CAPACITY WITH NEUTRAL AMMONIUM ACETATE AND SODIUM CHLORIDE SOLUTION OF PH 11.1

Soil no.	Am. ac. 7.0	Sod. chl. 11.1	Am. ac. 8.5
4	7.4	13.6	10.6
8	20.3	23.4	25.5
3	9.2	14.5	12.0
7	9.2	14.8	14.0
6	4.7	6.7	5.0
2	14.0	19.2	20.1

TABLE 7.—PH VALUES OF SOILS AFTER SATURATING THE EXCHANGE COMPLEX WITH Na, USING SODIUM SALT SOLUTIONS OF PH 7.0, 9.0, AND 10.0

PH of solutions	NaCl			Na_2SO_4			$\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$		
	7.0	9.0	10.0	7.0	9.0	10.0	7.0	9.0	10.0
Soil no. 2, paste	9.35	9.45	9.45	9.30	9.35	9.35	9.35	9.25	9.30
Soil no. 2, 1:10	10.05	10.00	10.45	10.10	10.00	10.10	9.90	10.05	10.05
Soil no. 4, paste	8.95	9.15	9.15	9.10	9.30	9.40	9.25	9.20	9.30
Soil no. 4, 1:10	9.90	9.85	9.90	9.90	9.95	10.10	9.90	9.90	9.90
Soil no. 6, paste	8.80	8.75	9.00	8.85	8.90	9.40	8.80	8.95	8.90
Soil no. 6, 1:10	9.25	9.35	9.75	9.45	9.35	9.40	9.55	9.50
Soil no. 7, paste	9.20	9.25	9.20	9.25	9.25	9.40	9.20	9.35	9.25
Soil no. 7, 1:10	9.95	9.95	9.90	9.90	9.90	10.00	9.85	9.90	9.85
Soil no. 3, paste	9.45	9.40	9.45	9.55	9.55	10.20	9.30	9.45	9.55
Soil no. 3, 1:10	10.05	9.95	9.90	9.95	9.95	10.20	9.80	9.90	9.90
Soil no. 5, paste	9.35	9.40	9.45	9.40	9.40	9.85	9.35	9.55	9.40
Soil no. 5, 1:10	10.25	10.20	10.20	10.15	10.15	10.35	10.10	10.15	10.10

by leaching the soils with salt solutions which had been adjusted to different pH values. The solutions used were normal solutions of sodium chloride, sodium sulphate, and sodium acetate adjusted to pH values of 7.0, 8.0, 9.0, and 10.0. The saturation with sodium was accomplished by weighing 20 grams of soil into 150-ml. beakers, adding the respective salt solutions, and transferring the whole to a filter where it was leached with 250 ml. of the respective salt solution. The soils were then washed on the filters with successive portions of 60 per cent methanol until they were free from excess salt. PH values were determined on these soils at the moisture equivalent and at 1:10 soil:water ratio. These data are given in Table 7. In spite of the fact that there is an increased adsorption of sodium when the soils are leached with sodium-salt solutions which have been adjusted to high pH values, the data given in Table 7 show that this increase in adsorption has little or no effect upon the pH value of the soil. All the values are in close agreement, considering the difficulties involved in washing an excess of alkali salts out of a soil. It is of interest that the Palos Verdes soil, number 6, which is noncalcareous, does not reach the maximum values exhibited by the calcareous soils.

SESQUIHYDRATES

Among the colloids commonly occurring in soils, the oxides and hydrates of iron and aluminum—the so-called sesquioxides or hydrates—are important. These colloids are electrical ampholytes and are electropositive in an acid medium and electronegative in alkaline media. Little is known about the extent to which these materials, at pH values above their isoelectric points, contribute to the pH of soils (18). Obviously in alkaline soils such colloids are electronegative, and Mattson (19) has shown that at pH values above their isoelectric points they possess cation exchange properties. The following isoelectric points are given by Mattson, depending upon whether the chloride or the sulphate is used to prepare the hydrate.

AlCl_3 and NaOH	pH 8.1
FeCl_3 and NaOH	pH 7.1
$\text{Al}_2(\text{SO}_4)_3$ and NaOH	pH 7.6
$\text{Al}_2(\text{SO}_4)_3$ and NaOH	pH 7.8

Most of the alkaline-calcareous soils of Arizona have pH values higher than the isoelectric points given by Mattson for these hydrates. In view of this, we should expect these sesquihydrates and oxides to function as exchange compounds and therefore to contribute to the pH of these soils.

In order to study this phase of the pH problem, hydrates of aluminum and iron were prepared in the laboratory. To a solution

of NaOH a solution of AlCl_3 was added at room temperature, with continuous stirring, and with frequent testing with a pH meter, until the pH value of the whole was reduced to pH 9.0. For the preparation of the ferric hydrate the same procedure was followed with solutions of FeCl_3 and NaOH. After having stood for twenty-four hours, both gels were shaken in a flask with distilled water and filtered three times in order to remove the excess of NaCl. After the gels were thus washed, the pH of the $\text{Al}(\text{OH})_3$ was 9.0 and that of the $\text{Fe}(\text{OH})_3$ was 8.9.

PH studies on small portions of these hydrates were made as follows. One portion of each was dried in the oven at 105 degrees C., another was dried in the air, and a third portion was reserved without drying to be studied as a gel. PH determinations were made on the gel at the gel stage, on the dry hydrates at low moisture content approximating the moisture equivalent, and on all three at 1:10 dilutions with boiled distilled water. These data are given in Table 8. The hydrates were then washed free of NaCl with distilled water and the pH values were again determined at 1:10 after just enough water was added to form a gel. These data are also given in Table 8.

TABLE 8.—PH VALUES EXHIBITED BY THE SESQUIHYDRATES

	PH before leaching		PH after leaching	
	Paste	1:10	Paste	1:10
$\text{Fe}(\text{OH})_3$, gel.....	9.90	10.10
$\text{Al}(\text{OH})_3$, gel.....	9.05	8.70
$\text{Fe}(\text{OH})_3$, air-dry.....	7.85	8.80	9.60	10.25
$\text{Al}(\text{OH})_3$, air-dry.....	7.85	8.70	9.50	9.15
$\text{Fe}(\text{OH})_3$, oven-dry.....	9.00	9.85	10.60	10.85
$\text{Al}(\text{OH})_3$, oven-dry.....	8.00	8.85	10.00	9.95

It is evident that these sesquihydrates may function as contributing factors in the high pH of alkali soils.

Gel. In the original gel form the pH of the $\text{Fe}(\text{OH})_3$ is higher than the $\text{Al}(\text{OH})_3$. The former is increased by dilution to 1:10 while the latter is reduced.

Air-dried hydrates. The air-dried hydrates, which should closely resemble the sesquihydrates in the soil, show that air-drying has reduced the pH value as compared with the original gel. Both hydrates show an increase in pH with dilution from the paste to the 1:10 ratio. After the air-dry hydrates were leached to rid them of NaCl, there was a notable increase in pH for both; but it is greater for the $\text{Fe}(\text{OH})_3$ than for the $\text{Al}(\text{OH})_3$, and as the original gel, the pH of the $\text{Al}(\text{OH})_3$ decreases with dilution while the pH of the $\text{Fe}(\text{OH})_3$ increases with dilution.

Oven-dried hydrates. The oven-dried hydrates have a higher pH than the air-dried, and before the NaCl is leached out the pH at 1:10 is appreciably higher than that for the paste. After the NaCl is leached out, this dilution effect is greatly reduced for $\text{Fe}(\text{OH})_3$ and completely absent for $\text{Al}(\text{OH})_3$.

There is evidence that the sesquihydrates at pH values above their isoelectric points possess permanent and high pH values and, as do the carbonates and the exchange silicates, will contribute to the high pH values of alkali soils—depending of course upon how extensively they are present. Both the iron and aluminum hydrates exhibit the dilution behavior, as has been noted for alkaline-calcareous soils; namely, an increase with dilution. However, in the absence of salts the dilution effect for $\text{Al}(\text{OH})_3$ is negative while the $\text{Fe}(\text{OH})_3$ is positive both in the presence and absence of salts.

Exchange capacity. As a matter of interest, the adsorbing capacity of the dried hydrates was determined by placing a quantitatively weighed portion of each on a filter where they were leached with normal ammonium acetate, pH 8.5, then with distilled water until free from ammonium acetate. The adsorbed NH_4 was then determined in the hydrates by distillation with MgO into standard acid. The following NH_4 adsorption was found.

$\text{Fe}(\text{OH})_3$ air-dried	22.2 m.e. per 100 gm.
$\text{Al}(\text{OH})_3$ air-dried	9.6 m.e. per 100 gm.
$\text{Fe}(\text{OH})_3$ oven-dried	20.2 m.e. per 100 gm.
$\text{Al}(\text{OH})_3$ oven-dried	8.1 m.e. per 100 gm.

The $\text{Fe}(\text{OH})_3$ apparently has a higher cation exchange capacity than has $\text{Al}(\text{OH})_3$, and this may explain the difference in pH values exhibited on dilution.

PH OF SOIL SEPARATES

The soil mass is composed of mineral particles varying from those of colloidal dimensions to particles of gravel or even larger, and the cations adsorbed by these particles are among the most reactive of those present in the soil. While some base exchange studies have been conducted with the different-sized soil particles, pH studies on them seem to be lacking. It seemed of interest, therefore, to study the contribution which the different-sized soil particles make to the pH of the soil mass as a whole. For a study of this phase of the problem, particle separates were prepared from ten different soils. A 500-gram portion of soil was worked in a mortar (a rubber pestle was used) with 60 per cent methanol and washed through a set of sieves of 20-mesh (0.84 m.m.) to 100-mesh (0.149 m.m.). The process of rubbing and washing was repeated as long as any clay appeared in the washings. Further separation of the portion passing the 100-mesh sieve was accomplished by sedimentation to obtain fractions of clay (.002 m.m.), silt (.002-.02 m.m.), and sand (.02-.149 m.m.). All these separates were dried in air and their weights calculated to percentage of the different-sized particles in air-dry soils. These percentages are given in Table 9. Some of the fractions were too small for pH determination and it was therefore necessary to combine some of the separates to increase the size of the sample.

TABLE 9.—PERCENTAGE MECHANICAL SEPARATES IN SOIL USED FOR PH DETERMINATION OF SOIL PARTICLES

	Soil no. 1	Soil no. 2	Soil no. 3	Soil no. 4	Soil no. 5	Soil no. 6	Soil no. 7	Soil R.I.	Soil N.J.	Soil K
.84 mm. plus	2.43	0.33	3.97	1.52	0.10	17.00	3.38	0.32	0.01	0.90
.59—.84 mm.	12.40	0.41	3.11	0.57	0.24	8.60	2.87	2.13	0.29	1.94
.42—.59 mm.	14.90	0.87	3.12	0.75	0.42	8.48	4.57	3.58	0.66	4.13
.29—.42 mm.	16.00	1.39	3.21	1.24	1.38	7.90	4.23	5.36	1.05	4.22
.25—.29 mm.	9.00	2.09	1.53	1.35	1.30	4.05	2.36	2.45	1.04	3.25
.177—.250 mm.	12.80	3.65	3.33	5.15	5.33	7.10	3.93	2.65	1.67	6.44
.149—.177 mm.	4.14	3.07	2.78	4.22	1.42	3.00	2.69	1.30	0.69	3.99
.020—.149 mm.	26.00	40.40	38.40	50.40	38.00	26.80	41.40	40.80	23.60	45.40
.002—.020 mm.	1.20	20.00	17.20	19.40	25.00	7.40	20.80	27.60	51.60	18.00
.002 mm. minus	1.20	24.00	20.40	11.80	26.00	9.60	11.00	8.80	15.00	6.60

In addition to the pH determinations on the separates for all the soils, pH determinations were made on five of the sets of separates after they were saturated with sodium, and in addition the adsorption capacity of these was determined. The separates on which the pH determinations were made were all free from salinity, and it is probable also that the pH values were changed somewhat during the prolonged washing process employed in the particle separation; but of course this was unavoidable. These data are given in Tables 10 and 11 and Figures 14 and 15. In order to increase the value of the data, some of the larger separates were ground in a ball mill to pass a 100-mesh sieve, and pH and adsorption capacity determinations were made on these for comparison with the unground particles.

The data show that all the different-sized particles, from the clay to 0.84 mm. fraction, have pH values more or less related to the pH of the soil mass as a whole.

For the calcareous soils 1, 2, 3, 4, and 5, the pH values of the sandy fractions are higher than the silt, and the silt, in turn, is higher than the clay both for the soil paste and at 1:10 soil:water ratio. This same behavior is exhibited by the sodium-saturated particles, but the pH values of the sand, silt, and clay are in close agreement at 1:10 soil:water ratio, just as are the sodium-saturated soils presented in Table 1.

For the noncalcareous soil, number 6, a somewhat different relation exists—namely, the pH of the silt and clay fractions are higher than the sand at 1:10 soil:water ratio, but the values are lower than the sand for the soil paste. The latter is therefore in agreement with the calcareous soils, but the pH at 1:10 is not.

The black alkali soils, K and 7, exhibit particle-separate pH values entirely different—especially soil K. This latter soil is from the San Joaquin Valley of California and contains much less CaCO_3 than does number 7. The coarse particles of soil K have higher pH values for the soil paste than at 1:10 soil:water ratio and show very little hydrolytic alkalinity. The clay fraction has a lower pH than the sand on the paste, but having a greater degree of hydrolysis, it has a higher pH at 1:10.

Soils N.J. and R.I. are acid soils from New Jersey and Rhode Island, respectively. These were included for a comparison with the semiarid soils, or of unsaturated with a saturated exchange complex. There is some agreement with the behavior of the other soil separates, for the pH of the sand fraction is highest and decreases toward silt and still further to the clay fraction.

In every case where the large soil particles were ground in a ball mill both the pH and replacement capacity were increased, but not to the values exhibited by the soil fraction which passed the 100-mesh sieve.

Replacement capacity for most of the separates was determined, and considerable variation is noted for the different soil types. For soils 6 and K the replacement capacity is practically negligible

TABLE 10.—PH VALUES FOR SOIL PARTICLE SEPARATES

Size of particle (m.m.)	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5	
	PH values		PH values		PH values		PH values		PH values	
	Paste	1:10	Paste	1:10	Paste	1:10	Paste	1:10	Paste	1:10
.149-.84*	8.80	9.00	8.25	8.90	8.10	8.65	8.55	9.20	—	—
.84 plus	8.95	9.15	8.60	9.20	8.65	9.10	8.15	8.85	—	—
.42-.84	8.75	9.45	8.75	9.30	8.70	9.20	8.55	9.25	7.75	8.80
.25-.42	8.65	9.40	8.75	9.15	8.60	9.15	8.50	9.15	—	—
.02-.149	8.05	8.90	8.20	8.85	8.20	8.85	8.75	9.25	8.45	9.05
.02	8.05	8.90	8.20	8.85	8.20	8.85	8.30	9.05	8.10	8.90
.002	8.15	8.95	7.95	8.80	7.95	8.85	8.05	8.85	7.10	8.20
	Soil 6		Soil 7		Soil R.I.		Soil N.J.		Soil K	
.149-.84*	8.00	8.65	—	—	—	—	—	—	—	—
.84 plus	7.70	7.70	9.25	9.70	5.25	5.90	6.25	6.95	10.00	9.35
.42-.84	8.10	8.20	9.70	9.90	4.95	5.50	6.25	6.75	10.05	9.90
.25-.42	7.85	8.25	9.60	9.95	5.35	5.85	6.35	7.20	10.30	10.15
.02-.149	8.10	8.20	9.05	9.60	5.75	6.20	7.15	7.45	8.25	9.25
.02	7.55	8.55	9.10	9.95	5.35	5.60	6.90	7.30	9.05	9.55
.002	7.40	8.35	8.80	10.10	5.25	5.45	6.50	7.15	9.20	10.15

*Ground in a ball mill to pass a 100-mesh sieve to determine effect of grinding on pH and replacement capacity.

TABLE 11.—PH OF SOIL PARTICLE SEPARATES AFTER SATURATION WITH Na, AND REPLACEMENT CAPACITY OF SEPARATES IN m.e. PER 100 GRAMS

Particle size (m.m.)	Soil 2			Soil 3			Soil 4		
	PH values			PH values			PH values		
	Paste	1:10	rep. cap.	Paste	1:10	rep. cap.	Paste	1:10	rep. cap.
.149-.84*	9.50	10.35	8.0	9.60	10.20	3.20	9.50	10.20	3.7
.84 plus	9.70	10.25	6.3	9.60	10.10	2.20	9.60	10.15	3.6
.42-.84									
.25-.42									
.149-.02	10.05	10.20	4.6	9.90	10.25	3.40	9.90	10.10	3.7
.02	9.20	10.25	15.4	9.20	10.25	7.50	9.10	10.10	11.1
.002	8.80	10.10	44.0	8.75	10.10	45.00	9.00	10.10	39.0
	Soil 6			Soil K					
.149-.84*	9.00	9.45	4.0	10.10	10.10	1.7			
.84 plus	8.90	9.15	0.3						
.42-.84	8.60	8.95	0.8	9.90	9.90	1.4			
.25-.42	9.20	9.70	1.9						
.149-.02	9.65	9.90	1.9	9.90	10.30	1.3			
.02	8.90	9.80	13.9	9.80	10.30	4.5			
.002	8.30	9.70	27.9	9.50	10.40	21.0			

*Ground in a ball mill to pass a 100-mesh sieve to determine effect of grinding on pH and replacement capacity.

for the particles of sand or those of greater diameter. For soils 3 and 4, it is somewhat higher and is highest for soil number 2. The replacement capacities for the different separates are shown graphically in Figure 16.

On close examination of the data in Tables 10 and 11 and Figures 14 and 15, it will be noted that the relative pH values of the different separates are similar—that is, the curves representing the pH values at the moisture equivalent follow the same general trend. Starting with low pH values at 40-mesh or coarser, the pH increases to a maximum value, usually the sand (0.02 to .129 m.m.), and then decreases again to a low pH value for the clay fraction. The low pH of the coarse particles is simply a low hydrolytic alkalinity, low exchange capacity, while the low pH for the other particle extreme, the clay fraction, is due to repressed hydrolysis

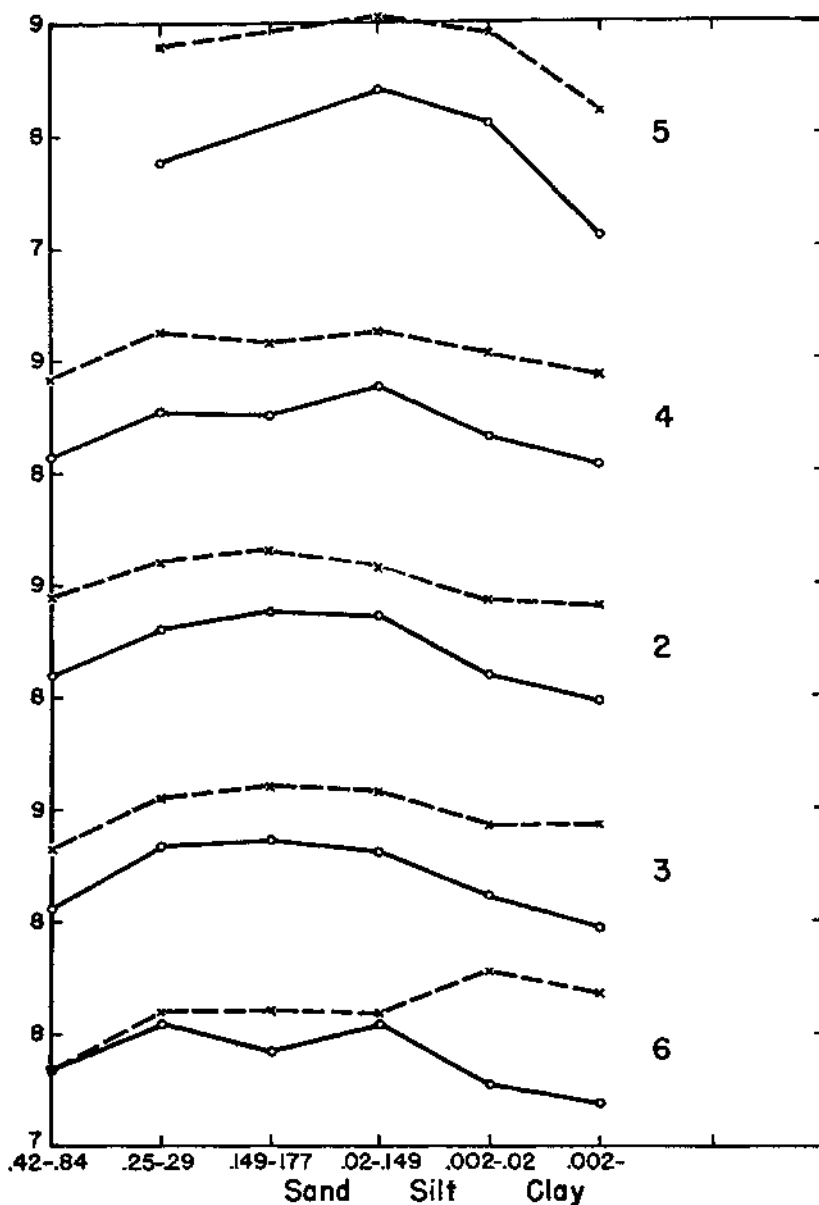


Figure 14.—PH of soil separates; solid lines represent pH of soil paste and broken lines pH of 1:10 soil:water ratio.

at the low moisture content represented by the soil paste. The data indicate that under field conditions higher pH values should exist in sandy soils, or be more easily attained in nature under

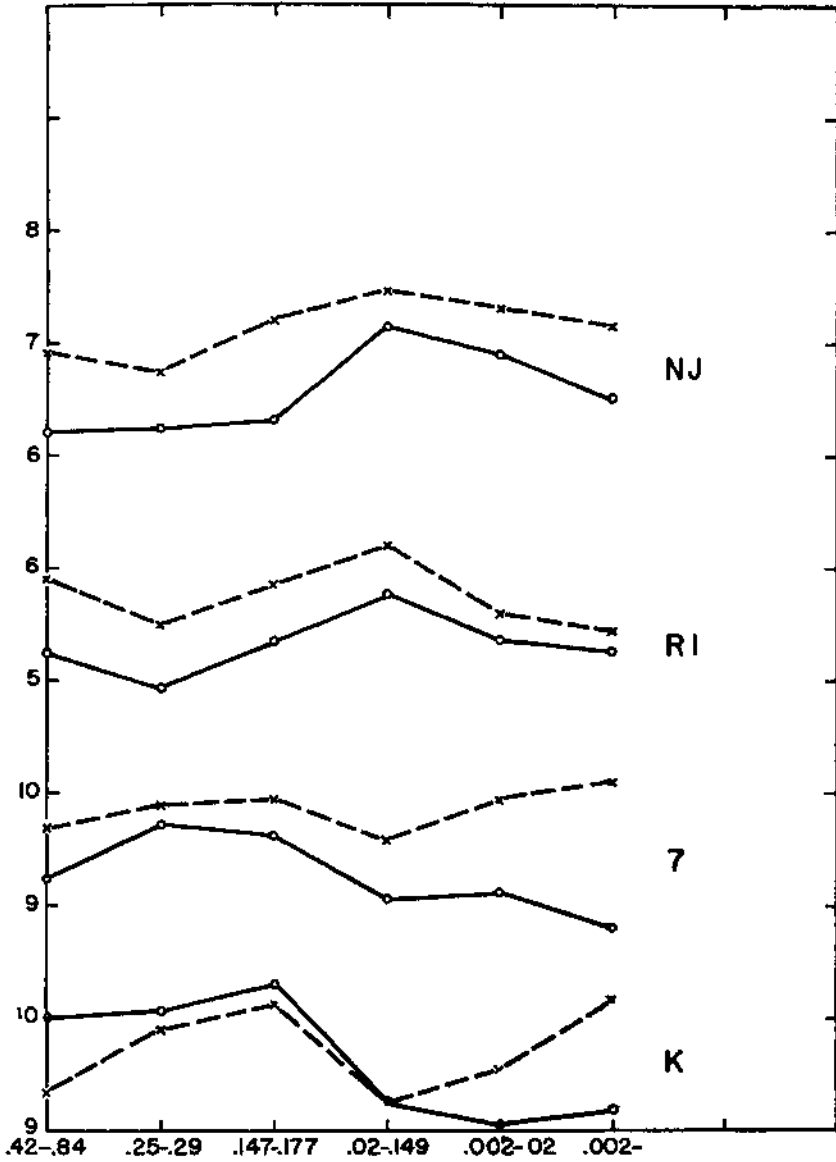


Figure 15.—PH of soil separates; solid lines represent pH of soil paste and broken lines pH of 1:10 soil:water ratio.

semiarid and salinity conditions, than in clay soils under similar conditions. But since the total hydrolytic alkalinity is much lower in sandy soils and the absorption capacity less, they should be less toxic toward crop growth and more easily reclaimed when black alkali is present. On examining the data for the pH values

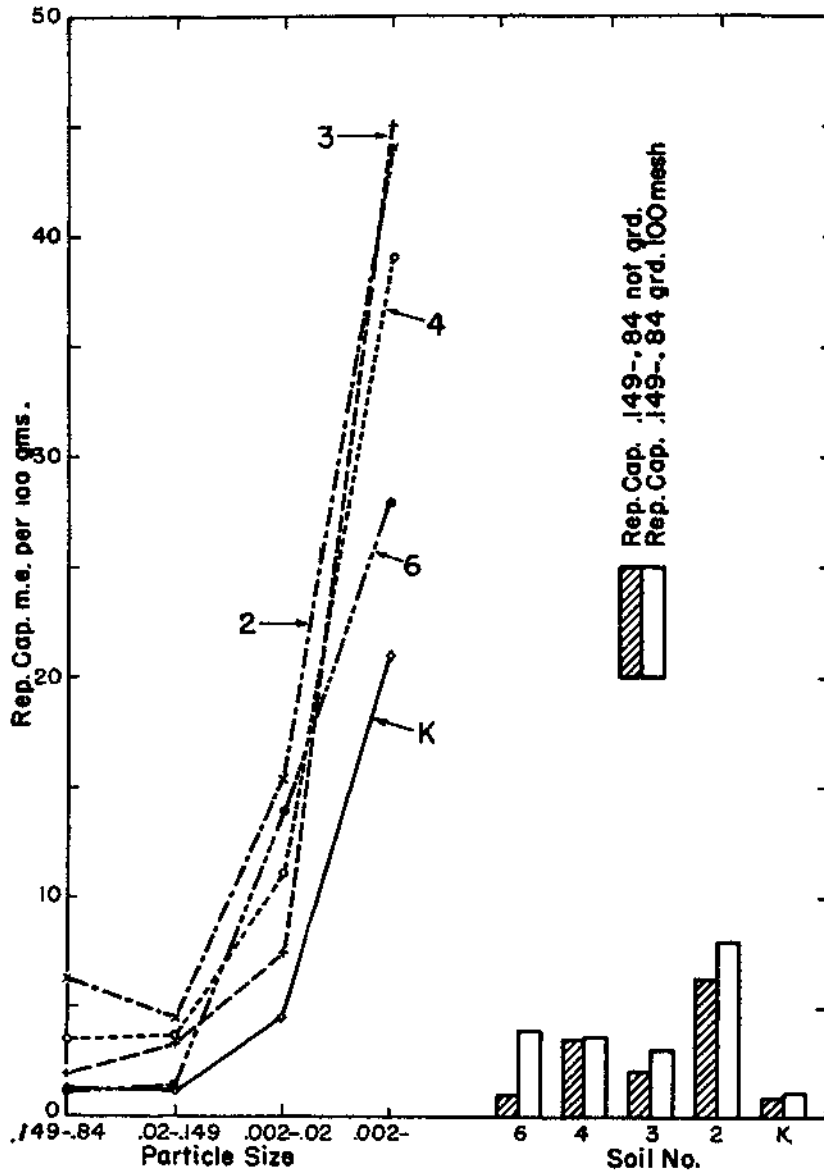


Figure 16.—Replacement capacity of soil separates and effect of grinding on the replacement capacity of coarse soil particles.

of the separates as determined at a 1:10 soil:water ratio, the difference in hydrolytic alkalinity is clearly shown. The pH values for the particle sizes of sand to 80-mesh, as determined at both moisture contents, approach one another more closely because of

the low hydrolytic alkalinity of these particle sizes. In the clay fraction where the hydrolytic alkalinity is highest, the two curves are farthest apart because of the greater hydrolysis on dilution.

ISOHYDRIC PH VALUES

When two solutions or a solution and a miscible material have the same hydrion concentration they are said to be isohydric. In alkali soils the OH ions are largely confined to the moisture film immediately in contact with the surface of the soil particles and in soil suspensions may be concentrated at the surface with more or less freedom of circulation. Obviously, then, the pH of the soil will vary with the variation in conditions under which the actual measurements are made, largely the soil:water ratio. To meet this situation we have suggested that the determination be made on a soil paste, approximately the moisture equivalent. This moisture content was chosen because it represents very closely the moisture content of the soil under field conditions soon after the soil has been irrigated and also because we found that pH values exhibited little or no change between the moisture equivalent and the water-holding capacity.

It has been suggested that buffer solutions should be useful for the determination of the pH value of a soil and that such values should approach the true pH value of the soil more closely than any other. On the basis that the ideal method for determining pH of the soil is one in which as little hydrolysis as possible is allowed to take place, Puri and Sarup (27) have suggested the isohydric pH. This isohydric pH is similar to the pH value suggested by Mattson (20) to express the exchange neutrality of the soil. In brief, the isohydric pH value of the soil is represented by the pH value of a buffer solution which is not changed when thoroughly shaken with a sample of soil. It may be determined by shaking weighed samples of soil with a series of buffer solutions of different pH values and ascertaining which buffer remains unchanged in pH during this process. Puri and Sarup (27) go so far as to refer to this isohydric pH value as an absolute pH value which does not fluctuate with alterations in experimental conditions.

During this investigation the question arose as to the relation between the pH of the soil paste and the isohydric pH, because both methods are specifically designed to reduce to a minimum the influence of ionization and hydrolysis on pH. The next experiment was designed to compare the isohydric pH of the soil and the pH of the soil paste which approximates the moisture equivalent. The buffer solution used in this experiment was the one suggested by Puri and Sarup (27); namely, 25 ml. of 0.2 normal KCl solution, 25 ml. of 0.2 normal boric acid, plus varying amounts of 0.2 normal KOH solution to be added before diluting the whole to 100 ml. to

TABLE 12.--VALUES OBTAINED IN TITRATION FOR ISOHYDRIC PH VALUES

PH buffer	PH buffer & soil	PH buffer	PH buffer & soil	PH buffer	PH buffer & soil
Soil no. 8 (7.55)*		Soil no. 4 (7.60)		Soil no. 3A (7.90)	
6.55	7.50	6.70	7.48	7.58	7.78
7.52	7.55	7.18	7.59	7.80	7.78
7.90	7.60	7.45	7.60	8.10	7.85
8.20	7.75	7.62	7.65	8.20	7.90
8.28	7.80	7.80	7.70	8.40	7.98
8.35	7.90	7.96	7.75		
8.55	8.05	8.10	7.84		
		8.20	7.92		
Soil no. 7 (9.55)		Soil no. 6 (7.20)		Soil no. 6A (7.75)	
8.30	8.50	6.70	7.10	7.40	7.68
8.55	8.75	7.20	7.20	7.60	7.70
8.75	8.90	7.50	7.32	7.72	7.72
8.85	9.00	7.70	7.40	7.80	7.72
8.92	9.05	7.80	7.46	7.98	7.76
9.00	9.10			8.12	7.80
9.10	9.15				
9.45	9.45				
9.82	9.75				
Soil no. 2 (7.85)		Soil no. 5 (7.60)		Soil no. 9A (8.30)	
7.58	7.75	6.70	7.52	8.03	8.17
7.71	7.78	7.20	7.52	8.12	8.20
7.83	8.78	7.42	7.56	8.30	8.30
7.92	7.82	7.62	7.59	8.45	8.38
8.00	7.85	7.80	7.65	8.55	8.42
		7.97	7.68	8.66	8.52
		8.10	7.70		
Soil no. 3 (7.75)		Soil no. 14 (8.95)		Soil no. 11A (8.15)	
7.35	7.55	8.15	8.50	7.35	7.90
7.46	7.60	8.43	8.65	7.65	8.00
7.65	7.60	8.60	8.72	7.87	8.02
7.80	7.65	8.71	8.80	8.02	8.05
7.90	7.68	8.85	8.65	8.12	8.10
7.98	7.70	9.06	8.92	8.35	8.15
				8.42	8.22
				8.60	8.35
Soil no. 1 (8.20)		Soil no. B (9.30)		Soil no. 12A (8.15)	
7.90	7.95	8.56	8.65	8.12	8.10
8.07	8.10	8.98	8.92	8.30	8.18
8.15	8.12	9.16	9.10	8.45	8.27
8.60	8.50	9.30	9.20		
8.71	8.60	9.50	9.35		
8.85	8.70	9.80	9.55		
8.95	8.60				
Soil no. C (9.25)		Soil no. 1A (7.90)		Soil no. 13A (8.40)	
8.65	8.82	7.50	7.85	7.90	8.20
8.90	9.00	7.82	7.85	8.14	8.25
9.05	9.10	8.00	7.90	8.15	8.25
9.22	9.28	8.10	7.92	8.43	8.35
9.42	9.40	8.22	7.95		
9.65	9.60				
Soil no. 25 (8.50)		Soil no. 92 (8.40)		Soil no. K (10.15)	
7.90	8.15	7.90	7.95	9.40	9.58
8.15	8.25	8.15	8.10	9.90	10.02
8.60	8.55	8.60	8.45	10.20	10.15
		8.85	8.67	11.00	10.70
				11.50	11.20
Soil no. 15A (8.15)					
8.12	8.13				
8.20	8.20				
8.45	8.30				
8.55	8.35				

*Values in parentheses represent pH of soil paste.

form the completed buffer solution. The method recommended by Puri and Sarup (27) was also followed for the determination of the isohydric pH value; namely, 20 grams of soil shaken for two hours with 100 ml. of buffer solution, filtered, and the pH of the filtrate determined and compared with the pH value of the same series of buffer solutions before they were shaken with the soil. These data are given in Table 12 and Figures 17, 18, and 19 for twenty-two soils, together with the pH of the same soils as determined on the soil paste.

The data presented in Figures 17, 18, and 19 are in the form of titration curves in which the pH values of the buffer series are plotted against the pH values of the same series of buffer solutions after having been shaken with the soil. One curve is obtained by using the X axis for the pH of the buffer solutions and the Y axis for the pH of the buffer solutions plus soil. The other curve is obtained by reversing this and using the X axis for the buffer solutions plus soil and the Y axis for the buffer solutions alone. The point at which the two curves meet and cross is taken as the isohydric pH, as it shows this point more accurately than the pH values of each member of the series because in some cases the actual isohydric point falls between two buffer solutions of the series.

There is very close agreement between the pH as determined on the soil paste and the isohydric pH in all but a few samples. Soil number 1, the Superstition sand, is closely isohydric with all the buffer solutions in the series, because with its low silt and clay content its buffer capacity is very low. This soil is essentially a blow sand and is located in the Yuma Mesa area.

There are twenty-two soils in the group examined. All the soils which did not contain Na_2CO_3 show a close agreement between the pH of the soil-paste method and the isohydric pH. Out of a total of twenty-two soils twelve of them were black alkali and showed appreciable amounts of Na_2CO_3 in the analysis of the water extracts. Out of these twelve black alkali soils there are four, designated as 92, C, B, and K, for which the pH of the paste and the isohydric point do not agree closely; but this is simply because they are already in more or less equilibrium with an Na_2CO_3 - NaHCO_3 buffer. The nature of the curves obtained for the black alkali soils are characteristically different from the titration curves representing the saline soils, in which Na_2CO_3 is absent. For the latter soils the curves tend to meet at an angle approaching a right angle and the isohydric point is sharply defined, while for the black alkali soils the curves tend to parallel each other and, as already mentioned, in four of the black alkali soils the point at which the two curves cross is not in very close agreement with the pH of the soil paste. However, the curves parallel each other so closely, both below and above the isohydric point, that the two curves are not widely separated at the pH value represented by the soil paste. That is, even though the iso-

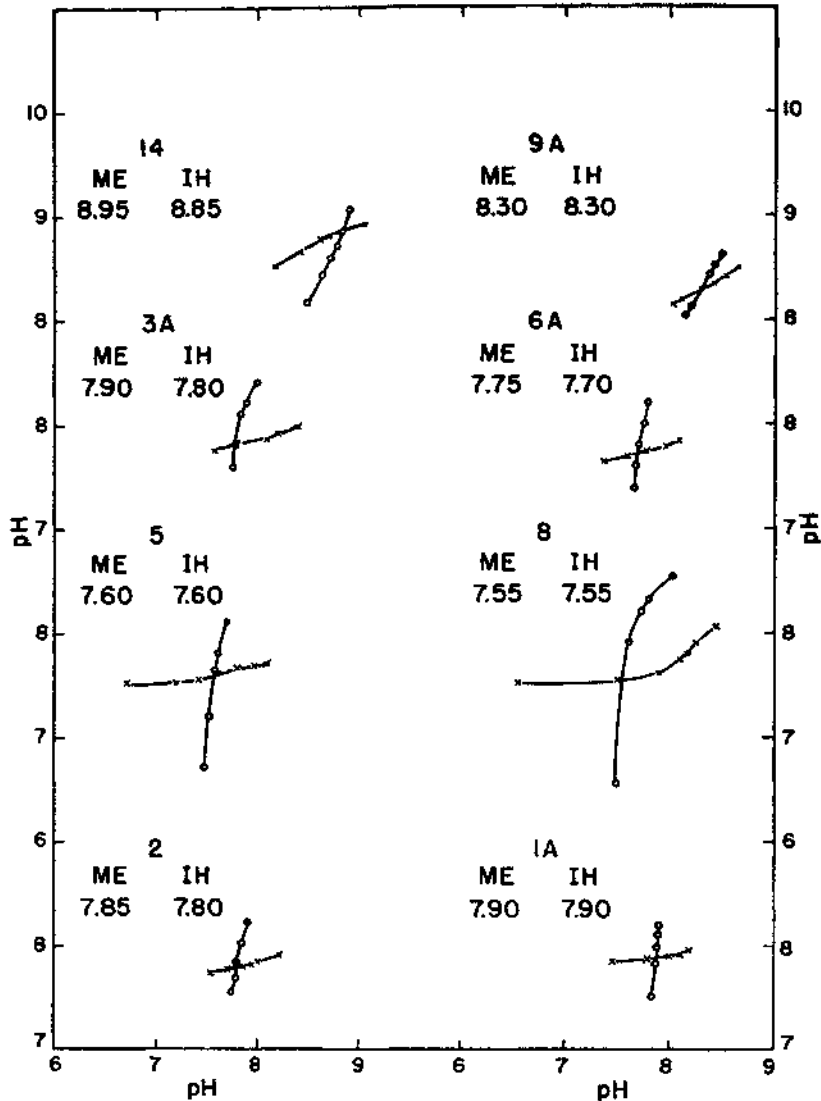


Figure 17.—Isohydric point obtained by plotting titration data. Point at which lines cross is isohydric point. ME designates pH of soil paste and IH the isohydric pH.

hydic pH does not agree with the pH of the soil paste in some black alkali soils, the isohydric curves are very close to each other at the pH of the soil paste.

It is believed that the pH of the soil paste yields a value which is the same pH as the isohydric value, and that in black alkali

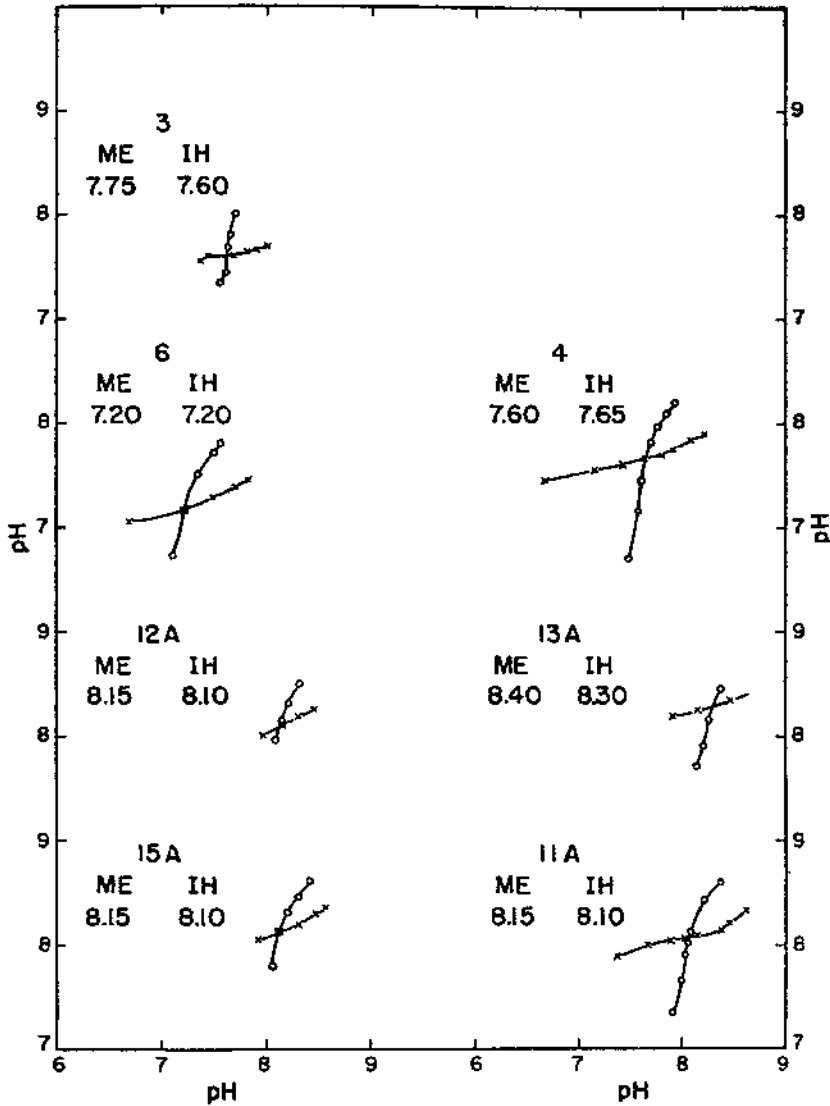


Figure 18.—Isohydric point obtained by plotting titration data. Point at which lines cross is isohydric point. ME designates pH of soil paste and IH the isohydric pH.

soils where there is antagonism between the $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ buffer in the soil and the boric acid-KCl-KOH the pH value of the soil paste is the more acceptable value. This experiment adds considerable support to the selection of the soil paste as being the most desirable moisture content for the determination of soil pH.

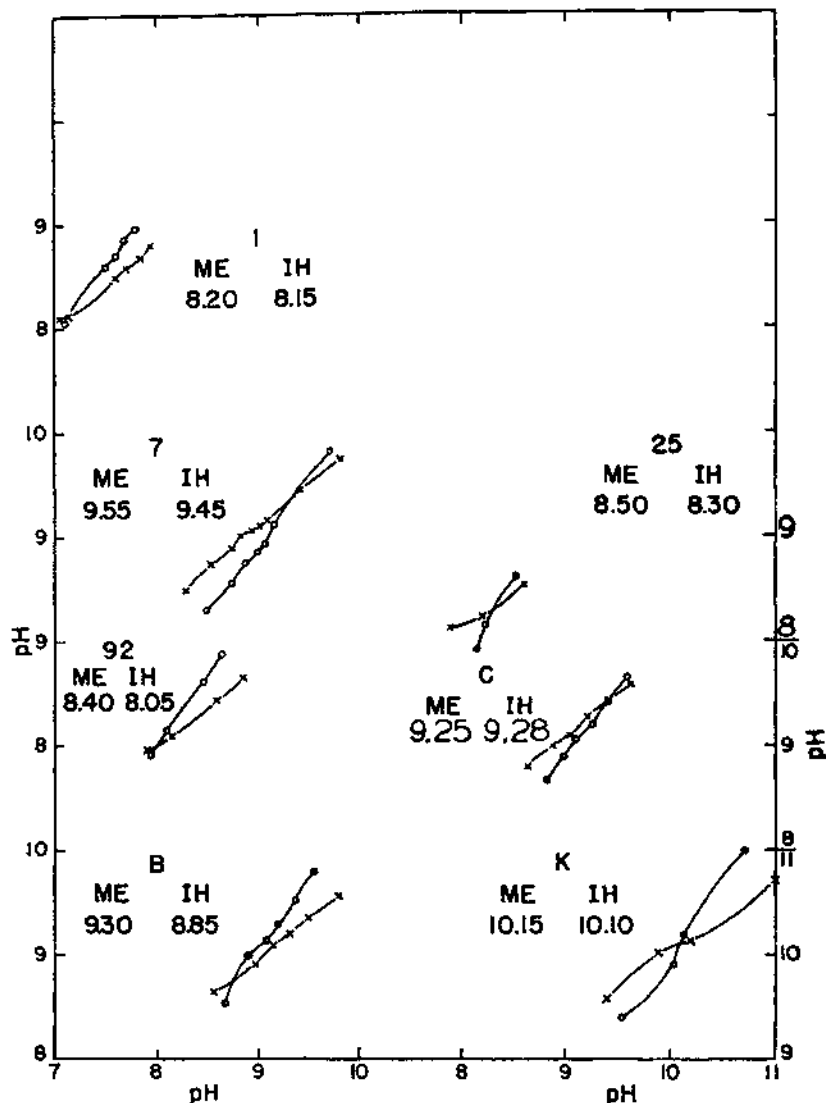


Figure 19.—Isohydric point obtained by plotting titration data. Point at which lines cross is isohydric point. ME designates pH of soil paste and IH the isohydric pH.

PH OF EXCHANGE NEUTRALITY

In one of a series of papers, "The Laws of Soil Colloidal Behavior," published in *Soil Science*, Mattson and his coworkers have emphasized two pH values; namely, the pH of exchange neutrality and the equi-ionic pH value (20). The latter represents

the pH at which the capacities of the soil to combine with the anions and cations of the solution are equal. The former is the point at which the addition of a neutral salt to a soil suspension does not affect the pH of the latter. In many soils these points do not vary greatly among one another.

In order to compare the pH of the soil as made on the soil paste, at approximately the moisture equivalent with the pH of exchange neutrality, an experiment was conducted with three noncalcareous soils. Noncalcareous soils were selected in order to avoid the influence of CaCO_3 on soil titration and the "breakdown" in exchange complex that might accompany the removal of CaCO_3 from the soil with dilute acid.

The experimental procedure was essentially that used by Mattson in which a suspension of 10 grams of soil in 20 ml. of distilled water and another of 10 grams of soil in 20 ml. of normal Na_2SO_4 solution were titrated with .02 normal solutions of H_2SO_4 and NaOH . The points at which the two curves for each soil cross when the titrations are plotted on cross-section paper were taken as the pH of exchange neutrality. The data and curves are given in Figure 20.

In all three soils these points agree closely with the pH of the soil paste, and they therefore add further support to the selection of the soil-paste method as being best suited for the determination of the pH value of soils.

CALCULATION OF PH VALUES

Puri and Sarup (27), in their study of isohydric pH values in soils, did not recommend the method for the determination of pH in highly alkaline soils because such soils invariably contain more or less Na_2CO_3 and NaHCO_3 . Since such soils are already in equilibrium with a Na_2CO_3 - NaHCO_3 buffer, they have proposed a formula for calculating the pH value of highly alkaline soils. In order to obtain the values for the formula, they recommend the determination of the pH value, CO_3 , and HCO_3 in a 0.1 normal KCl extract of the soil, one part soil in five parts KCl solution. The values thus obtained are substituted in the following equation:

$$\text{PH value} = 8.67 + 0.018A - .0032B$$

in which B represents ml. of 0.1 normal alkali ($\text{CO}_3 + \text{HCO}_3$) in 100 ml., and A equals per cent Na_2CO_3 in B. Having first determined the pH values of various mixtures of Na_2CO_3 in distilled water and in 0.1 normal KCl and having found the difference to be 0.2 pH, they add this value to the calculated pH. On applying this formula to a number of black alkali soils, they found a close agreement between the calculated pH and the pH determined with the antimony electrode.

In view of the fact that several of the highly alkaline soils examined in our experiments gave pH values at the isohydric point

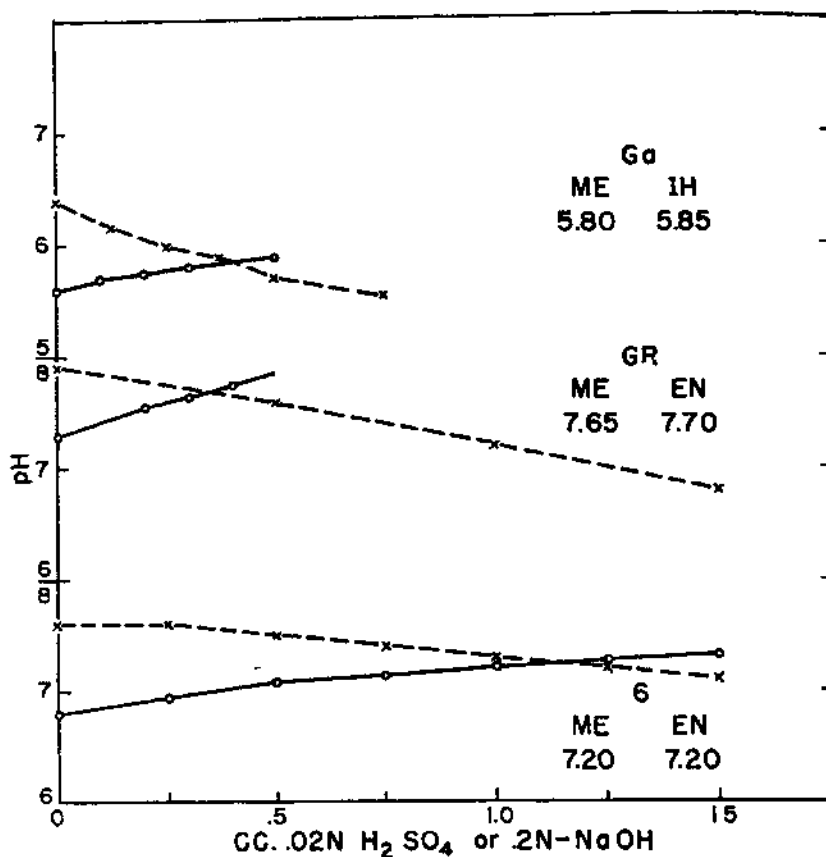


Figure 20.—pH of exchange neutrality. ME designates pH of soil paste and EN pH of exchange neutrality or point at which curves cross.

which were not in close agreement with the pH of the soil paste, it seemed of interest to calculate the pH values for several highly alkaline Arizona soils, using the above formula, and to compare these calculated values with the pH values obtained on the soil paste and at 1:10 soil:water ratio. These data are given in Table 13 and indicate that the method of calculating pH values for black alkali soils does not yield values which agree with those obtained on the soil paste nearly so closely as the isohydric pH values obtained with the buffer solutions. It is probable that the correction value, 0.2 pH, is not widely enough adapted to meet the many variables which influence the pH of alkali soils in Arizona, or that Puri was interested only in the pH of a 1:5 soil:water extract.

TABLE 13.—COMPARISON OF PH VALUES, OBTAINED ON THE SOIL PASTE AND AT 1:10, WITH CALCULATED PH VALUES

Soil no.	PH paste	PH 1:10	PH cal.
A	9.60	10.40	9.73
B	8.95	9.85	9.68
C	8.55	9.65	9.54
D	8.35	9.40	9.22
E	8.35	9.40	9.40
F	8.40	9.65	9.09
G	9.65	10.35	9.97
H	8.85	10.00	9.35
I	8.55	10.00	8.98
J	8.50	9.60	9.32

VARIATION IN ABSOLUTE WEIGHT OF SOIL

In addition to the established fact that pH values for soils vary with the soil:water ratio at which the determination is made, Buehrer and Williams (4) have shown that the pH value of a soil will increase with an increase in the absolute weight of soil and volume of water, even though the ratio of soil to water is maintained at a constant. For example, they showed that the pH value of a soil suspension of one part soil in ten parts of water increased from 8.2 for 3 grams of soil in 30 ml. of water to 9.11 for 20 grams of soil in 200 ml. of water. Huberty and Haas (14) studied the influence of absolute weight of soil at constant soil:water ratio, using 4 to 50 grams of soil. They used soils with pH values of 6.42, 6.81, 7.28, and 10.28 and both 1:5 and 1:10 soil:water ratios and obtained the same pH values with all absolute weights of soil. In view of the fact that Buehrer and Williams used only one soil, it seemed advisable to examine a little further the subject of absolute weight of soil and its influence on the pH by using a larger number of soils. The data thus obtained are given in Figure 21.

The pH values of eight different soils were determined at 1:10 soil:water ratio, using 1, 2, 4, 6, 8, 10, 15, 20, 25, 30, 40, and 50 grams of soil with 10, 20, 40, 60, 80, 100, 150, 200, 250, 300, 400, and 500 ml. of boiled distilled water. The data confirm our previous observations (Buehrer and Williams), that when pH determinations are made on a soil suspension of 1:10, the absolute weight of soil used is an important consideration. When 10 grams of soil or less are used, the pH values obtained are not reliable. Consistently reproducible results are obtained only when the absolute weight of soil is 20 to 40 grams.

This variation in pH with variation in absolute weight of soil is shown to exist for the black alkali soils, for both the calcareous and noncalcareous soils, and for the soils with both high and low salinity, and is not related to the CaCO_3 in the soil. The soil which

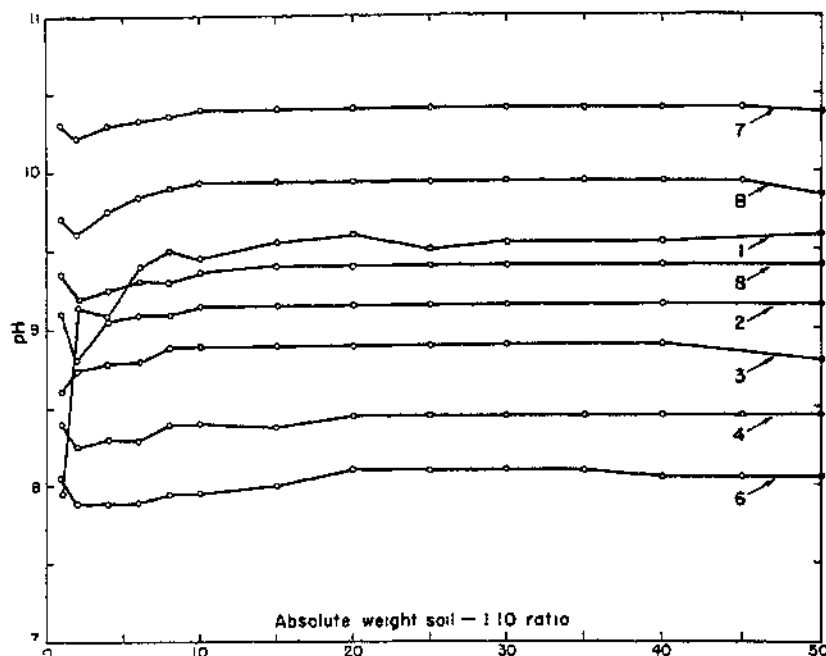


Figure 21.—Relation between absolute weight of soil and pH at constant soil:water ratio.

shows the greatest variation with change in absolute weight of soil from 1 to 20 grams is the Superstition sand. This suggests that a minimum weight of 20 grams of soil is required for uniform saturation of the soil suspension with the hydrolytic products of the potentially alkaline compounds in the soil.

PH STUDIES AT LOW MOISTURE CONTENT

In our original research on the pH determination in soils at low moisture contents in this laboratory, it was shown that apparent pH readings could be made with the glass electrode at moisture contents well below the moisture equivalent. It should be mentioned in this connection that most of the semiarid soils of Arizona contain very little organic matter and are therefore very low in actual moisture content under atmospheric conditions. A close agreement in pH values for soils can be obtained for moisture contents within the range extending from the moisture equivalent to the water-holding capacity. Above the water-holding capacity there is a considerable increase in pH with dilution up to a soil:water ratio of 1:10 at which point it becomes practically constant. At moisture contents below the moisture equivalent the glass electrode gives values which decrease at a rather rapid rate with decrease in moisture content, but it is sometimes difficult to ob-

tain consistent and reproducible readings. This may be due to poor electrode contacts, to insufficient continuity of the moisture films on the soil particles, or, as Davis (9) has pointed out, to the effect of increased resistance on the product of the grid current and resistance. For this reason Davis has referred to these low pH values as apparent pH values.

We have continued to make all routine pH determinations on the soil paste or approximately the moisture equivalent in this laboratory. However, there is still some interest in pH values of the soil below the moisture equivalent, both in field soils *in situ* and in the analysis of laboratory samples. This is in large part due to the low pH values reported for field tests by Haas and Huberty (14). These authors report extensive studies on orchard soils in the field, in which appreciably acid pH values were found under field conditions for soils which by the regular procedure yielded pH values on the alkaline side of neutrality, and these values appeared to be related to tree performance in the orchards. Davis (9) obtained equilibrium values with the glass electrode at these low moisture contents, but there was a slow yet appreciable drift before equilibrium was reached. This is more or less in agreement with our own experiences, except that we have found that these apparent pH values are more consistent and reproducible if the low soil moisture samples are enclosed for twenty-four hours in a glass weighing bottle with a ground glass cover in order to establish complete moisture equilibrium in the soil before inserting the electrodes. Since Davis has shown that commercial vacuum tubes may give erroneous results under these conditions, there is as yet no acceptable evidence that air-dry soils are characteristically more acid or alkaline than moist soils. Heintze (13) obtained pH values of 5.6 to 6.2 for dry soils, and he concluded that these values represent "the pH value of a thin moist film in equilibrium with the carbon dioxide content of the air and with the glass but not in equilibrium with the soil moisture."

In our original work the moisture equivalent was selected as a desirable moisture content for the pH determination of soils, because it is a frequently used value for characterizing the moisture relations in soils. It represents closely the moisture present in the small pores and that imbibed by the soil colloids. All soils are equally wet at the moisture equivalent. It is slightly below the field moisture capacity, well above the wilting point, and is about the optimum moisture content for seed germination.

In the work on pH determination at low moisture contents, especially below the moisture equivalent, no recognition seems to have been given to the fact that the soil is worked into a paste (before inserting the electrodes) when the determination is made at the moisture equivalent. In so doing, a large part of the water becomes bound and therefore the amount of free water present is reduced well below that represented by the moisture equivalent. Bouyoucos has defined bound water as that portion

(1) of the total water which fails to freeze when the soil is placed in a freezing chamber and reduced to -1 degree C. Ewing and Spurway (11) found a reduction in the dielectric constant of water from 81 to 22 in the binding of water by silica gel. There was likewise a reduction in solvent power for salts, and the water became less polar and less active. It has been shown that Arizona soils are most severely puddled when worked at the moisture equivalent and that this moisture content is a critical point for physical changes in the soil (24). Buehrer and Rose (6) have shown that maximum binding of water takes place when soils are puddled at the moisture equivalent. An examination of seven soils showed that 37 to 98 per cent of the moisture was bound when they were puddled at the moisture equivalent. There is evidence, then, that when a pH determination is made on a prepared soil paste the free or active water is far less than the content actually represented by the moisture equivalent percentage.

An experiment was conducted to determine, by puddling, the effect of reduction in free water on the pH of the soil. Fifty grams of soil, in two series, were weighed into 100-ml. beakers and sufficient distilled water added to bring the moisture content to the moisture equivalent. One series was thoroughly puddled into a paste, allowed to stand in a saturated atmosphere for twenty-four hours, and the pH determined on this paste (Table 14, col. 1). The other series was left unpuddled but also left in the water-saturated atmosphere for twenty-four hours in order for the soil and moisture to come to equilibrium before inserting the electrodes for the pH determination (Table 14, col. 2) after which this portion was worked into a paste and the pH again determined (Table 14, col. 3).

TABLE 14.—COMPARISON OF PH VALUES AT THE MOISTURE EQUIVALENT FOR PUDDLED AND UNPUDDLED SOILS

Soil no.	PH			Per cent clay in soils	P.p.m. total salts in soils
	Puddled	Not puddled	Puddled		
C	8.85	8.80	8.80	----	-----
2	7.90	7.75	7.85	29	1,105
3	7.75	7.70	7.80	16	1,555
4	7.50	7.65	7.60	29	10,200
5	7.70	7.55	7.60	29	2,800
7	9.05	9.05	9.05	25	8,020
8	7.85	7.70	7.80	42	1,230

Practically all soils, especially when they contain appreciable amounts of clay, have a certain percentage of moisture bound, and this is merely increased by puddling. The data in Table 14 indicate that there are only small differences in pH values of puddled and unpuddled soils at the moisture equivalent. For five soils the pH is slightly higher for the puddled soils, in one it is slightly lower, and in another there is no difference in pH. All these pH determinations may be considered within the range of

experimental error, especially in view of the fact that there was some drift in the readings made on the unpuddled soil. This experiment shows that if reduction in free water by puddling is in any way related to reduction of moisture by evaporation, there should be little or no change in the pH of the soil on reducing the moisture content below the moisture equivalent.

The subject of pH determinations on soils at moisture contents below the moisture equivalent has been approached from another angle. That is, pH studies have been conducted on soil suspensions or mixtures of soil in alcohol instead of water. This experiment had two objectives. First, to study the possibility of using alcohol as a medium for the suspension of air-dry soils, thus obtaining pH values for soils at low moisture percentages; and second, to study the possibility of selecting an alcohol-water mixture that would yield the same pH values as those obtained on the soil paste. In making a large number of routine soil analyses it takes some time to prepare soil pastes of the proper moisture content. This is especially true of clay soils, which are usually sticky, and on the other extreme, for sandy soils where it is difficult to avoid going beyond the moisture equivalent and having present an excess of water. Routine pH determinations in soils could be greatly expedited if a 1:1 mixture of soil and alcohol could be used to obtain a pH value which agreed with that of the soil paste. This is especially true since we now know that the pH of the soil paste is closely the isohydric pH and since Davis (9) has shown that pH values obtained at very low moisture contents are erroneous, or at least of questionable value.

There are several things one might expect from the use of alcohol as a medium for the soil suspension. Mixing alcohol with the soil should change the concentration of the water present, depending upon the amount of water in the soil, but it should not change the absolute amount present. The amount of water present can be varied by using different ratios of water and alcohol in the suspension. Since water has a dielectric constant of 80, methanol of 33, and ethanol of 25, the use of alcohol suspensions should reduce the dissociation and hydrolysis of the salts and soil minerals. In a qualitative examination of five saline soils and two black alkali soils shaken with distilled water, 95 per cent ethanol, and absolute methanol, 1:5 ratio, conductivity readings with an L. & N. soil conductivity bridge showed the lowest conductivity for methanol, next lowest for ethanol, and highest for water.

Alcohols act as dehydrating agents and as flocculants for soil colloids. Since they are dehydrating agents they should increase the apparent resistance of the glass electrode, and it would not be advisable to use strong alcohol solutions. Also the activity of water decreases with increase in per cent alcohol. It has been shown by Dole (10) that the presence of alcohol introduces an error into the pH readings of the glass electrode; but within the range of 33 to 66 per cent alcohol he found the error, at least in

acid solutions, was very small. In another experiment in which NaOH solution was gradually added to an alcoholic solution of NaI the error was low between pH 7.73 and 8.09. Thus there is very little encouragement in the literature for the use of alcohol in the pH determination of soils.

For the study of the pH values of soils in alcohol suspensions, nine soils were selected. Both ethanol and methanol were used, and both were redistilled from pyrex flasks in which an excess of CaO was present. For ethanol the pH determinations were made with 10, 25, 50, 80, and 95 per cent solutions and soil alcohol ratios of 1:1, 1:5, and 1:10. For methanol the solutions were 10, 25, 50, and 80 per cent solutions, and ratios of 1:1 and 1:5 were used. The technic employed for the determinations was the same as that used in the pH determination of water suspensions. The pH readings were made approximately fifteen minutes after the suspensions were prepared. This arbitrary time was selected after determinations made over a period of twenty-four hours showed no change in pH. The data are given in Table 15 together with values obtained with boiled distilled water at 1:1, 1:5, and 1:10 soil:water ratios and on the soil paste.

These data show that the pH values obtained with 50 per cent ethanol and 50 per cent methanol at a 1:1 ratio are very closely the values obtained on the soil paste at a moisture content approximating the moisture equivalent. The values obtained with ethanol are in closer agreement than those obtained with methanol and are sufficiently close to warrant consideration of the method in the routine determination of soil pH values which may be considered equivalent to the values of the soil paste. It is of interest that 50 per cent alcohol is within the range of concentration where Dole found the least alcohol error.

With the encouragement of the above, thirty samples of soil were selected at random from the soil samples on file in the laboratory and pH determinations were made on the soil paste, at 1:10 soil:water ratio, and at 1:1 soil alcohol ratios for 50 per cent ethanol and 50 per cent methanol. These data are given in Table 16, where a close agreement was obtained with both alcohols and the soil paste with only a few exceptions. These exceptions are fewer for the ethanol than for methanol.

Briefly summarizing the pH studies at low moisture content of soils, there is considerable evidence that in the soil-paste method the active or free moisture content of the soil paste is considerably less than the per cent moisture represented by the moisture equivalent percentage. There is also strong evidence that an approach to the pH of soils at low moisture content can be attained by using dilute alcohol as a suspension medium. It is noted that Davis (9) employed an acetone soil paste to a limited extent.

TABLE 15.—PH VALUES OBTAINED BY USING ALCOHOLS AS SUSPENSION MEDIA

Soil:water ratios	Soil number								
	2	3	5	4	6	7	R.I.	8	C
Distilled water									
Paste	7.95	7.75	7.70	7.60	7.20	9.55	4.45	8.00	8.95
1:1	8.15	7.90	7.85	7.70	7.45	9.95	4.30	8.55	9.30
1:5	8.70	8.30	8.30	7.95	7.80	10.10	4.45	9.15	9.85
1:10	9.10	8.85	8.35	8.45	8.15	10.40	4.75	9.40	10.30
10 per cent ethanol									
1:1	8.10	7.80	7.80	7.70	7.45	9.90	4.20	8.60	9.30
1:5	8.65	8.20	8.20	8.00	7.80	10.15	4.30	9.15	9.85
1:10	8.85	8.55	8.45	8.15	7.90	10.15	4.55	9.30	9.95
25 per cent ethanol									
1:1	8.00	7.70	7.75	7.60	7.35	9.75	4.20	8.35	9.10
1:5	8.50	8.10	8.10	7.90	7.65	10.20	4.30	9.05	9.90
1:10	8.75	8.35	8.35	8.05	7.80	10.10	4.50	9.20	9.90
50 per cent ethanol									
1:1	7.85	7.60	7.65	7.45	7.25	9.55	4.20	7.85	8.90
1:5	8.35	7.85	8.00	7.70	7.55	9.95	4.40	8.80	9.45
1:10	8.55	8.10	8.30	7.95	7.60	9.80	4.65	8.90	9.55
80 per cent ethanol									
1:1	7.65	7.35	7.40	7.10	7.00	9.25	4.15	7.60	8.65
1:5	8.00	7.60	7.75	7.30	7.30	9.55	4.40	8.35	9.15
1:10	8.20	7.70	8.05	7.55	7.40	9.35	4.60	8.55	9.15
95 per cent ethanol									
1:1	7.40	6.90	6.95	6.80	6.65	8.40	4.20	7.30	8.00
1:5	7.65	7.30	7.15	6.80	6.95	8.70	4.15	7.90	8.50
1:10	7.60	7.30	7.30	7.15	7.05	8.50	4.35	8.00	8.45
10 per cent methanol									
1:1	8.10	7.85	7.80	7.75	7.30	9.85	4.30	8.60	9.40
1:5	8.60	8.20	8.20	8.00	7.45	10.10	4.40	9.05	9.65
25 per cent methanol									
1:1	8.05	7.70	7.70	7.70	7.25	9.90	4.30	8.25	9.35
1:5	8.45	8.00	8.10	7.90	7.45	9.75	4.45	8.90	9.50
50 per cent methanol									
1:1	7.95	7.65	7.60	7.60	7.30	9.60	4.35	8.25	9.15
1:5	8.40	7.90	8.00	7.80	7.10	9.70	4.50	8.95	9.50
80 per cent methanol									
1:1	7.85	7.40	7.40	7.45	7.05	9.35	4.05	8.25	8.90
1:5	8.15	7.70	7.80	7.55	7.10	9.40	4.30	8.90	9.50

SUMMARY

As our knowledge of the chemical and physical properties of soils progressively increases, we find more and more emphasis on their dynamic character—that is, on the property of the soil to respond to changes in environment. Mention is often noted in the literature that there is no such thing as a definite or true soil solution, that there is no such thing as a definite or true base exchange capacity, and finally that there is no such thing as a definite or true pH value. There is plenty of experimental evidence

TABLE 16.—COMPARISON OF PH VALUES USING WATER AT 1:10 AND SOIL PASTE, 50 PER CENT ETHANOL, AND 50 PER CENT METHANOL

Soil no.	Water		Methanol 1:1	Ethanol 1:1
	Paste	1:10		
50	7.65	7.85	7.65	7.60
51	7.75	8.80	7.85	7.80
52	7.65	8.65	7.65	7.55
53	7.70	8.45	7.75	7.65
N	5.80	6.10	5.80	5.70
K	9.85	10.20	9.95	10.20
54	7.80	8.85	7.80	7.80
55	7.75	8.50	7.80	7.80
56	7.85	8.35	7.85	7.75
1	8.60	8.95	8.65	8.65
2	7.95	9.10	8.05	7.95
6	7.40	8.10	7.40	7.35
3	7.70	8.85	7.65	7.60
4	7.65	8.45	7.65	7.60
5	7.60	8.35	7.60	7.65
PV	7.20	8.15	7.25	7.20
C	8.95	10.30	9.15	8.90
7	9.60	10.40	9.60	9.55
57	7.90	8.80	7.90	7.80
R	4.45	4.75	4.25	4.20
8	8.00	9.35	8.25	8.15
S1	7.25	8.00	7.25	7.25
S3	8.10	9.45	8.50	8.45
58	7.20	7.65	7.70	7.75
G1	6.90	7.80	6.90	7.00
G4	5.90	6.55	5.95	5.85
F8	8.10	9.25	8.35	8.35
F9	8.10	9.05	8.20	7.95
23	9.15	10.05	9.40	9.25
24	8.75	9.90	8.75	8.65

on which to base such statements, for the soil is a product of environment. But the same may be said of crops, for the plant, too, is a product of environment. However the soil solution, the exchange capacity, and the pH value are all contributing factors in soil behavior and crop production. The dynamic character of the soil merely emphasizes the necessity for continued research to clarify as many of the variables as possible. Environment is essentially the summation of these variables.

When electrometric and colorimetric methods were first developed for the determination of pH values of soils, they immediately assumed an important place in soil research and control. The technic of the early methods was such as to require a soil suspension in water totally unlike the soil-moisture relations existing in the field. Definitely, the values thus obtained were not true pH values. The development of the glass electrode greatly expanded research in soil pH, for it is applicable under conditions of low moisture content within the range at which roots make con-

tact with the soil particles in the field. Based upon research conducted in this laboratory, it was suggested that a moisture content approximating the moisture equivalent be adopted for pH determinations in soils to replace the older methods which employed soil:water ratios varying from 1:1 to 1:10. The selection of the moisture equivalent point was more or less arbitrary but was based in large part upon the fact that we found little variation in pH at moisture contents slightly below and above this point, and because the moisture equivalent represents a moisture content at which all soils are equally wet. The pH value at this point is usually considerably lower than the pH values obtained at dilutions previously used, but it is higher than apparent values obtained with the glass electrode at moisture contents well below the moisture equivalent and approaching air-dryness. In a study of these low pH or equilibrium values obtained at low moisture contents Davis (9) has found evidence that these equilibrium values do not represent true pH values, and he suggests a soil paste approximating the moisture equivalent as a satisfactory moisture content for the pH determination. At present there seems to be general agreement that this moisture content is most satisfactory for semiarid soils; but while there has been much to commend the method, there still remains much to be learned about the pH values of soils and their interpretation. The data presented in this bulletin present much evidence that the pH value of the soil paste is a true soil pH value.

Because of the great variation in soil pH values obtained at different soil:water ratios and the opinion that none of them represented true pH values, Puri (27) has suggested the isohydric pH value and Mattson (20) the pH of exchange neutrality as being most useful and as approaching an absolute value. The isohydric pH value is the pH of a buffer solution which is not changed by shaking it with a soil. The pH of exchange neutrality is defined as that point at which the addition of a neutral salt to a soil suspension does not affect the pH of the latter. Since both these values agree very closely with the pH value of the soil paste, this investigation has yielded considerable support to the recommendation that pH values of soils be determined on a soil paste.

The equi-ionic pH is defined as that pH of a salt solution which is not affected by the addition of a completely unsaturated soil (free acid-base ampholytoid). In other words, it is the pH at which the capacities of the soil to combine with the cations and the anions of the solution are equal. Mattson has shown this point to approximate closely the pH of exchange neutrality, and obviously, then, it will closely approximate the pH value of the soil paste.

Among the variables affecting pH are salinity, both concentration and character, and the anions and cations as individuals, the character of the base exchange complex, and the mechanical composition of the soil. The influence of all these factors on the

pH is reduced to a minimum at the moisture equivalent. In fact, all the information obtained in this investigation further commends the use of the soil paste for the pH determination, especially in view of the fact that the value is in close agreement with Mattson's pH of exchange neutrality and Puri's isohydric pH to which he refers as an absolute value.

The salinity-pH relationship is greatly clarified by this investigation. It has been known for many years that salts have a profound influence on the pH value of soils. This is largely because the activity of water is reduced and thus becomes less active as a hydrolyzing agent, and because salts tend to flocculate and thus reduce the soil surface exposed to the hydrolyzing solution. The common ion effect is also often mentioned. We have been somewhat puzzled by the failure to find any correlation between pH and total salts in the soil, actually determined or calculated from conductivity. This failure is now explained by the observation that HCO_3 and CO_3 ions have opposite effects on pH to the Cl and SO_4 ions and may thus confuse the effect of total salinity depending entirely on the composition and ratio of the different ions present in solution. The hydrolysis of the exchange complex and CaCO_3 , taking place both in the absence of salts and at variable degrees in the presence of salts also contributes to the multiplicity of factors affecting pH. It is evident from the experiments presented that one should not necessarily expect any relation between total salinity and pH, nor between sodium and pH. The salinity effect on pH appears to be largely due to the anions. It is true that there was a highly significant correlation between Ca and pH (Fig. 5), but it must be recognized that calcium is precipitated as carbonate in the presence of Na_2CO_3 , and so this significant correlation, decrease in Ca with increase in pH, may be a simple fact that the calcium is removed from solution in the high pH soils by the precipitation as carbonate. Actually the data do not necessarily prove that pH decreases with increase in concentration of soluble calcium, although we know from other experiments that it does.

The base exchange complex contributes to soil pH by hydrolysis; therefore its influence depends, in large part, upon the nature of the attached cations and the activity of the water in contact with the soil. The pH of the soil increases with increase in percentage of replaceable sodium and the ratio of sodium to the total exchange capacity of the soil. However all sodium-saturated soils were found to have closely the same pH at 1:10 soil: water ratio, regardless of the m.e. sodium per 100 grams. At the moisture content represented by the moisture equivalent the soils highest in replaceable sodium, m.e. per 100 grams, had the lowest pH, while the soils lowest in replaceable sodium, the sandy soils, had the highest pH. When the adsorbing fraction of the soil is saturated with sodium it apparently acts similarly to CaCO_3 , in that, regardless of the total amount present, they both hydrolyze to a

constant and maximum pH value when conditions are such as to permit complete hydrolysis.

In the study of the soil particle separates from ten soils, the separates from clay to 0.84 m.m. exhibited pH values somewhat related to the pH of the soil mass as a whole. The hydrolytic alkalinity increases with decrease in particle size. However, the OH-ion concentration is greatest for the sand particles showing a wide difference between the intensity and quantity factors in alkali soils.

The value of pH determinations in dry soils—that is, well below the moisture equivalent—is still an open question. It is generally agreed that equilibrium values can be obtained with the glass electrode at these low moisture contents. Even though they may not be true pH values, Haas and Huberty (14) have found that these low values are related to certain tree conditions in orchards. Plant experiments conducted in this laboratory have shown that roots can absorb ions from dry soils (3) but that they do so by moisture movement from the deep roots to the roots in the layer of dry soil where the moisture is exuded to form a root-soil contact film in the dry soil layer. This moist film is probably close to the moisture equivalent and therefore it seems that the pH at this moisture content should be low enough and have the widest application in soil research and plant nutrition, and there should be no place for pH values of dry soils where one is concerned primarily with nutrition. The use of alcohol-water solutions offers an approach to the problem of low pH values. Alcohol is a dehydrating agent and a flocculant, but it may introduce certain characteristic errors into the pH determination when the glass electrode is used. In spite of this property of alcohol the pH values obtained with 50 per cent alcohol, at a 1:1 ratio, agree very closely with the pH of the soil paste.

Above all, in a consideration of the pH values of soil at low moisture content, one should not ignore the fact that in preparing a soil paste for the pH determination, most of the water becomes bound and therefore the free water present amounts to only a small percentage of that present before the soil was worked into a paste. Yet there is very little or no difference between the pH of puddled and unpuddled soils at the moisture content represented by the moisture equivalent.

CONCLUSIONS

1. Calcareous semiarid soils have higher pH values than non-calcareous soils, but there is no relation between the percentage of CaCO_3 and pH in the calcareous soils.

2. Soil pH values are repressed by increasing salinity, but there is no correlation between total salinity and pH values when the analyses of a large number of soils are compared.

3. Of the anions, pH increases with increase in concentration of CO_3 and HCO_3 and decreases with increase in Cl and SO_4 . For the cations the pH decreases with increase in concentration of Ca , but there is no correlation between pH and the concentration of Na when the salts are predominantly sodium salts and CO_3 , HCO_3 , Cl , and SO_4 are all present.

4. The total salinity-pH relationship can best be demonstrated by centrifugal separation of the soil and water extracts. The pH of the soil-water mixture, the water separate, and the soil paste increase in pH with successive extractions except in the black alkali soils where the pH of the soil paste decreases.

5. By employing the Hehner method for determining the black alkali content of soils, a correlation between the magnitude of the Hehner value and the pH was shown.

6. The pH value of the soil increases with an increase in the percentage of replaceable sodium in the exchange complex and the ratio of sodium to the total exchange capacity of the soil.

7. The pH value of the soil increases with dilution, both in the presence and the absence of neutral salts.

8. All sodium-saturated soils, in the absence of neutral salts, have pH values approximating pH 10.0 to 10.2 when the pH value is determined at a 1:10 soil:water ratio. At the moisture equivalent the pH decreases with increase in replaceable sodium.

9. The adsorbing capacity of the soil is increased by leaching the soil with salt solutions of high pH values but not by salt solutions of pH 8.5 or lower. This increased cation adsorption increases the potential alkalinity of the soil but does not increase the pH of the soil.

10. Sesquihydrates exhibit base exchange properties and high pH values which are affected by salinity and dilution.

11. All the soil separates possess an adsorption capacity for cations and exhibit high pH values in semiarid soils. The sand particles usually have a higher pH than the silt and clay.

12. The pH value of a soil when determined on the soil paste agrees closely with the isohydric pH and the pH of exchange neutrality.

13. For the determination of soil pH at low moisture contents, the use of dilute and strong alcohol solutions has been studied. The pH values obtained with 50 per cent ethanol or 50 per cent methanol at 1:1 soil:alcohol ratio agree very closely with the pH values obtained on the soil paste.

14. Variation in absolute weight of soil with constant soil:water ratios materially affects the pH value of a soil suspension in water. For pH determinations where dilute suspensions are used, an absolute weight of 20 grams of soil should be used for a 1:10 soil:water ratio.

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