



University of Arizona
College of Agriculture
Agricultural Experiment Station

SODIUM HYDROXIDE RATHER
THAN SODIUM CARBONATE
THE SOURCE OF ALKALINITY
IN BLACK ALKALI SOILS

By J. F. BREAZEALE AND W. T. McGEORGE

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FOREWORD

Practically all black alkali soils are calcareous and while for the past 2 years we have realized the utter impossibility of carbon dioxide, or carbonic acid, existing in such soils in any but the most minute amounts, if at all, it has but recently been possible for us to complete the necessary work herein presented. Very little evidence has ever been advanced in proof of the statement that sodium carbonate, to any considerable extent, exists in black alkali soils, although since the early work of Hilgard, it has been generally accepted as a fact that the titratable alkalinity here present is the result of the hydrolysis of this salt. Doubtless, reasoning largely from soils from humid climates, which are usually acidic in character and often carry large amounts of carbon dioxide, it has been taken for granted that like conditions prevail in arid, desert soils, low in organic matter and almost invariably calcareous in nature.

The fact that no hydroxyl-ion concentration, above that of calcium carbonate, from whatsoever source is normally present in the soil solution of black alkali soils when at optimum moisture content for crop growth, is new and of far-reaching significance.

The above, as well as other related phenomena, are interestingly presented and proved by the data appearing in this bulletin.

P. S. BURGESS,
Agricultural Chemist.

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SODIUM HYDROXIDE RATHER THAN SODIUM CARBONATE THE SOURCE OF ALKALINITY IN BLACK ALKALI SOILS

By J. F. BREAZEALE AND W. T. McGEORGE

INTRODUCTION

The term "black alkali soil" is used ordinarily to designate a soil that is supposed to contain enough sodium carbonate to interfere with the growth of plants. In the West such soils are prevalent, and they present more difficulties in the way of reclamation and drainage than do soils that contain excessive amounts of other alkalis.

Black alkali soils are dreaded by the farmer, for reasons that heretofore have not been definitely understood. Recent investigations upon the zeolites, or colloidal silicates, in these soils, have developed many facts that tend to explain their peculiar behavior when they are brought under cultivation. The zeolites are concerned chiefly with the penetration of water, and with the structure of the soil, and these physical effects will not be discussed in detail. This bulletin deals with black alkali from a chemical standpoint.

During many years' work upon soils of the Southwest, no evidence has been found, except in rare cases, that indicates that sodium carbonate exists in appreciable amounts in the so-called "black alkali soils." In the following discussion, therefore, the term "black alkali" will be used to designate those soils that contain hydroxyl ions in solution, but not necessarily sodium carbonate. It will be shown that the black alkali, that is usually reported in a chemical analysis as sodium carbonate, exists in the soil solution largely as sodium hydroxide.

BLACK ALKALI AND SODIUM CARBONATE

The soil from the old University Farm is a typical black alkali soil. It contains some sodium chloride and sodium sulphate, and when analyzed by the usual method, that is, when digested with distilled water in the proportions of 1 part of soil to 20 of water, it yields a solution whose alkalinity, when calculated to the basis of dry soil, often equals .5 percent of sodium carbonate. If this strongly alkaline soil is diluted with neutral soils from the same locality, and wheat seedlings are planted in these soil mixtures, the wheat will grow in all concentrations below .25 percent sodium carbonate in the soil, while above this concentration no growth is possible. The limit of endurance for wheat in

this soil is, therefore, about .25 percent, or 2,500 parts per million on the basis of dry soil. The moisture content of this soil at optimum, is about 10 percent, so in each kilogram of soil there would be 100 cc. of water, or more than enough to dissolve all of the soluble salts that are found in the soil.

In this soil, at the limit of endurance of wheat seedlings, there would be a concentration of 25,000 parts per million of sodium carbonate, if all of this alkali were dissolved in the soil solution. It will be shown that wheat seedlings cease growing at about 900 parts per million of sodium carbonate, so it is evident that all, or at least a greater part of this alkali, is not in solution in the soil when it is near or below the optimum moisture content.

It has been known for a long time that in order to extract all of the black alkali from a soil, it is necessary to use a high proportion of water to soil. It has been found by many trials, that, usually, a digestion of a soil in 20 times its weight of water, at 100° C., will yield practically all of the black alkali. Many experiments have been made recently, in which the ratio of water to soil was varied, and the data of one of these experiments are given in Table I.

Samples of soil from the old University Farm were placed in jars, and water was added in the ratios that are shown in Table I. The jars were corked and allowed to stand, with frequent shakings, for 5 days and the solutions were then filtered and analyzed. The results for total solids, hydroxyl ions, and bicarbonates are shown in the following table.

TABLE I.—SOLUBILITY OF TOTAL SOLIDS, HYDROXYL IONS, AND BICARBONATES IN VARYING RATIOS OF WATER TO SOIL. (RESULTS IN PERCENTAGE OF DRY SOIL.)

No.	Ratio water to soil	Total solids	Hydroxyl calculated to CO ₂	HCO ₃
		Percent		Percent
1	25.0 1	.470	.0600	.1800
2	10.0 1	.392	.0420	.1320
3	5.0 1	.330	.0450	.0600
4	2.5 1	.269	.0255	.0570
5	1.0 1	.220	.0132	.0456
6	0.5 1	.200	.0078	.0456
7	0.4 1	.189	.0057	.0389
8	0.3 1	.199	.0050	.0353

It will be seen from the table, that, when the results of these analyses of the solutions are calculated to dry soil, there is a decrease in the percentage of total solids, hydroxyl ions, and bicarbonates, as the ratio of water to soil is reduced.

In the present discussion we are not concerned with any of the ions except OH and HCO_3 . The determinations of these were made by titration in solutions containing black organic matter, and this made it difficult to get very accurate end points. These errors are not large enough to affect materially the results of the experiment, although they may make the results appear a little irregular. If these are plotted with the ratio of soil to water as ordinates and the percentages of alkali as abscissa, a fairly regular curve will be obtained.

THE SOIL SOLUTION

In all studies of alkali in soils and of alkali tolerance of plants, we have been handicapped by our ignorance of the nature and composition of the true soil solution, that is, the solution with which plant roots actually come in contact. The plant feeds in all of the soil moisture, from the outer edge of the thick film that is represented by the optimum moisture content of the soil, down to the innermost layer that surrounds the soil particles, represented by the hygroscopic moisture.

No one has yet separated completely the soil from the true soil solution. If the true soil solution could only be obtained for analysis, many phenomena of alkali tolerance might be explained. Analyses of soil extracts that are made by digesting the soil with an excess of water have led many into mistaken ideas about the true soil solution. Briggs and McLane, with the centrifugal machine, succeeded in obtaining a little of the outer film of water from the soil particles, while Parker, Burd, Martin, and others, by partially replacing the soil solution with alcohol or other liquids, have obtained a larger part of the soil solution, a portion that is probably nearer the soil particle than that removed by the centrifugal force that was employed by Briggs and McLane. However, there is much unexplored territory in the region of and below the wilting point of the plant. The water in a soil at and below optimum may be considered as static, that is, it moves very slowly from one part of the soil to another. The water in a saturated soil, or the water that is added in excess in order to make soil extracts, is largely dynamic. The analyses of the soil extracts that are shown in Table II indicate that, when the ratio of water to soil is reduced to a point where all the water becomes static, an abrupt change takes place in the concentration of the solution, especially with respect to hydroxyl and bicarbonate ions.

HYDROXYL AND BICARBONATE IONS IN STATIC SOIL MOISTURE

Three large samples of the University Farm soil were made up to 8, 12, and 18 percent, respectively, with water, packed into large brass

tubes, and allowed to stand overnight. Twelve percent of moisture represented approximately the optimum of this soil, 8 percent a little above the wilting point, and 18 percent a little below saturation.

The moisture in the tubes was displaced under pressure by alcohol, according to the method described by Burd and Martin,* and the displaced solutions were analyzed for all of the common ions. At the same time, a set of soil extracts of the same soil was prepared by digesting the soil with water in the ratios shown in Table II, and these extracts were also analyzed.

The analyses for hydroxyl and bicarbonate ions, expressed in percentages of the dry soil, are given in Table II.

TABLE II.—THE EFFECT OF DILUTION UPON THE CONCENTRATION OF HYDROXYL AND BICARBONATE IONS IN SOIL EXTRACTS AND DISPLACED SOIL SOLUTIONS.

Soil extracts	Ratio water to soil	CO ₂	HCO ₃
		Percent	Percent
1	20:1	.0720	.1680
2	10:1	.0720	.1080
3	6:1	.0612	.0792
4	5:1	.0450	.0720
5	4:1	.0432	.0624
6	3:1	.0396	.0558
7	2:1	.0240	.0552
8	1:1	.0120	.0528
9	.5:1	.0078	.0528
10	.3:1	.0036	.0509
<i>Displaced solutions</i>			
11 (18%)	.18:1	Tr.	.0475
12 (12%)	.12:1	Tr.	.0360
13 (8%)	.08:1	Tr.	.0254

In order to show the points of interest in these tables, it is necessary to plot the results in two separate graphs, each with different values for the axis and abscissa. In figure 1 are shown the percentages of the extracts in terms of dry soil from a dilution of 20 parts of water to 1 of soil, down to a dilution of 1 part of water and 1 of soil.

In figure 2 are shown the data from a solution of 1 part of water to 1 of soil down to 0.08 parts of water to 1 of soil, or to a moisture content of 8 percent.

It will be seen from figure 1 that there is a gradual decrease in the percentages of both carbonates and bicarbonates as the ratio of water to soil is reduced. The hydroxyl ions seem to disappear very rapidly

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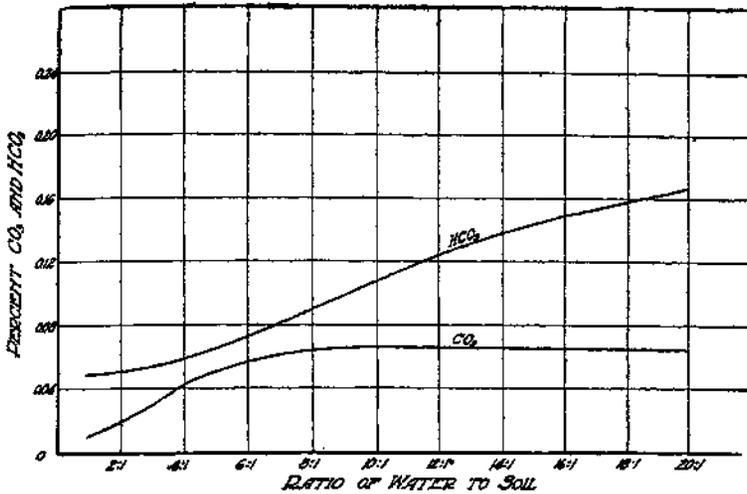


Fig. 1.—Graph illustrating effect of dilution upon the concentration of hydroxyl and bicarbonate ions in soil extracts.

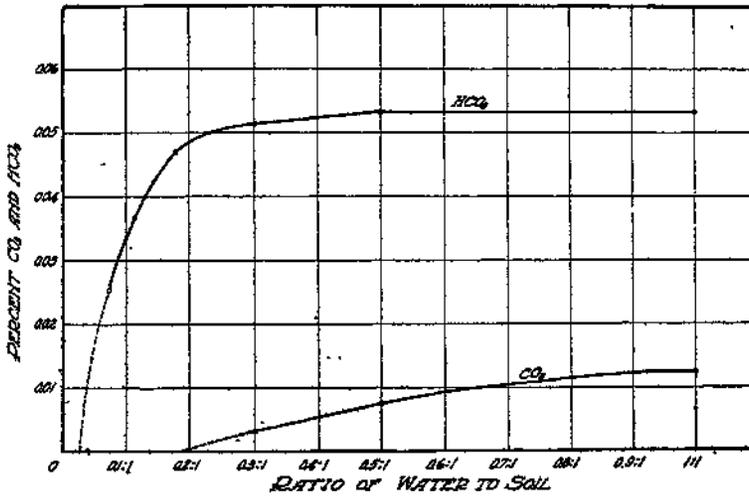


Fig. 2.—Graph illustrating effect of dilution upon the concentration of hydroxyl and bicarbonate ions in soil solutions.

in the lower ratios of water and soil, while there is a tendency of the bicarbonates to maintain the same concentration. It is quite likely that a part of the hydroxyl is being transferred into bicarbonates, in these lower ratios.

Figure 2 is of special interest. Beginning with an extract made by digesting 1 part of water to 1 of soil, the hydroxyl ions disappear rapidly from the solution until they show only a trace at and below a dilution of 18 parts of water to 1 of soil, or at a soil-moisture content of 18 percent. This alkalinity in the lower dilution is due, probably, to the slight solubility of calcium carbonate. It is evident that, in the static water of this soil or in the true soil solution, there is very little, if any normal sodium carbonate.

The bicarbonate curve makes an abrupt break when the percentage of water is lowered to the point where it becomes static, and falls off rapidly as the soil moisture is further decreased. If the curve is projected from the last point, it will be seen that only a trace of bicarbonates can remain in the soil when it is reduced to the dry state.

ELECTROMETRIC TITRATION OF BLACK ALKALI SOILS

Since the pH was not determined in these experiments, two other samples of black alkali soils were prepared, using carbon-dioxide-free water, and the reactions determined electrometrically in a suspension of soil in water of the ratios given. Sample 1 was the University Farm soil that had been used in the experiment just described, and Sample 2 was a badly dispersed soil from the Salt River Valley.

TABLE III.—EFFECT OF DILUTION UPON THE REACTION OF BLACK ALKALI SOILS.

Ratio water to soil	pH of soil	
	No 1	No 2
25 0 1	10.15	10.20
10 0 1	10.10	10.20
5 0 1	10.00	10.05
2 5 1	9.90	9.90
1 0 1	9.75	9.60
1 5 1	9.45	--

These results serve to confirm those that were given in tables I and II. There is a reduction in pH of OH ions, as the ratio of water to soil is decreased.

TITRATION OF THE SOIL SOLUTION AS COMPARED WITH SOLUTIONS OF ALKALI

The nature of the curves obtained in the titration of hydroxides, carbonates, and bicarbonates in pure solutions, show definite characters from which soil alkali identification should be possible. In view of

this, by means of such titrations, further proof was sought of the absence of normal carbonates in alkaline soils.

In these experiments, titrations were first made of solutions of sodium hydroxide, sodium carbonate, sodium bicarbonate, calcium carbonate, and calcium bicarbonate, with hydrochloric or sulphuric acids. The data obtained were plotted graphically, the pH against cc. of acid.

For the titration of sodium carbonate solution, 20 cc. of .05 N solution were added to each of a series of test tubes, and .05 N hydrochloric acid added in amounts varying from 1 to 20 cc. The reactions of the resulting solutions were then determined colorimetrically. Titrations were also made of solutions of equal parts of .05 N sodium carbonate, and .05 N sodium hydroxide, as well as .05 N sodium carbonate and .05 N sodium bicarbonate separately by the same procedure as that described above. These results are shown in figure 3. For the titration of sodium hydroxide, the procedure described above was followed, using .05 N sodium hydroxide, with the addition to the experiment of a solution containing equal parts of all three alkalis. The results of these titrations are shown in figure 4. The sodium hydroxide titrations were made electrometrically, but when sodium carbonate or sodium bicarbonate was present the titrations were made colorimetrically.

The sodium bicarbonate titrations were also made with .05 N solutions in the above manner and all readings made colorimetrically. These are shown in figure 5.

It will be noted that each curve has a distinctive character. This is especially true in comparing each alkali alone with the others both singly and in combination.

For the titration of the calcium carbonate and bicarbonate a saturated solution of the former was made by shaking precipitated calcium carbonate with carbon-dioxide-free, distilled water and of the latter by passing carbon dioxide through a suspension of calcium carbonate in distilled water. Titrations were made by adding 10 cc. of the foregoing solutions to a series of test tubes and adding the .05 N acid in varying amounts. The readings on these solutions were made colorimetrically. In the latter case the true curve is not obtained, although it is similar in character. With the smallest additions of acid, that is, those which do not completely neutralize the bicarbonate, the passing of hydrogen through the solution in the electrometric titration removes carbon dioxide. The effect of this is to give a high pH in the early stages of the titration. In this case the reaction was pH 6.6 before passing the hydrogen through, which was raised to 8.4. Otherwise, there is little difference in the character of the curves and with a knowledge of the foregoing it is possible to interpret correctly the results.

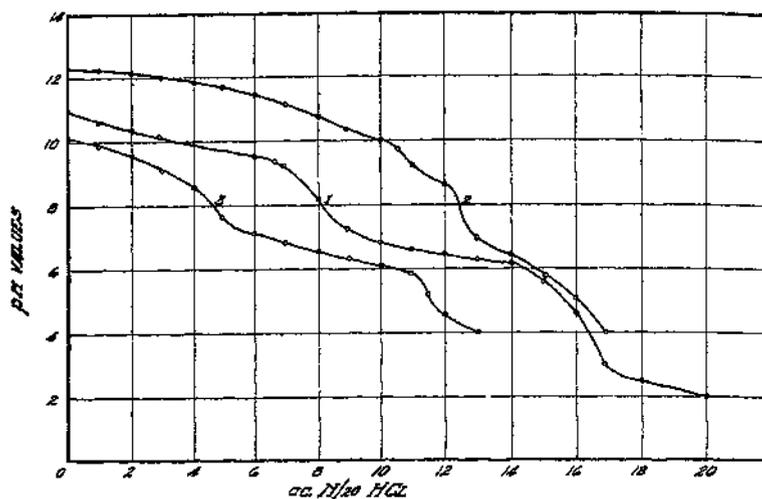


Fig. 3.—Graph illustrating nature of curves when sodium carbonate alone, and mixtures of sodium carbonate with sodium hydroxide and sodium bicarbonate, are titrated against hydrochloric acid.

1. 20 cc. N/20 Na_2CO_3 , against N/20 HCl.
2. 10 cc. N/20 Na_2CO_3 +10 cc. N/20 NaOH, against N/20 HCl.
3. 10 cc. N/20 Na_2CO_3 +10 cc. N/20 NaHCO_3 , against N/20 HCl.

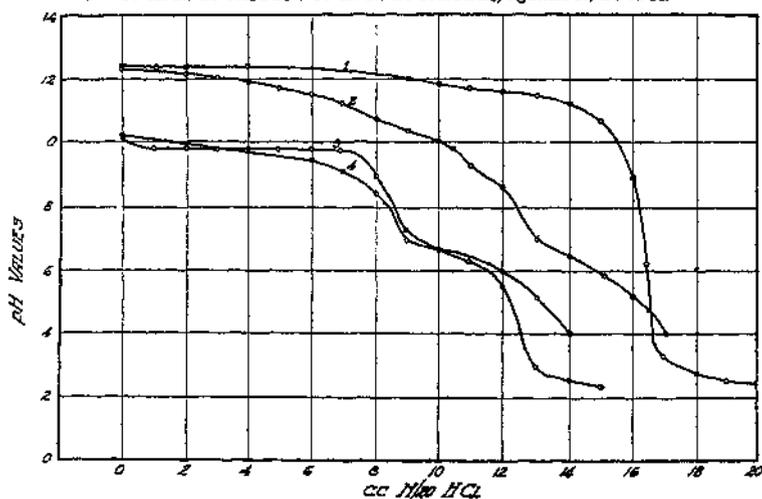


Fig. 4.—Graph illustrating nature of curves when sodium hydroxide alone, and mixtures of sodium hydroxide, sodium carbonate, and sodium bicarbonate are titrated against hydrochloric acid.

1. 20 cc. N/20 NaOH, against N/20 HCl.
2. 10 cc. N/20 NaOH+10 cc. N/20 Na_2CO_3 , against N/20 HCl.
3. 10 cc. N/20 NaOH+10 cc. N/20 NaHCO_3 , against N/20 HCl.
4. 6.6 cc. N/20 NaOH+6.6 cc. N/20 Na_2CO_3 +6.6 cc. N/20 NaHCO_3 , against N/20 HCl.

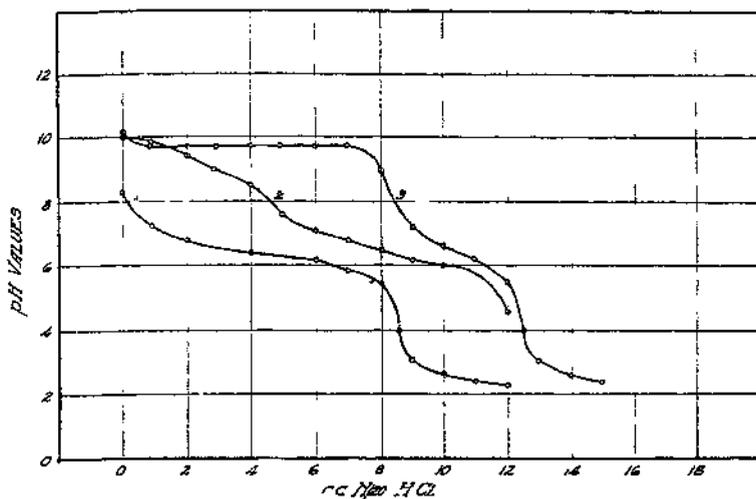


Fig. 5.—Graph illustrating nature of curves when sodium bicarbonate alone and mixtures of sodium bicarbonate, sodium carbonate, and sodium hydroxide are titrated against hydrochloric acid.

1. 20 cc. N/20 NaHCO_3 , against N/20 HCl
2. 10 cc. N/20 NaHCO_3 +10 cc. N/20 Na_2CO_3 , against N/20 HCl
3. 10 cc N/20 NaHCO_3 +10 cc N/20 NaOH, against N/20 HCl.

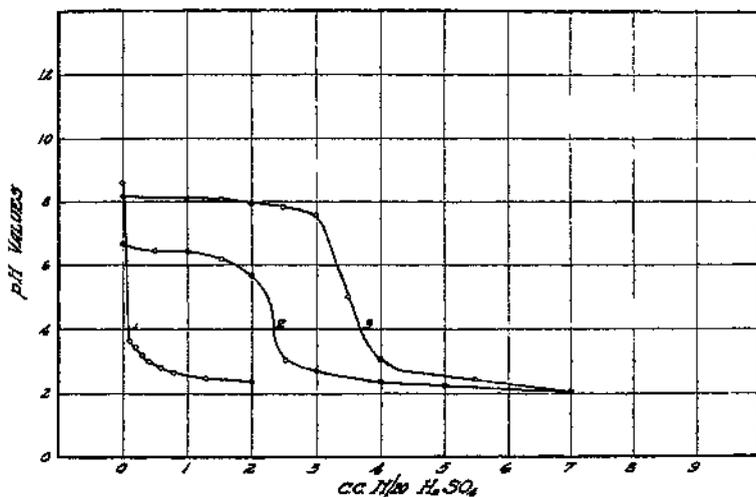


Fig. 6.—Graph illustrating nature of curves when calcium carbonate and calcium bicarbonate are titrated against sulphuric acid.

1. CaCO_3 , against N/20 H_2SO_4 colorimetrically.
2. $\text{Ca}(\text{HCO}_3)_2$, against N/20 H_2SO_4 colorimetrically.
3. $\text{Ca}(\text{HCO}_3)_2$, against N/20 H_2SO_4 electrometrically.

After obtaining the preceding data which are shown graphically in figures 3, 4, 5, and 6, a sample of black alkali soil which was also high in soluble salts was brought to the laboratory and, without drying out, packed in glass percolators. The soil solution was then obtained by displacement with alcohol and was of a very black color. The reaction of this soil as determined electrometrically on the hydrogen electrode in a suspension of 5 parts of water to 1 of soil, was pH 9.90. The moisture content as taken from the field and as packed in the percolators was 7 percent. The air-dry moisture content of this soil is 1 percent and the optimum about 10 percent.

The soil solution obtained in the above displacement was analyzed with the following results:

TABLE IV.—ANALYSES OF SOIL SOLUTIONS OF A BLACK ALKALI SOIL.

	Parts per million in soil solution	Percent soil, water-free basis
Total solids	89,672	.675
Inorganic solids	77,272	.582
Organic solids	12,400	.093
Hydroxyl or carbonate.....	No color with	phenolphthalein
Bicarbonate HCO ₃ (meth. Or).....	2,074	.015
Chlorine Cl	12,110	.091
Sulphur trioxide SO ₃	20,200	.152
Calcium Ca	73.6	.0005
Magnesium Mg	2.2	.00002
Iron and aluminum	Trace	Trace
Manganese	Trace	Trace
Silica	Trace	Trace
Reaction (electrometrically)	pH 7.7	

As shown in a previous experiment, it is plainly evident that there are few or no hydroxyl or normal carbonate ions present in the soil solution of this black alkali soil at a moisture content slightly below optimum. To verify this titrations were made on the solution. The electrometric titration was made by placing 10 cc. of the solution in the vessel containing the hydrogen electrode and the KCl-agar bridge. After taking the initial reading, 0.05 N sulphuric acid was added from a burette and readings taken after progressive additions of acid. The results of this titration are shown graphically in figure 7. The soil solution was too black to permit a colorimetric titration.

On the other hand, we have shown in the titration of calcium bicarbonate, and have subsequently determined in an electrometric titration of sodium bicarbonate, that while the points on the curve preceding the complete neutralization of the sodium bicarbonate are above the

true alkalinity of the solution, due to some normal carbonate being formed by loss of carbon dioxide, the general character of the curve is not greatly different from that obtained colorimetrically. It is to be noted that there is only one break in the curve showing a bicarbonate salt. The buffer effect of the organic matter and possibly the dissolved salts have shown their effects upon the curve by elimination of the sharper breaks characteristic of pure bicarbonate solutions.

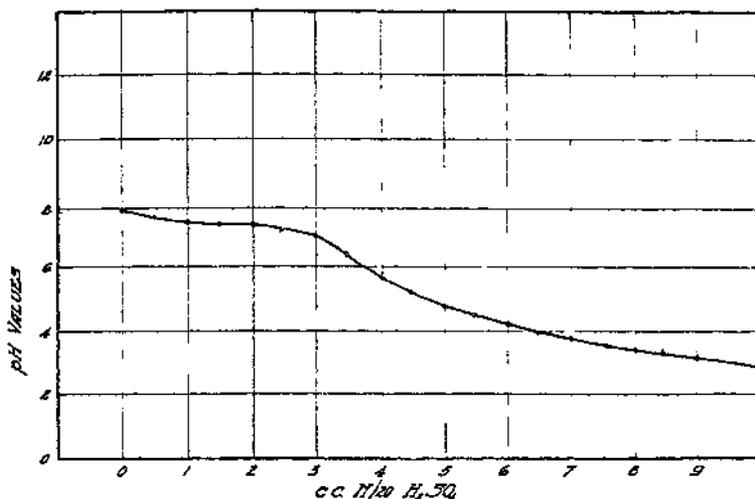
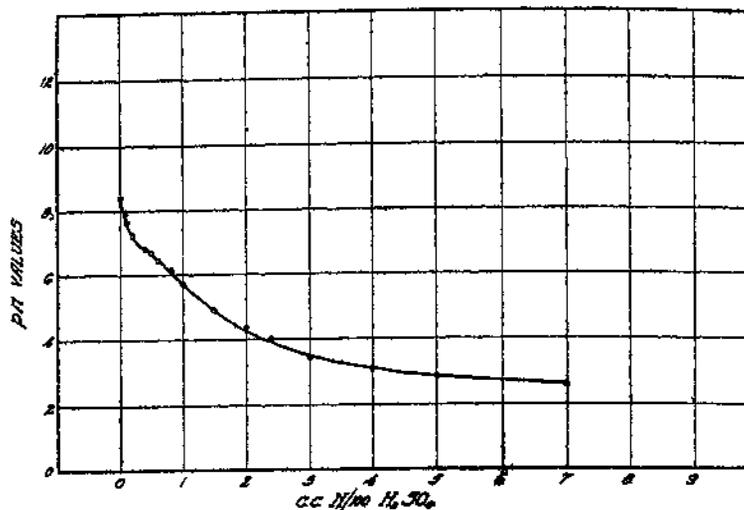
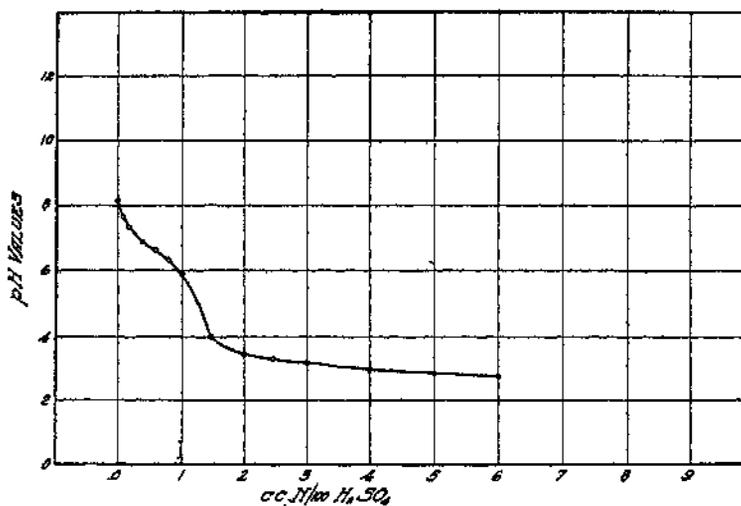


Fig. 7.—Electrometric titration of soil solution against N/20 H₂SO₄.

Since the soil solution was too dark for colorimetric titration, 10 cc. of this solution were diluted to 250 cc. with carbon-dioxide-free water at which dilution it was possible to make colorimetric comparisons. The titration of the undiluted soil solution showed a concentration of 2,074 parts per million bicarbonate (HCO₃) by titration with methyl orange. A solution of sodium bicarbonate was, therefore, made up of the same dilution as the diluted soil solution for comparative titration. For these titrations 10 cc. of solution were added to each of a series of test tubes and .01 N sulphuric acid added as a variant. These were then all made to the same volume, 20 cc., well shaken and the pH determined colorimetrically with a La Motte comparator. The data obtained in these titrations are given graphically in figures 8 and 9. The results tend to confirm the electrometric titrations of the undiluted soil solution and show that a soluble bicarbonate is the principal salt present and that it is probably sodium bicarbonate. The reaction of the soil solution, pH 7.7, shows however that a trace of OH-ion is present. It has been shown in figure 6 that the solubility of calcium carbonate is

Fig. 8.—Colorimetric titration of soil solution against N/100 H₂SO₄.Fig. 9.—Colorimetric titration of sodium bicarbonate against N/100 H₂SO₄.

sufficient to give a pH of 8.5. In the analysis of the soil solution only small amounts of Ca were found. This would permit the hydrolysis of calcium carbonate of which this soil contains approximately 5 percent. Then again sodium bicarbonate solutions in distilled water, unless an excess of carbon dioxide is intentionally added, will often show a pH of 7.7 or even more.

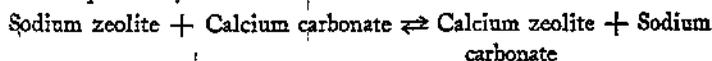
It is an apparent contradiction, but nevertheless a fact, that under field conditions, practically all of the "black alkali" soils contain no sodium carbonate and usually little sodium bicarbonate.

HYDROLYSIS OF SOIL ZEOLITES

A detailed discussion of the soil zeolites will not be undertaken here. It is sufficient to say that the presence of hydroxyl ions in extracts of black alkali soils is due primarily to the hydrolysis of sodium zeolite. In the presence of soil moisture the sodium aluminosilicates hydrolyze, and a certain amount of sodium hydroxide is formed in the soil solution. If a soil that contains no calcium carbonate is leached, the sodium hydroxide may be leached out as such, and the soil will gradually become acid, due to the replacement of the sodium in the zeolite by hydrogen. If, however, the soil is calcareous, the sodium zeolite will hydrolyze slightly, and sodium in the zeolite will be replaced by calcium from the calcium carbonate, and a little sodium carbonate will be formed. This, in turn, will hydrolyze and form sodium hydroxide, and unless the products of the reaction are removed the presence of this alkali will put an end to the hydrolysis of the sodium zeolite.

A tenth-normal solution of sodium carbonate will hydrolyze 85 to 90 percent. At concentrations usually found in soil solutions, the sodium carbonate will almost completely hydrolyze and ionize, so the hydroxyl ions will appear on both sides of the equation, which will make the reaction very limited. It is only in soils where there is an excess of sodium combined with hydroxyl ions, over that required to combine with silica and aluminum to form a zeolite, that much sodium carbonate can exist, under field conditions.

When calcareous, black alkali soils are leached with water, or when they are digested with a high ratio of water to soil, 20 to 1, for example, the extracts usually show varying amounts of hydroxyl ions, as well as carbonates and bicarbonates. The carbonates exist in the untreated dry soil largely as calcium carbonate, and not as sodium carbonate. The degree of hydrolysis of the sodium zeolite depends largely upon the volume of water that is used in the digestion. If sufficient water is used, practically all of the sodium zeolite will be hydrolyzed and the sodium replaced by calcium of the calcium carbonate.



This reaction will bring a small amount of sodium carbonate into solution, which will in turn hydrolyze, and ionize, and bring Na, OH, H, HCO₃, and CO₃ ions into solution. The carbonates noticed in alka-

line soil extracts are, therefore, derived almost entirely from the calcium carbonate in the soil.

The fact that there can be only a small amount of sodium hydroxide in the soil solution at one time, explains why, in saturated soils in the field or in drainage waters, we seldom find but a small amount of "black alkali" in solution. Under field conditions there is always a limited amount of water in the soil, the water seldom rises above that required to saturate the soil. The sodium zeolites are in equilibrium with this water and the amount of the salt that is hydrolyzed will depend upon the volume of water. The drainage waters, therefore, seldom have more than a trace of black alkali.

If a sample of black alkali soil is leached repeatedly with distilled water, the leachings will be alkaline to phenolphthalein, and this alkalinity will continue, with repeated leachings, until all of the sodium zeolite has been hydrolyzed and the sodium hydroxide removed from the soil. A sample of 2,000 grams of University Farm soil, that contained about five percent of calcium carbonate, was shaken with 3,000 cc. of water, allowed to stand overnight, and 2,000 cc. of solution filtered off through a porous filter. The solutions were stoppered and set aside and 2,000 cc. more of water were added to the soil, shaken, allowed to stand, and filtered off as before. This was continued for 14 days and all of the extracts were then analyzed. The results are given in Table V.

TABLE V—ANALYSES OF LEACHINGS FROM A BLACK ALKALI SOIL
(RESULTS EXPRESSED IN PARTS PER MILLION OF SOLUTION)

No.	pH of solution	Total solids	Hydroxyl calculated to CO ₂	HCO ₂	Cl	SO ₄
		ppm	ppm.	ppm	ppm	ppm
1	8.67	2200	Trace	432	378	474
2	9.58	1148	72	216	175	254
3	9.48	1080	60	168	98	88
4	9.38	522	60	168	63	33
5	9.32	480	48	180	42	29
6	9.42	436	60	180	14	0
7	9.60	368	60	132	0	0
8	9.66	360	60	120	0	0
9	9.48	280	48	108	0	0
10	9.48	296	48	96	0	0
11	9.54	272	48	84	0	0
12	9.50	248	48	48	0	0
13	9.47	248	36	60	0	0
14	8.99	220	30	60	0	0

It will be noted that the hydroxyl ions continue to appear in the extracts after repeated leachings. The original soil contained .039%

percent replaceable calcium, representing calcium zeolite, and .1725 percent replaceable sodium, representing sodium zeolite. The sodium zeolite, therefore, predominated over the calcium zeolite. After the soil had been leached, the conditions were reversed, the calcium zeolite was greatly in excess of the sodium zeolite. The sodium zeolite had been largely hydrolyzed during the leaching process, and the sodium had been replaced by calcium from the calcium carbonate in the soil.

REACTION BETWEEN SODIUM ZEOLITE AND CALCIUM CARBONATE DURING THE RECLAMATION OF BLACK ALKALI SOILS

Six samples of 2 kg. each of a calcareous, black alkali soil from the University Farm, were treated as follows:

Soil sample	Treatment
1	Control, saturated with water and dried out.
2	Leached upon 3 successive days, 2,000 cc. water each day, 6,000 cc. total percolate.
3	Leached 6 days, 2,000 cc. each day, 12,000 cc. total percolate.
4	Leached 9 days, 18,000 cc. total percolate.
5	Leached 12 days, 24,000 cc. total percolate.
6	Leached 15 days, 30,000 cc total percolate.

After the soils had been leached, they were dried, and the replaceable calcium determined by percolating a sub-sample of each soil with a tenth-normal solution of barium chloride. The replaceable sodium was also determined by percolating another sub-sample with a tenth-normal solution of calcium chloride.*

The percentages of replaceable calcium, replaceable sodium, and the pH of the different soils are shown in Table VI.

It will be noted that there was a gradual decrease in the replaceable sodium and an increase in the replaceable calcium as the leaching proceeded. The sodium zeolite hydrolyzed gradually, and to that extent, the sodium was replaced by the calcium of the calcium carbonate. This brought sodium carbonate into the solution, which in turn hydrolyzed and ionized and brought OH, CO₃, and HCO₃ ions into the solution. The presence of HCO₃ and to a slight degree, OH, in the percolate, as shown in Table IV, was due to the reaction above cited. The gain in replaceable calcium during the leaching process amounted to .0720 percent, while the loss in replaceable sodium amounted to .1173 percent.

*For method, see Technical Bulletin No. 9, Ariz Agr Exp. Sta. 1926.

TABLE VI—EFFECT OF LEACHING UPON THE REPLACEABLE BASES OF A BLACK ALKALI SOIL.

Soil	Total percolated	pH soil 5 water— 1 soil	Replaceable	Replaceable	Total
			calcium	sodium	replaceable bases as sodium
	cc		Percent	Percent	Percent
1	0	9.95	0.390	1.725	2.173
2	4,000	10.08	0.645	.1325	2.067
3	12,000	10.00	0.705	1.165	1.976
4	18,000	9.90	.0915	0.878	.1930
5	24,000	9.73	0.945	0.811	.1898
6	30,000	9.63	.1110	0.552	.1828

The loss in sodium was, therefore, not fully balanced by the gain in calcium.

In figure 10 is shown the replaceable sodium plotted against the replaceable calcium; and the regularity of the reaction between sodium zeolite and calcium carbonate is indicated by a straight line.

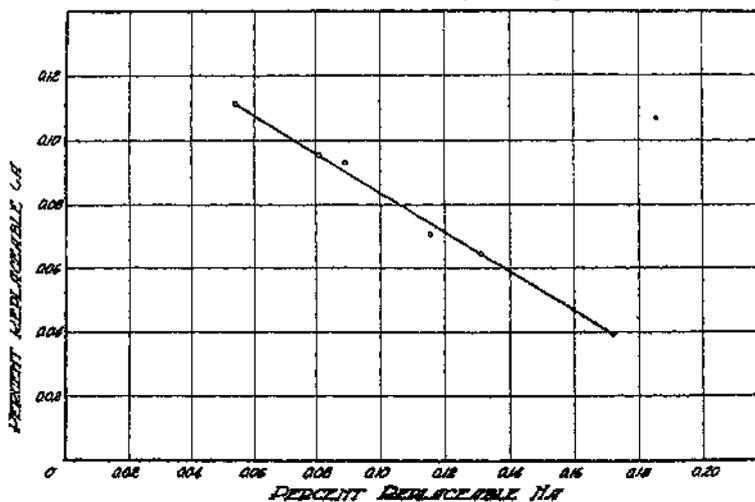


Fig. 10—Graph illustrating the gradual replacement of sodium by calcium during the leaching of black alkali soils.

The gradual change of sodium zeolite into calcium zeolite during leaching or reclamation is shown more clearly in figure 11.

In the last column of Table VI is shown the total base replacement in terms of sodium. To obtain these figures the calcium was calculated to its equivalent of sodium, and this was added to the replaceable sodium. It will be noted that there was a gradual decrease in the percentage of

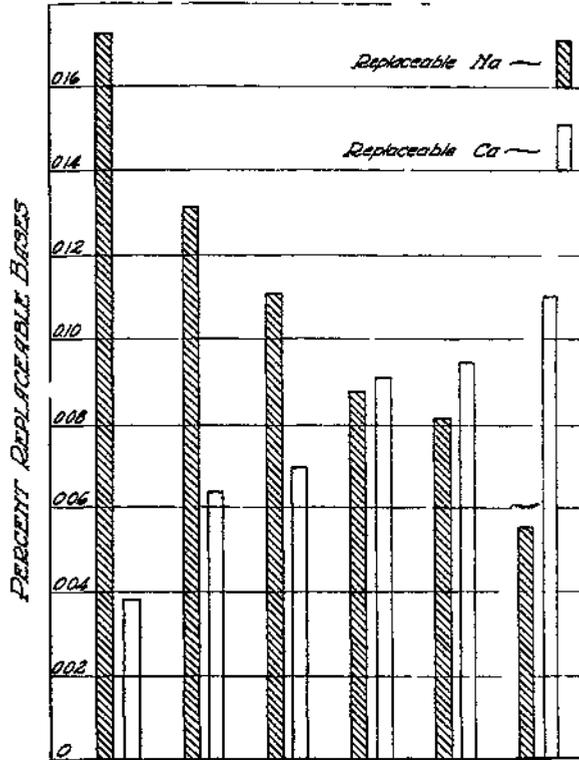


Fig 11—Graph illustrating the change in the ratio of replaceable sodium to replaceable calcium during the leaching of black alkali soils

total replaceable bases as the leaching proceeded. This is explained by the fact that during the leaching process, a part of the sodium zeolite was hydrolyzed and the sodium was replaced by calcium. At the same time another fraction of the sodium zeolite molecules was broken down, and soluble aluminum and soluble silica appeared in the solution. These two components were then leached out, and to that extent the total base replacement of the soil was reduced. The percentage loss in base replacement in the soil during the leaching, is accounted for by the soluble aluminum and soluble silica in the percolate.

Neither the original soil nor the leached samples contained any sodium carbonate. The alkalinity of the soil solution and of the percolate was due to the presence of sodium hydroxide.

EFFECT OF SODIUM CHLORIDE AND SODIUM SULPHATE UPON THE HYDROLYSIS OF SODIUM ZEOLITE

It will be noted also that the pH in Extract No. 1, or that obtained from the untreated soil in Table V was 8.67, and that this was raised

to 9.58 by one leaching. The pH continued to stand at about 9.50 for successive leachings. At the same time that the pH was raised from 8.67 to 9.58, it will be noticed that much of the sodium chloride and sodium sulphate was removed from the soil.

The same phenomenon was shown in Table VI when the pH of the soil itself, in a 5 to 1 extract, was measured. The untreated soil gave a pH of 9.95, which was raised to 10.08 by leaching. It will be noticed also that hydroxyl ions did not appear in the solutions in appreciable amounts, until after the soils had been partly leached.

It is well known that if a salt of a strong base and a weak acid, is hydrolyzed and ionized in solution, the introduction of a common ion into the solution will force back the ionization of the dissociated salt. This phenomenon is very pronounced in the case of sodium zeolite, and it is illustrated in both of the experiments just described.

Practically all black alkali soils contain varying amounts of either sodium chloride or sodium sulphate, or both of these salts, and in the analysis of an alkaline soil by the usual method of extraction, the percentage of these two salts has an important effect upon the hydrolysis of the sodium zeolite. If they are present in sufficient concentrations, they may force all of the sodium zeolite back into the undissociated state, or even into a solid phase, and in such a case, an alkaline soil that would otherwise show a large amount of hydroxyl ions in solution, may, upon analysis, show none whatever. The effect of sodium chloride in forcing back the ionization of the sodium zeolite is shown in the experiments which follow.

As it is almost impossible to obtain a sample of black alkali soil that contains no sodium chloride or sodium sulphate, a sample was taken from the University Farm that contained .141 percent sodium chloride and .098 percent sodium sulphate, in addition to black alkali. This amount of soluble salts would, of course, bring some error into the experiment, but this percentage was evidently not great enough to force back the ionization of all of the sodium zeolite, for the soil, when digested with 20 parts of water to 1 of soil, gave hydroxyl ions equivalent to about .25 percent of sodium carbonate.

Samples of soil were digested with water and with 5-percent solutions of sodium chloride in the ratios that are shown in Table VII. The results of the analyses of the extracts for hydroxyl and bicarbonate ions are given in the table.

These results show that, even in a digestion of 20 parts of solvent to 1 of soil, a greater part of the hydroxyl ion, that is usually titrated and reported as a carbonate, disappears from solution upon the addition of 5 percent sodium chloride. In the lower ratios, the hydroxyl ion

disappears completely from solution. The bicarbonates, however, were but slightly affected by the presence of the sodium chloride.

TABLE VII.—SOLUBILITY OF BLACK ALKALI IN WATER AND IN A FIVE-PERCENT SOLUTION OF SODIUM CHLORIDE. (RESULTS IN PERCENTAGE OF DRY SOIL.)

No.	Ratio water to soil	Soil digested with:			
		Water	5% NaCl	Water	5% NaCl
		OH calculated to CO ₂	OH calculated to CO ₂	HCO ₃	HCO ₃
		Percent	Percent	Percent	Percent
1	20.0:1	.072	.024	.168	.168
2	10.0:1	.072	.012	.108	.108
3	6.0:1	.061	.007	.079	.086
4	5.0:1	.045	.006	.072	.078
5	4.0:1	.043	.007	.062	.067
6	3.0:1	.039	.004	.056	.061
7	2.0:1	.024	Tr.	.055	.055
8	1.0:1	.012	.0	.053	.044
9	0.5:1	.008	.0	.053	.032

This same phenomenon is true when instead of sodium chloride, a 5-percent solution of potassium chloride is used, as is shown in Table VIII.

TABLE VIII.—SOLUBILITY OF BLACK ALKALI IN WATER AND IN A FIVE-PERCENT SOLUTION OF POTASSIUM CHLORIDE. (RESULTS IN PERCENTAGE OF DRY SOIL.)

No.	Ratio water to soil	Soil digested with:			
		Water	5% KCl	Water	5% KCl
		OH calculated to CO ₂	OH calculated to CO ₂	HCO ₃	HCO ₃
		Percent	Percent	Percent	Percent
1	20.0:1	.072	.048	.168	.192
2	10.0:1	.048	.030	.160	.168
3	6.0:1	.037	.018	.151	.154
4	5.0:1	.034	.006	.138	.144
5	4.0:1	.030	Tr.	.134	.132
6	3.0:1	.025	Tr.	.124	.133
7	2.0:1	.019	Tr.	.120	.120
8	1.0:1	.011	.0	.098	.096
9	0.5:1	.007	.0	.049	.049

Upon first thought it might seem that the introduction of potassium chloride into the solution would not force back the ionization of the

sodium zeolite, as no common ion is involved. This would be the case if base replacement did not enter into consideration. When potassium chloride is added to a soil that contains sodium zeolite, the sodium is, in part, replaced by potassium, and sodium chloride appears in solution. If an exact percentage of potassium chloride is added, there may be a 50-percent replacement, then potassium zeolite and sodium zeolite will appear in the soil in equal amounts, while potassium chloride and sodium chloride will appear in the solution. The potassium chloride in solution will then force back the ionization of the potassium zeolite, while the sodium chloride will have the same influence upon the sodium zeolite, so that no hydroxyl ions will be left in solution.

THE PRESENCE OF HYDROXYL OR CARBONATE IONS AS AFFECTED BY THE SALINE CONCENTRATION OF THE SOIL SOLUTION

In obtaining data on this phase of the problem two soils were made up to different moisture contents, soil solutions obtained from these by displacement, and these soil solutions tested for phenolphthalein alkalinity. In the first soil, pH 10.2 as determined electrometrically in a 1 to 5 water suspension, sufficient water was added to bring the moisture to 5, 8, and 12 percent, respectively. The soils were then packed in percolators and allowed to stand overnight before displacement. The soil solutions were analyzed with the following results, expressed in parts per million of soil solution.

Molsture content of soil	5 percent	8 percent	12 percent
Phenolphthalein alkalinity	None	None	Trace
	p.p.m.	p.p.m.	p.p.m.
Bicarbonate (HCO ₃) (methyl orange)	1110	1380	1500
Total solids	61960	42500	26200
Reaction pH	8.2	8.4	8.5

These results show that at a concentration of 26,200 parts per million in the soil solution there is sufficient hydrolysis of the sodium zeolite to give phenolphthalein alkalinity. The amount was, however, only a trace and not sufficient for a quantitative determination. Therefore, at the saline concentration of 26,000 parts per million or at a moisture content slightly above optimum this black alkali soil will show phenolphthalein alkalinity.

A similar experiment was carried out with the soil containing 89,672 parts per million solids in the soil solution. This soil was made to moisture contents of 8, 10, 11, 12, and 14 percent, respectively, and the soil solution obtained by displacement with alcohol. The saline

concentration of the soil solutions is shown as follows expressed in parts per million of the soil solution.

Moisture content	8	10	11	12	14
	Percent	Percent	Percent	Percent	Percent
Total solids.....	91,920	73,440	74,290	64,250	55,300
Bicarbonate HCO ₃	2,562	2,318	2,318	2,196	2,013
Phenolphthalein alk.....	None	None	None	None	None

It was impossible to bring this soil to a moisture content above 14 percent without making it too wet to pack in the percolators. In view of this, the moisture content of phenolphthalein alkalinity was determined in a different manner. Fifty grams of soil were placed in each of a series of 200 cc. test tubes and water added as follows: 30, 25, 20, 15 and 10 cc. They were well mixed and after standing overnight tested with phenolphthalein. Ten cc. or 20 percent of water showed no color while 15 cc. or 30 percent gave a faint pink color. These data show that this soil will show no phenolphthalein alkalinity below approximately 25 percent moisture or a saline concentration in the soil solution of 25,000 parts per million.

THE EFFECT OF A COMMON ION IN THE APPLICATION OF GYPSUM AS A CORRECTIVE, TO BLACK ALKALI SOILS

The effect of a common ion, as shown in the experiments just described, is exceedingly important in agricultural practice. It has been observed many times that an application of gypsum is not always effective in flocculating soils, and in neutralizing black alkali, and the reasons for certain failures have not been explained. Often it is found necessary to apply two or three times as much gypsum as is actually required to neutralize the known amount of black alkali in the soil, before the desired results are obtained. In practice it has been found necessary, also, to leach the soil thoroughly after an application of gypsum. This is thought to be advisable, in order to remove the sodium sulphate that is formed in the reaction between gypsum and sodium carbonate. Many such phenomena connected with the use of gypsum have been observed but not explained. In the light of the experiments just described, however, the explanations are evident.

Nearly all black alkali soils contain sodium chloride and sodium sulphate in varying amounts, in addition to sodium zeolite. The beneficial effects of gypsum rest in its power to react with sodium zeolite. It is a well-known law, that no chemical reaction is possible between salts

in solution, unless there is a certain amount of ionization of the salt involved. Therefore, if either sodium chloride or sodium sulphate exists in a black alkali soil, they will furnish a common ion, Na, to the soil solution, which will tend to force back the ionization of the sodium zeolite. If the concentration of soluble sodium salt is high enough, all of the sodium zeolite may be forced back into the undissociated state or even into the solid phase. This phenomenon is shown in the following experiment.

Samples of 100 grams each of a black alkali soil from the University Farm, were placed in tubes, percolated with 210 cc. of the solutions described in Table IX, and the amount of calcium that was removed from the solutions, by the soils, determined by analyzing the solutions before and after the percolations. The amount of calcium that was fixed by the soil represents the extent of the reaction between gypsum and the sodium zeolite. These results are shown in Table IX and figure 12.

TABLE IX.—EFFECT OF SODIUM CHLORIDE UPON THE REACTION BETWEEN CALCIUM SULPHATE AND SODIUM ZEOLITE.

Soil	Percolating solutions	Grams Ca removed from solution by soil
1	Distilled water plus .1259 grams Ca as CaSO ₄1259
2	.5% solution NaCl plus .1259 gms. Ca.....	.1055
3	1.0% solution NaCl plus .1259 gms. Ca.....	.0805
4	2.0% solution NaCl plus .1259 gms. Ca.....	.0536
5	4.0% solution NaCl plus .1259 gms. Ca.....	.0189
6	8.0% solution NaCl plus .1259 gms. Ca.....	.0063
7	12.0% solution NaCl plus .1259 gms. Ca.....	.0

This experiment was repeated, using calcium chloride instead of calcium sulphate in the percolating solution, and the same results were obtained. The presence of even a small amount of sodium chloride reduced the reaction, while the higher concentrations of sodium chloride prevented all reaction between gypsum and sodium zeolite. When much sodium chloride is present, no ionization of the sodium zeolite takes place, and no reaction is possible, so the calcium sulphate passes through the soil, and leaves it in much the same condition, with respect to its permeability and zeolitic content, that it was in originally.

After the soils had been leached with the solutions described in Table IX they were leached with distilled water. The soil column that had received calcium sulphate only, No. 1, was thoroughly flocculated and freely permeable to water, while the columns that had received the salt

solutions in addition to the calcium sulphate, after the salt had been washed out, gradually became impermeable, and the tubes that had received higher concentrations of salt, finally became almost impermeable.

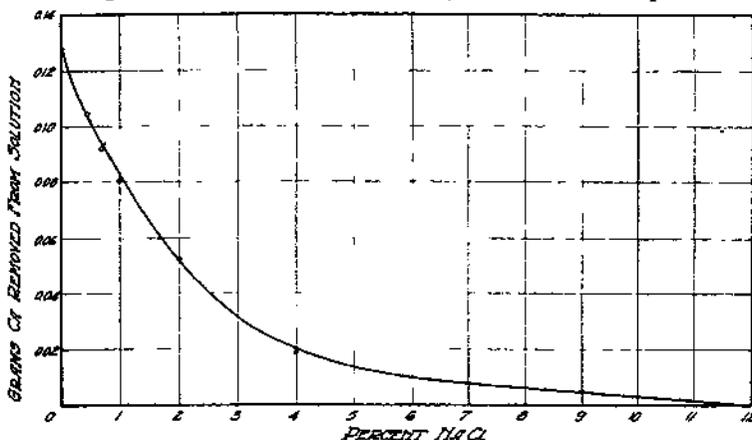


Fig. 12.—Graph illustrating effect of sodium chloride in preventing the reaction between gypsum and sodium zeolite

This experiment has a practical application in the treatment of soils in the field. If gypsum is applied to a black alkali soil that contains very much sodium chloride or sodium sulphate, the gypsum will be partially or wholly leached out of the soil with the sodium salts, and will be lost in the drainage. The amount of gypsum that will be lost in this way will depend upon the percentage of soluble sodium salts in the soil. The presence of gypsum in the soil solution may stimulate the percolation of water, although it may not have any power of replacement with the sodium zeolite. In certain cases, when gypsum is very cheap, it may be economical to use it for this purpose only. However, no difficulty is usually experienced in percolating the soil, as long as it contains an appreciable amount of soluble sodium salt. The final congealing, or "freezing up" of soils under reclamation, takes place after practically all the soluble sodium salts have been removed. In practical reclamation work, before applying gypsum, it seems advisable to leach first the soil with one or more heavy irrigations, in order to remove the excess soluble sodium salts. When the soil begins to show a tendency to become impermeable, the gypsum may be applied, and the soil leached again. It is fairly safe to assume that the "slick spots," or those spots in the fields that are impermeable to water, yet contain little soluble sodium salts, will respond to an application of gypsum more readily than will a field that has an alkali sodium crust, or one that contains very much soluble salt.

The effect of a common ion in solution has also an important bearing upon the quality of an irrigation water, but this phase of reclamation work will be discussed in a future paper.

A COMMON ERROR IN THE DETERMINATION OF SODIUM CARBONATE IN BLACK ALKALI SOILS

In the methods commonly used in determining sodium carbonate in soils, a certain weight of soil is digested with a large excess of water and the extract used for analysis. From the experiments just described it is evident that an error exists in such determinations, that is usually overlooked. If the soil contains sodium zeolite and no soluble salts, the hydrolyzation may be nearly complete, but in soils that contain very much sodium chloride or sodium sulphate these salts will introduce a common ion (Na) into the solution, which will force back the ionization of the sodium zeolite. If the concentration of the soluble sodium salts is high enough it may prevent all hydrolysis of the sodium zeolite. Therefore, if a black alkali soil that contains no soluble sodium salts is analyzed by the usual method, it may show a high percentage of hydroxyl ions, commonly calculated as sodium carbonate. If the same soil contains a sufficient amount of sodium chloride or sodium sulphate to prevent the ionization of the sodium zeolite, it will apparently contain no sodium carbonate.

A fairly accurate determination of the sodium carbonate that exists, as such, in a soil, may be made by digesting the soil in a 5-percent solution of sodium chloride instead of digesting it in water, and titrating the hydroxyl ion that comes into solution. The sodium chloride will force back the ionization of the sodium zeolite and keep the hydroxyl ions out of solution, while it will have little effect upon the ionization of the sodium carbonate. In this way a separation may be made between the hydroxyl ion that is derived from the sodium zeolite and the ion that comes from the sodium carbonate. It is true that sodium carbonate hydrolyzes and ionizes in the same way as does sodium zeolite, and that a common ion will also tend to force the salt back into an undissociated state. Sodium carbonate, however, in dilute solutions, is so completely ionized that the effect of a common ion in the solution does not introduce an appreciable error.

EXPERIMENTS WITH AN ALKALINE SPOT ON THE OLD UNIVERSITY FARM

As little or no sodium carbonate can exist in a black alkali soil, except when the Na ion occurs combined with the OH radical in amounts more than sufficient to combine as sodium zeolite, we should not expect

to find appreciable amounts of sodium carbonate in any soil except in low places, and in poorly drained spots in a field that contains black alkali. Such places occur upon the University Farm.

The upper half-inch of an alkaline spot, that was suspected of having some sodium carbonate as such, was collected from the University Farm, and extracts were made by digesting the soil in different ratios of water. The analyses are given in Table X.

TABLE X.—ANALYSES OF EXTRACTS FROM AN ALKALINE SPOT ON THE OLD UNIVERSITY FARM.
(RESULTS IN PERCENTAGE OF DRY SOIL.)

No.	Ratio water to soil	Total solids	Hydroxyl ions calculated to CO ₂	HCO ₃	Cl	SO ₄
		Percent	Percent	Percent	Percent	Percent
1	50.0:1	4.640	.420	.540	.665	1.555
2	25.0:1	4.250	.450	.450	.630	1.349
3	10.0:1	4.000	.455	.300	.630	1.263
4	5.0:1	3.980	.444	.306	.630	1.261
5	2.5:1	3.795	.420	.300	.612	1.188
6	1.0:1	3.695	.405	.339	.630	1.097
7	0.5:1	3.805	.381	.323	.616	1.225

It will be seen from the table that this alkaline crust ran very high in both sodium chloride and sodium sulphate, about 1.1 percent of the former and 2.3 percent of the latter. It will also be noted that the hydroxyl ions showed little tendency to disappear from solution as the ratio of water to soil was decreased. Evidently the salines were forcing back the ionization of the sodium zeolite and no sodium hydroxide was obtained from this source. The titrations for the hydroxyl radical, which were fairly constant in all ratios, therefore, indicated the presence of sodium carbonate as such in the alkaline salts.

The above-mentioned alkaline top soil was diluted by mixing it with a relatively good soil from the same field, in the ratio of 20 percent of the crust to 80 percent of the good soil. Extracts were then made of this soil mixture and analyzed as before.

It will be seen from the following table that, when the alkaline top soil was diluted with good soil until the sodium chloride and sodium sulphate amounted to only about one-half percent in the aggregate, the tendency was shown again for the hydroxyl ions to disappear from solution as the ratio of soil to water was decreased. The percentage of sodium chloride and sodium sulphate in the mixture, while checking hydrolysis, was not high enough to prevent completely the partial hydrolysis of the soil zeolite.

TABLE XI.—ANALYSES OF EXTRACTS OF DILUTED ALKALINE SOIL FROM THE OLD UNIVERSITY FARM.
(RESULTS IN PERCENTAGE OF DRY SOIL.)

No.	Ratio water to soil	Total solids	Hydroxyl ions calculated to CO ₂	HCO ₃	Cl	SO ₄
		Percent	Percent	Percent	Percent	Percent
1	50 0 1	1.12	1500	2400	.140	.245
2	25.0 1	1.12	1500	1500	.140	.232
3	10 0 1	0.99	1200	0840	140	.256
4	5 0 1	0.94	0840	1020	133	.257
5	2.5 1	0.87	0660	0930	122	.257
6	1 0 1	0.82	0396	1128	126	.271
7	0.5 1	0.77	.0246	0996	.133	.266

SODIUM BICARBONATE IN BLACK ALKALI SOILS

It may be stated, also, that sodium bicarbonate cannot exist in the true soil solution of a black alkali soil in large amounts, except when there are sufficient soluble sodium salts present to prevent the sodium zeolite from ionizing. The hydrolysis of sodium zeolite is slight, and it is checked by the sodium hydroxide that is formed in the reaction. No great amount of sodium hydroxide can be present in a soil at one time, therefore, if sodium bicarbonate is added to a black alkali soil, this salt immediately gives up a part of its carbon dioxide to the sodium hydroxide, and both become the normal carbonate. The sodium zeolite then further ionizes, more sodium hydroxide is formed, and this in turn reacts with the sodium bicarbonate. Unless interfered with, and if the products of the reaction are removed, the reaction will continue until practically all of the sodium zeolite is decomposed.

EFFECT OF CARBON DIOXIDE IN THE SOIL SOLUTION

It has been shown in a previous bulletin* that free carbon dioxide cannot exist in a soil that contains any sodium hydroxide, sodium carbonate, or hydroxyl ions. It has been shown repeatedly in this laboratory, that distilled water saturated with carbon dioxide, will flocculate a dispersed, calcareous soil quite as readily as will a solution of gypsum. This is accounted for, in part, by the fact that carbon dioxide converts the sodium hydroxide into sodium carbonate, and then into sodium bicarbonate, and thus removes the hydroxyl from solution, and allows the sodium zeolite to hydrolyze completely. Under eastern conditions, when carbon dioxide, but no calcium carbonate, is present, the sodium zeolite will hydrolyze, the sodium hydroxide will be converted into

*Technical Bulletin No. 6, Ariz. Agri. Exp. Sta. 1926.

sodium bicarbonate and be leached from the soil, and the sodium in the zeolite will be replaced by hydrogen. In the course of time this reaction will produce an acid soil.

In a calcareous soil under the same conditions, carbon dioxide, if present, will unite with calcium carbonate and form calcium bicarbonate, and the sodium in the zeolite will be replaced by the calcium of the calcium bicarbonate as fast as the sodium zeolite ionizes. This reaction will take place to a limited extent only, unless the soluble product of the reaction, sodium bicarbonate, is removed by leaching. If this is done the reaction will run to an end. As a matter of course, under western conditions, where an excess of calcium carbonate is nearly always present in the soil, the reaction will proceed only to where nearly all of the sodium in the zeolite is replaced by the calcium. It is probable that the reactions involved in the replacement of sodium by calcium, or of calcium by sodium in the zeolites do not run to an end. In leaching a black alkali soil with gypsum, it is difficult to replace the sodium completely, there may be some sodium zeolite left in the soil, even after repeated leachings.

EFFECT OF CARBON DIOXIDE UPON UNIVERSITY FARM SOIL

Two samples of black alkali soil that contained about 5 percent of calcium carbonate were weighed out, placed in jars, and 2,000 cc. of water added to each jar. Carbon dioxide gas was passed through each solution for about five minutes, then solution No. 1 was placed in the open air and all of the water was allowed to evaporate. Solution No. 2 was filtered from the soil, the solution discarded, and the soil washed twice with 2,000 cc. of water for each washing. Both samples of soil were dried, and the amounts of the replaceable sodium and replaceable calcium determined. These results are shown in the following table.

TABLE XII.—EFFECT OF CARBON DIOXIDE UPON REPLACEABLE BASES IN A BLACK ALKALI SOIL.

No.		Replaceable Ca	Replaceable Na
		Percent	Percent
1	Soil saturated with CO ₂ dried in the open air.....	.055	.183
2	Soil saturated with CO ₂ extract filtered off.....	.135	.043

Immediately following the addition of the carbon dioxide, both of these soils were in the same condition. No water was removed from

No. 1 except by evaporation. The carbon dioxide which was added, and which produced base replacement in the soil, was driven off during evaporation of the water, and the soil reverted to its original chemical condition. The solution from No. 2, however, was filtered off, and the soluble products of the reaction partly removed, and the effect of the carbon dioxide upon the zeolites is shown. The percentage of replaceable calcium, which represents the calcium zeolite, was increased, while the percentage of replaceable sodium, or sodium zeolite was decreased. If the experiment had been carried further, if carbon dioxide and water had been added again to the soil, the sodium would have been almost entirely replaced by calcium.

This experiment is cited to show how impossible it is for carbon dioxide, calcium carbonate, and hydroxyl ions from sodium zeolite, to exist in a soil at the same time. Calcium carbonate and sodium zeolite exist together in practically all black alkali soils, but carbon dioxide cannot enter into the system unless the moisture content of the soil is low enough to prevent the ionization of the sodium zeolite, or unless the salt content is high enough to accomplish the same purpose.

CONCLUSIONS

1. In making up extracts of black alkali soils for analyses, it is necessary to use at least 20 parts of water to 1 of soil, in order to extract practically all of the sodium salts.
2. If the results of analyses of soil extracts are expressed in terms of dry soil, there is an apparent decrease in the hydroxyl and bicarbonate ions as the ratio of water to soil is decreased.
3. The true soil solution, or the static water, in most black alkali soils, contains few or no hydroxyl ions, no sodium carbonate, and usually very little sodium bicarbonate in solution.
4. It is possible, by titrating the soil solution electrometrically or colorimetrically, to identify the nature of the components that produce the alkaline reaction of black alkali soils.
5. The alkalinity of sodium hydroxide that is produced by the hydrolysis of sodium zeolite is usually mistaken for sodium carbonate and is reported as such.
6. In the reclamation of black alkali soils by leaching, there is a gradual reaction between the sodium zeolite and calcium carbonate as reclamation proceeds, with the formation of calcium zeolite and sodium carbonate.
7. A common ion in solution, sodium as sodium chloride, for example,

will force back the ionization of sodium zeolite, and prevent any hydroxyl ions from appearing in solution.

8. If a black alkali soil contains soluble sodium salts in excessive amounts, little or no effect from an application of gypsum is possible, until the sodium salts are removed by leaching.

9. Free carbon dioxide does not exist in a black alkali soil, either in the soil solution or in the soil atmosphere.

