



University of Arizona
College of Agriculture
Agricultural Experiment Station

THE REACTION BETWEEN
CALCIUM SULPHATE AND
SODIUM CARBONATE, AND ITS
RELATION TO THE
RECLAMATION OF BLACK ALKALI
LANDS

By J. F. BREAZEALF AND P. S. BURGESS

PUBLISHED BY
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TUCSON, ARIZONA

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FOREWORD

This technical bulletin is the first of a series that will appear from the Agricultural Chemistry Section dealing with problems relating to alkali soils, and to plant growth under irrigation.

In the arid Southwest, practically all agricultural lands must first be reclaimed from the desert, and the reclamation of desert lands is by no means an easy problem. Even if successfully reclaimed and brought under cultivation, the natural tendency of all our arid lands is to revert to their natural desert condition, and nothing but the most intelligent efforts of man can prevent this.

In the history of mankind this fight against the slow forces of nature in arid countries has been a losing one, and, except in the Valley of the Nile, where irrigation has been carried on under peculiar conditions, we have yet to find a single example of a permanent irrigation agriculture.

Foremost among these destructive agencies that bring about this reversion is alkali, and it is believed that the problems relating to alkali are the most important problems now facing the irrigation farmers of Arizona.

In handling problems that are as complex as are those of reclamation, a knowledge of the fundamental factors involved is most essential. We must have a thorough understanding of many phases of soil alkali and methods of controlling it if we can hope to maintain a permanent agriculture.

The present paper deals with one of the most important chemical reactions that take place in the reclamation of alkali lands—that involved when gypsum is added to black alkali soil. A study of this reaction has brought about some new conceptions of several conditions that are associated with black alkali, for example, it explains why it is impossible to neutralize completely black alkali or sodium carbonate by the addition of gypsum or calcium sulphate, it explains why the addition of organic matter with an application of gypsum is so essential, and why carbon dioxide cannot be present in a black-alkali soil.

J. J. THORNBURGH,
Director

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THE REACTION BETWEEN CALCIUM SULPHATE AND SODIUM CARBONATE, AND ITS RELATION TO THE RECLAMATION OF BLACK ALKALI LANDS

BY J. F. BREAZEALE AND P. S. BURGESS

INTRODUCTION

The application of gypsum to soils as a corrective for black alkali is a common practice. A great deal of field work has been done upon this subject during the last two decades, and a large amount of practical data is available concerning the injurious effects of black alkali upon crop plants, and concerning the benefits that are often derived from applications of gypsum. However, no data have been found that bear directly upon the mechanism of the reaction that takes place when a solution of calcium sulphate or gypsum is brought into contact with a solution of sodium carbonate or black alkali.

In the irrigated regions of the West, black alkali (sodium carbonate) is very prevalent, in fact it is much more so than is ordinarily supposed. To the ordinary observer, the presence of this alkali in soils is indicated in three ways—first, by the corrosive or toxic action upon the crop, second, by the dissolving of the organic matter in the soil with the formation of soluble black substances, and third, by the dispersing or flocculating effect upon the finer particles of the soil, which in turn makes the soil impermeable to water.

In probably a great majority of soils that are affected with black alkali, the alkali does not exist in amounts sufficient to be toxic to plants. Wheat plants, for example, will endure a concentration of about 800 parts per million of sodium carbonate in solution, which is a concentration much higher than is ordinarily found in solution in black-alkali soils. Soils that show relatively high amounts of black alkali when subjected to ordinary methods of analysis, that is, when they are digested with large amounts of water, really have much smaller percentages of that alkali actually in the soil solution under field conditions. This apparent error is caused by the gradual hydrolysis of the hydrated, sodium-aluminum silicates, or the so-called zeolites of the soil upon the addition of water. However, this phenomenon will not be discussed here. It is sufficient to say that, under field conditions, black-alkali soils, as a rule, contain relatively little sodium carbonate in solution.

Many soils contain enough black alkali to cause them to become dispersed, yet not enough to give the soil that characteristic black color

which often distinguishes this salt. An exceedingly small amount of black alkali will cause the clay fraction, that is, that finely divided colloidal part of a soil to disperse, so it is evident that the dispersed condition of a soil or subsoil is often the only, as well as the most accurate, indication of the presence of sodium carbonate.

One of the fundamental principles of irrigation agriculture is that soils must "take" water. Dispersed soils are hard and impermeable and will not take water readily. If enough black alkali is present, soils may be dispersed through their entire depth, or they may contain dispersed layers in the subsoil at any level. Sometimes these dispersed layers are only a few inches in thickness, but they tend to exclude the air from the lower levels of the root zones, and this in addition to the injury caused by the soil's inability to take water, prevents the aeration of soils and the action of the aerobic bacteria. Aerobic bacteria split off carbon dioxide during organic decomposition, and this of itself has an exceedingly important bearing upon crop production. This dispersing, or deflocculating effect of black alkali is responsible, directly or indirectly, for probably two-thirds of the injury that may be attributed to it. On the other hand, soils that originally contain an excess of gypsum are usually not dispersed, and will take water more or less readily, and ordinarily, an application of a sufficient amount of gypsum to black-alkali soil will greatly improve its permeability.

The effect of an application of gypsum to a black-alkali soil is often very pronounced. The soil that had previously been deflocculated or puddled, and impermeable to water, soon becomes granular and will take water readily. The barren or slick spots disappear from the field and crops grow normally where nothing grew before. However, an application of gypsum is occasionally disappointing, and the probable reasons will be shown later.

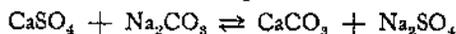
In alkali reclamation work, when soils containing large amounts of sodium chloride and sodium sulphate but no black alkali, are leached with comparatively fresh water, near the end of the leaching process a certain amount of black alkali is invariably formed in situ, due to silicate hydrolysis, and the soil that otherwise would be reclaimed, becomes puddled and impermeable, and is often less valuable for agricultural purposes than it was before the sodium salts were removed. An application of gypsum to a soil that has been thus leached is then necessary, in order to make the soil tillable.

No flocculating agent, that can be used extensively in place of gypsum, has yet been found. Many salts will flocculate soils as well, if not better, than gypsum, but the price of these materials is usually so great as to make their use impractical. Fortunately, gypsum occurs in

great abundance in the regions that are affected with black alkali, and deposits are often so convenient to the railroads that they may be handled with steam shovels. This lowers the cost of production, and under such conditions, makes the use of gypsum feasible even upon moderately priced land. In many cases of black alkali, the application of gypsum is the only practical remedy, so it will be seen how important is any information relative to the reaction involved between calcium sulphate and sodium carbonate when they are brought together in soil solutions.

EQUILIBRIUM BETWEEN CALCIUM SULPHATE AND SODIUM CARBONATE.

It is known that when a solution of calcium sulphate is added to a solution of sodium carbonate, a reaction takes place with the formation of calcium carbonate and sodium sulphate.



Calcium sulphate is soluble to the extent of about .210 percent, so, when this concentration is used, the reaction runs almost to completion from left to right, and the calcium is almost completely precipitated out of solution as calcium carbonate. While this is not the most accurate way of determining calcium, it is a method that may be used for quantitative determinations. It was a knowledge of the extent of this reaction that has caused many investigators, particularly Hilgard, to advocate early the use of gypsum upon black-alkali soils.

But, like most other reactions between two salt solutions, this reaction is reversible, that is, the precipitation of calcium as the carbonate is never quite complete, even from a saturated solution of calcium sulphate. The calcium carbonate that is formed in the reaction has a certain solubility, although small, and this tends to check the reaction and to keep a certain amount of sodium carbonate in solution. At equilibrium, when equivalent amounts of calcium sulphate and sodium carbonate are used, the amount of calcium carbonate that remains in solution will be exactly balanced by the sodium carbonate in solution and depends upon the solubility of the former. In other words, if calcium carbonate were absolutely insoluble there would be no sodium carbonate left in solution. The following experiments indicate that the amount of sodium carbonate that remains in solution in the reaction with calcium sulphate, depends upon several factors, but principally upon the concentrations of the solutions used.

Seven 50-cc. portions of a saturated solution of gypsum, each containing .0308 gram of calcium, were diluted to nearly a liter with carbon-dioxide-free water and sodium carbonate in solution was added to the gypsum solutions in increasing amounts as is shown in Table I. In

the first few cases it will be noticed that the sodium carbonate was not added in sufficient amounts to precipitate all of the calcium, while in the last few instances sodium carbonate was added in excess. The solutions were made up at once to 1,000 cc. volumes, stoppered, and shaken in a machine for 1 hour each day for 9 days. They were then allowed to settle for 1 day, and duplicate analyses were made to determine the amounts of calcium that were left in solution. The solutions were shaken and allowed to stand for another day, and another set of analyses was made. The two sets of analyses checked so well that the solutions were assumed to be at equilibrium.

TABLE No. I.—EQUILIBRIUM BETWEEN CALCIUM SULPHATE AND SODIUM CARBONATE IN DIFFERENT CONCENTRATIONS OF SODIUM CARBONATE. GRAMS PER LITER.

| No. | Ca as CaSO ₄ added | Na ₂ CO ₃ added | Ca left in solution | Theoretical precipitation of Ca as CaCO ₃ | Actual precipitation of Ca as CaCO ₃ | pH of solutions |
|-----|-------------------------------|---------------------------------------|---------------------|--|---|-----------------|
| 1. | .0308 | .0111 | .0308 | .0042 | 0 | 8.27 |
| 2. | .0308 | .0278 | .0308 | .0105 | 0 | 8.43 |
| 3. | .0308 | .0444 | .0240 | .0168 | .0068 | 8.57 |
| 4. | .0308 | .0612 | .0181 | .0231 | .0127 | 8.67 |
| 5. | .0308 | .0778 | .0120 | .0294 | .0188 | 8.78 |
| 6. | .0308 | .0945 | .0090 | .0308 | .0218 | 8.80 |
| 7. | .0308 | .1112 | .0053 | .0308 | .0255 | 8.97 |

The solubility of calcium carbonate in carbon-dioxide-free water was determined under these conditions, and was found to be .0030 gram calcium per liter. This experiment was repeated with practically the same results.

It will be seen from the fifth and sixth columns of the table, that the full effect of sodium carbonate in precipitating calcium as calcium carbonate, was not obtained in any of the concentrations used. In numbers 1 and 2, when there was a possible theoretical precipitation of .0042 and .0105 gram of calcium respectively, no precipitation was obtained. In other words, in No. 2, .0278 gram of sodium carbonate remained in each liter of the solution, together with .0308 gram of calcium or .1050 gram of calcium sulphate, without any visible precipitation. Expressed in parts per million, there were 27.8 parts per million of sodium carbonate or black alkali remaining in solution in No. 2, 26.5 parts, in No. 3, 27.6, in No. 4, 28.1, in No. 5, and 23.8 parts per million in No. 6. This amount of black alkali existed in

contact with calcium sulphate or gypsum without any apparent reaction. In solution No. 7, where there was a considerable excess of sodium carbonate, the reaction was carried further.

That all of the solutions contained free hydroxyl ions is shown by the pH measurements given in the last column of the table. As will be seen, the hydroxyl-ion concentrations increase regularly with the amounts of sodium carbonate added, although there were doubtless two factors involved, the direct hydrolysis of that part of the sodium carbonate that had not entered into combination with the calcium sulphate, and the solubility and ultimate hydrolysis of the slightly larger amounts of calcium carbonate brought into solution by the presence of the dissolved sodium sulphate. The hydroxyl-ion concentration of a 25-part-per-million solution of pure sodium carbonate in carbon-dioxide-free water is pH 8.45. An important fact thus shown by the pH determinations listed in Table I is that, in the presence of a saturated solution of gypsum, dissolved sodium carbonate is able to exist in such concentration as to furnish sufficient hydroxyl ions to give readings of the same degree of magnitude as a *pure* aqueous solution of sodium carbonate of 25 parts-per-million concentration. That the sodium carbonate in the former case is not removed completely from solution is due, of course, to the comparatively slight solubility of gypsum. Other experiments performed in this laboratory, using calcium chloride in concentrations of 1 percent and greater, completely precipitated soluble carbonates and reduced hydroxyl-ion concentrations practically to neutrality.

It must be remembered that, in the concentrations that occurred in these mixtures, the salts were largely ionized, and that the Na and CO₃ ions, for example, existed as separate charges and not as a combined salt. This chemical aspect is not being considered. From a practical standpoint we are interested only in the removal of all of the toxic sodium carbonate from solution, and this can be accomplished only by the precipitation of the carbonate as calcium carbonate. In the first five solutions we have appreciable amounts of black alkali, sodium carbonate, existing in the presence of an excess of gypsum.

The results that are given in Table I are in harmony with the experience of the writers. Often in analyzing irrigation or groundwaters and soils that contain a relatively high amount of calcium sulphate, we get a pink color when phenolphthalein is added to the aqueous solution. This pink color with phenolphthalein is ordinarily supposed to indicate the presence of a soluble carbonate, or black alkali, and the question has often been asked, "How can black alkali exist in the presence of an excess of gypsum?" In the experiment just described, under controlled

conditions, we have reproduced this phenomenon, and it is evident that sodium carbonate and calcium sulphate can exist together in the same solution, and that sodium carbonate can hydrolyze under such conditions and form enough hydroxyl ion to give a pink color with a phenolphthalein solution. The color itself indicates a pH above 8. From the standpoint of soil dispersion and water penetration these results are significant.

THE DISPERSION OF SOIL

In the field, soils are either flocculated or deflocculated, depending upon whether or not sodium hydroxide exists in the soil solution. This sodium hydroxide may be derived from the hydrolysis of sodium carbonate, from the hydrolysis of sodium silicates, or from hydrated sodium-aluminum silicates. The problems of the hydrolysis of sodium salts and the replacement of one base by another, are being extensively studied at the present time by many investigators, and it is not the purpose of this paper to go into a discussion of these phenomena. It is sufficient to say that, under western conditions, the presence of sodium hydroxide or potassium hydroxide is necessary in order to bring about the deflocculation or dispersion of soils. Whether it is the cation or the anion that is responsible for soil dispersion has not been definitely proved. The writers are of the opinion that both the cation and anion are concerned in the dispersion, but that the cation, particularly sodium, is the more potent factor.

If water is added to a soil that contains black alkali in considerable amounts, the sodium carbonate will hydrolyze in part, to sodium hydroxide, and the sodium hydroxide will then ionize as Na and OH. If the alkali soil solution is further diluted with water, and this water removed from the soil by filtration or otherwise, a part of the alkali will be removed, but, contrary to what might be expected, as the amount of black alkali is thus decreased the soil usually becomes more dispersed and impermeable. If this dilution and filtration is continued, as by being thoroughly leached with pure water, the concentration of alkali in solution in the soil may become so low as to give only a slight color with phenolphthalein, indicating a concentration of only a few parts per million of hydroxyl ions in solution, yet the soil will become almost impermeable to water. As long as there are any free sodium or hydroxyl ions in solution, however small in amount, the soil usually remains dispersed. This shows that the absolute amount of sodium hydroxide in the soil solution is not an index to permeability, and that the small amounts of sodium carbonate that are found to persist in solution, as is shown in Table I, are sufficient to cause soil dispersion, provided that there are no other factors that counteract their influence.

If, instead of diluting the alkali in the soil and filtering off the solutions, gypsum is gradually added to the soil, a different condition is obtained. Calcium sulphate and sodium hydroxide do not react until a relatively high concentration of calcium sulphate is reached, so in the concentrations usually found in soils, there will probably be no action that involves a precipitation between these two compounds. But calcium sulphate does react with sodium carbonate, and in this way it may remove the source of the sodium hydroxide and thereby tend to reduce its concentration. If more and more gypsum is added to a soil, the concentration of sodium hydroxide may be reduced to a certain point, *but no further*. Whether this last trace of sodium hydroxide that cannot be removed from solution by gypsum, can cause soil dispersion, is an exceedingly important question.

In the experiment just described, Table I, the amount of gypsum and the volumes of the solutions were kept constant, while the sodium carbonate was added in increasing amounts. In the experiments to follow, the same amounts of gypsum and the same amounts of sodium carbonate were added to each solution, while the volumes of the solutions were varied. In no case was enough sodium carbonate added to precipitate completely the calcium sulphate.

TABLE No. II.—EQUILIBRIUM BETWEEN CALCIUM SULPHATE AND SODIUM CARBONATE IN DIFFERENT CONCENTRATIONS.

| No. | Ca as CaSO ₄ added | Na ₂ CO ₃ added | Volume of solution | Total Ca left in solution | Theoretical precipitation of Ca as CaCO ₃ | Actual precipitation of Ca | pH of solution |
|-----|-------------------------------|---------------------------------------|--------------------|---------------------------|--|----------------------------|----------------|
| 1. | .0308 | .0556 | 100 cc | .0103 | .0210 | .0205 | 7.88 |
| 2 | .0308 | .0556 | 200 cc | .0117 | .0210 | .0191 | 8.00 |
| 3 | .0308 | .0556 | 400 cc | .0138 | .0210 | .0170 | 8.11 |
| 4 | .0308 | .0556 | 600 cc | .0154 | .0210 | .0154 | 8.22 |
| 5. | .0308 | .0556 | 800 cc | .0178 | .0210 | .0130 | 8.33 |
| 6. | .0308 | .0556 | 1000 cc | .0208 | .0210 | .0100 | 8.50 |

Fifty cc. of a saturated solution of gypsum, containing .0308 gram of calcium were diluted with carbon-dioxide-free water to within about 10 cc. of the volumes shown in Table II, and 10 cc. of the solutions of sodium carbonate, containing .0556 gram, were added to each gypsum solution and the whole then made up to volume. This amount of sodium carbonate was sufficient to precipitate .0210 gram of calcium. The precipitations were thus made in gypsum solutions of varying dilutions.

These were stoppered and shaken 1 hour a day for 9 days in order to bring about equilibrium. They were allowed to settle for 1 day and then analyzed for the calcium that remained in solution. The averages of several duplicate experiments are shown in Table II.

In the next experiment the same procedure was followed except that the strong sodium carbonate solutions were added to the saturated solutions of gypsum. The solutions were allowed to precipitate and to stand 6 hours, then each solution was diluted to the volume shown in Table III. The solutions were shaken 1 hour a day for 8 days, allowed to settle, and then analyzed for the calcium that remained in solution. The results of these analyses are shown in Table III.

TABLE No. III—EQUILIBRIUM BETWEEN CALCIUM SULPHATE AND SODIUM CARBONATE IN DIFFERENT CONCENTRATIONS.

| No. | Ca as CaSO_4 added | Na_2CO_3 added | Volume of solution | Total Ca left in solution | Theoretical precipitation of Ca as CaCO_3 | Actual precipitation of Ca | pH of solution |
|-----|-----------------------------|--------------------------------|--------------------|---------------------------|--|----------------------------|----------------|
| 1. | .0308 | .0556 | 100 cc | .0108 | .0210 | .0200 | 7.79 |
| 2. | .0308 | .0556 | 200 cc | .0118 | .0210 | .0190 | 7.86 |
| 3. | .0308 | .0556 | 400 cc | .0128 | .0210 | .0180 | 8.16 |
| 4. | .0308 | .0556 | 600 cc | .0139 | .0210 | .0169 | 8.33 |
| 5. | .0308 | .0556 | 800 cc | .0174 | .0210 | .0134 | 8.38 |
| 6. | .0308 | .0556 | 1000 cc | .0184 | .0210 | .0124 | 8.78 |

The last two experiments varied from each other only to the extent that the original precipitations of the first were made in dilute solutions while those in the last were made in concentrated solutions, but, as might be expected, the final equilibrium was practically the same in both cases.

Both of these experiments indicate, that as the solution of calcium sulphate is diluted, less and less precipitation of calcium carbonate is obtained from a given addition of sodium carbonate. In Solution No. 6, Table II, 0.0110 gram of calcium failed to precipitate. The sodium carbonate equivalent of this amount of calcium is .0292 gram, so in this solution, 29.2 parts per million of sodium carbonate existed in the presence of gypsum. In both tables II and III it will be noted also that the pH measurements kept pace with the amounts of calcium precipitated out, that is, the greater the precipitation of calcium carbonate, the more of the sodium carbonate reacted, and the lower was the hydrogen-ion concentration.

GYPSUM NOT ALWAYS EFFECTIVE UPON BLACK-ALKALI SOILS

For a long time there has been a tendency to over-rate the reaction that takes place between calcium sulphate and sodium carbonate under field conditions, and to consider gypsum a panacea for all black-alkali trouble, but in so doing many mistakes have been made. The application of gypsum does not always accomplish what is expected of it, and this failure may be explained, in part at least, by the results of the experiments that have been given. Hilgard calls attention to the fact that the beneficial change that is brought about by the application of gypsum may go backward, if the land thus treated is allowed to become water-logged by irrigation water or otherwise. He also emphasizes the fact that good aeration and good cultivation of the soil are necessary in maintaining the effect of an application of gypsum. It has been known for a long time that it requires more gypsum to reclaim alkaline soils than is actually indicated by their sodium carbonate contents; that the beneficial effect may go backward after a time, and that the soils often slowly revert to an impermeable condition. There are apparently factors coming into play other than those directly concerned with the reaction between calcium sulphate and sodium carbonate.

A badly dispersed soil, that is, a soil that will not allow percolation of pure water to any appreciable extent, will percolate freely water that has been saturated with carbon dioxide. *Carbon dioxide is, therefore, one of the most important factors in the reclamation of black-alkali lands.* It is a fact that soils cannot contain black alkali, if water and free carbon dioxide are both present. The reverse is also true; in a soil containing an excess of black alkali, carbon dioxide cannot exist. We think ordinarily of the soil atmosphere as being high in carbon dioxide, but this is not always the case. Many soils contain no carbon dioxide. If they did contain carbon dioxide *they could not carry black alkali.* If carbon dioxide is brought into contact with sodium carbonate, this alkali will be converted into the much less harmful sodium bicarbonate. Sodium bicarbonate as such does not disperse soil because it does not hydrolyze and form sodium hydroxide to any great extent. When black alkali occurs in a soil or subsoil, we, therefore, may be safe in assuming that there is no free carbon dioxide present. Carbon dioxide in soil is formed largely by the action of bacteria upon organic matter, and in the dispersed soils of the West, especially in the soils that are inclined to be heavy, often there is very little organic matter for the bacteria to decompose. These soils are also tight, and when placed under irrigation are inclined to become water-logged, so that air does not readily enter them. Without a fair supply of both oxygen

and carbon (organic matter) it is impossible for bacteria to generate carbon dioxide. It is under such conditions as these that we usually find black alkali, dispersion, and impermeability. It is the opinion of the writers that a great many cases of citrus chlorosis may be traced to the above condition, that is, to dispersion in the subsoil, and to subsequent water-logging in the root zone. It has long been known that manure has a beneficial effect on black-alkali soils and that manure and gypsum when applied together are probably the best ameliorative treatments that can be given them. This beneficial effect of manure is explained by the fact that it furnishes organic material upon which the bacteria work, and from which they generate carbon dioxide.

As has been previously shown, after an application of gypsum to a soil containing black alkali, there is a small amount of sodium carbonate left in solution. In the surface layers of the soil which are exposed to the carbon dioxide of the air, and which often contain living roots and decomposing organic matter, we usually find an excess of carbon dioxide formed. Here the last traces of sodium carbonate will be removed from solution as the bicarbonate, and the soil will become flocculated and permeable, and if it contains appreciable amounts of alkali, this may then be removed by leaching. In the lower layers, however, where there is no carbon dioxide to complete the reduction, the traces of sodium carbonate will persist and the soil will remain dispersed. This shows how important is thorough manuring and aeration after an application of gypsum, as was advocated by Hilgard (3)* and also doubtless explains the presence of impervious layers often encountered in the lower strata of black-alkali soils.

REACTION BETWEEN GYPSUM AND BLACK ALKALI IN THE PRESENCE OF SODIUM SALTS

A few years ago one of the writers studied the reaction between calcium carbonate and sodium salts, from another point of view, namely, the formation of black alkali in calcareous soils (1). As these reactions apply to soil dispersion as well as to the formation of black alkali, more work has been done upon them, and additional data will be presented.

The application of gypsum as a corrective for black alkali is made to soils that almost invariably contain at least small amounts of either sodium chloride, sodium sulphate, or both, in addition to black alkali. Black-alkali soils are also nearly always calcareous, and the resulting reaction between gypsum and black alkali is necessarily affected by the presence of these other salts. The reactions between sodium sulphate and sodium chloride, and calcium carbonate were, therefore, studied separately.

*See Bibliography at end.

THE REACTION BETWEEN SODIUM SULPHATE AND
CALCIUM CARBONATE

Solutions of sodium sulphate in concentrations shown in Table IV, were prepared with carbon-dioxide-free water, placed in 200 cc. shaker bottles, and 0.5 gram of calcium carbonate was added to each bottle. The solutions were allowed to stand at room temperature, (about 25°C.) with occasional shakings for 8 days, when they were analyzed for soluble calcium and for the total carbonate that had gone into solution. The calcium was determined by titration against a standard soap solution, while the carbonates were titrated against 25th normal sulphuric acid with erythrosin as indicator. After subtracting errors due to slight impurities in the reagents, the results of these analyses are shown in Table IV.

TABLE No. IV.—FORMATION OF SODIUM CARBONATE IN THE REACTION BETWEEN SODIUM SULPHATE AND CALCIUM CARBONATE.

| No. | Percent Na ₂ SO ₄ added. | Grams CaCO ₃ added. | Parts per million calcium found in solution. | Parts per million carbonate as CO ₂ found in solution. |
|-----|--|--------------------------------|--|---|
| 1. | 0.00 | 0.5 | 6 | 10 |
| 2. | 0.50 | 0.5 | 15 | 26 |
| 3. | 1.00 | 0.5 | 19 | 28 |
| 4. | 3.00 | 0.5 | 21 | 42 |
| 5. | 5.00 | 0.5 | 26 | 54 |
| 6. | 10.00 | 0.5 | 44 | 70 |
| 7. | 15.00 | 0.5 | 55 | 85 |
| 8. | 20.00 | 0.5 | 60 | 91 |

It will be seen that the amount of calcium that had gone into solution increased from 6 parts per million in the control that contained only calcium carbonate and carbon-dioxide-free water, to 60 parts per million in the solution of 20 percent of sodium sulphate, and that the soluble carbonate (CO₂), under similar conditions, increased from 10 parts to 91 parts per million.

These determinations were carried on under carefully controlled conditions, but are not presented as absolutely accurate measurements, as it is almost impossible to eliminate completely carbon dioxide, which is the main disturbing factor in this reaction. The measurements show the nature of the reaction that takes place when sodium sulphate comes in contact with calcium carbonate in a soil that is practically free from

carbon dioxide. When a large amount of carbon dioxide is present, the reaction between the sodium sulphate and calcium carbonate will go much further, with the formation of a considerable amount of sodium bicarbonate. This reaction has been studied by Hilgard and others (2).

The reaction between sodium sulphate and calcium carbonate, Table IV, may be represented



The calcium carbonate is itself slightly soluble, but the increase in the calcium content of the solutions upon the addition of sodium sulphate is ascribed largely to the formation of the more soluble calcium sulphate. Consequently at equilibrium, as shown in the equation, sodium carbonate and calcium sulphate must exist in the same solution in molecularly equivalent quantities. It appears that a considerable amount of black alkali was thus formed,—91 parts per million of CO_3 , for example, is equivalent to 161 parts per million of sodium carbonate.

EFFECT OF CALCIUM SULPHATE UPON THE FORMATION OF SODIUM CARBONATE IN THE REACTION BETWEEN SODIUM SULPHATE AND CALCIUM CARBONATE

The reaction just cited, Table IV, is one that might be expected when sodium sulphate comes in contact with calcium carbonate in the soil. With the application of gypsum, however, the condition is changed, the presence of calcium sulphate in the solution tending to check the formation of sodium carbonate in the reaction. The nature of the reaction that involves the presence of calcium sulphate is shown in Table V.

Calcium carbonate was added in excess to shaker bottles that contained the solutions of sodium sulphate, and calcium sulphate was then added in the concentrations shown in the table. The solutions were allowed to stand with occasional shakings, for 9 days, and then analyzed for total soluble carbonate, by titrating against 25th normal sulphuric acid with erythrosin as indicator. The results of these analyses are shown in Table V.

It will be seen that, as the amount of calcium sulphate in the solution is increased, the amount of soluble carbonate formed gradually decreases, until a concentration of about 23 parts per million of CO_3 is reached, where the solution is saturated with gypsum. This concentration of soluble carbonate represents approximate equilibrium when a 20-percent solution of sodium sulphate comes in contact with gypsum and an excess of calcium carbonate in the soil that is practically free from carbon dioxide. By subtracting the amount of CO_3 that was con-

tained in the control, 9 parts per million, from that formed in the presence of a saturated solution of calcium sulphate, 23 parts per million, we have 14 parts per million of CO_2 that may safely be assumed to be associated with sodium as sodium carbonate, or we may have about 24 parts per million of black alkali formed under the conditions of this experiment. The amount of black alkali that was thus formed is practically the same as that formed in the other experiments that have been previously described. *All our work indicates that approximately 25 parts per million of black alkali will persist at ordinary temperature in the presence of a saturated solution of gypsum.*

TABLE No. V.—EFFECT OF VARYING AMOUNTS OF CALCIUM SULPHATE UPON THE FORMATION OF SODIUM CARBONATE IN THE REACTION BETWEEN SODIUM SULPHATE AND CALCIUM CARBONATE.

| No. | Percent Na_2SO_4 added. | Grams CaCO_3 to each bottle. | Parts per million calcium sulphate added. | Parts per million CO_2 found in solution. |
|---------|---|---------------------------------------|---|--|
| Control | 0.0 | 0.5 | 0 | 9.0 |
| 1. | 20.0 | 0.5 | 0 | 94.0 |
| 2. | 20.0 | 0.5 | 50 | 90.0 |
| 3. | 20.0 | 0.5 | 100 | 84.0 |
| 4. | 20.0 | 0.5 | 250 | 71.0 |
| 5. | 20.0 | 0.5 | 500 | 48.0 |
| 6. | 20.0 | 0.5 | 1000 | 31.0 |
| 7. | 20.0 | 0.5 | 2100* | 23.0 |

*Saturated solution.

THE REACTION BETWEEN SODIUM CHLORIDE AND CALCIUM CARBONATE

Solutions of sodium chloride were prepared from carbon-dioxide-free water in concentrations shown in Table VI, placed in shaker bottles of about 200 cc. capacity, 0.5 gram of calcium carbonate added to each bottle, and the solutions brought to equilibrium as was done in the case of sodium sulphate. These solutions were analyzed for soluble carbonate only, and the result of the analyses are shown in Table VI.

As the percentage of sodium chloride was increased, more and more sodium carbonate was brought into solution, however, in much smaller amounts than that brought into solution by similar concentrations of sodium sulphate.

TABLE No. VI.—FORMATION OF SODIUM CARBONATE IN THE REACTION BETWEEN SODIUM CHLORIDE AND CALCIUM CARBONATE.

| No. | Percent NaCl added. | Grams CaCO ₃ added. | Parts per million carbonate, (CO ₃) found in solution |
|-----|---------------------|--------------------------------|---|
| 1. | 0.00 | 0.5 | 9.6 |
| 2. | 0.25 | 0.5 | 14.4 |
| 3. | 0.50 | 0.5 | 20.4 |
| 4. | 1.00 | 0.5 | 22.8 |
| 5. | 5.00 | 0.5 | 31.2 |
| 6. | 10.00 | 0.5 | 36.0 |
| 7. | 15.00 | 0.5 | 33.6 |
| 8. | 20.00 | 0.5 | 33.1 |

THE EFFECT OF CALCIUM SULPHATE UPON THE FORMATION OF SODIUM CARBONATE IN THE REACTION BETWEEN SODIUM CHLORIDE AND CALCIUM CARBONATE

A series of shaker bottles was prepared containing 20-percent solutions of sodium chloride, an excess of calcium carbonate, and the amounts of calcium sulphate that are shown in Table VII. These were brought to equilibrium, analyzed for soluble carbonates, and the results are given in Table VII.

TABLE No. VII.—THE EFFECT OF CALCIUM SULPHATE UPON THE FORMATION OF SODIUM CARBONATE IN THE REACTION BETWEEN SODIUM CHLORIDE AND CALCIUM CARBONATE.

| No. | Percent NaCl added. | Grams CaCO ₃ to each bottle. | Parts per million calcium sulphate added. | Parts per million CO ₃ found in solution. |
|-----|---------------------|---|---|--|
| 1. | 0 | 0.5 | 0 | 9.6 |
| 2. | 20 | 0.5 | 0 | 31.0 |
| 3. | 20 | 0.5 | 50 | 26.0 |
| 4. | 20 | 0.5 | 100 | 19.2 |
| 5. | 20 | 0.5 | 250 | 13.2 |
| 6. | 20 | 0.5 | 500 | 9.6 |
| 7. | 20 | 0.5 | 1000 | 9.6 |
| 8. | 20 | 0.5 | Saturated solution | 9.6 |

As shown in Table VI, a 20-percent solution of sodium chloride, in the presence of an excess of calcium carbonate, will bring about 24 parts per million of CO_2 . If calcium sulphate, in increasing amounts, is then added to portions of such a solution, as shown in Table VII, the concentration of CO_2 will gradually decrease until the concentration of 500 parts per million of calcium sulphate is reached, when no more hydroxyl ions will appear in the solution.

In a mixture of these two salts, it seems to require a concentration of about 20 percent of sodium chloride and .05 percent (500 parts per million) of calcium sulphate to prevent the formation of sodium carbonate in the solution.

The inability of gypsum, when acting alone, to neutralize completely black alkali, is due to the relatively low solubility of calcium sulphate. Calcium chloride and calcium nitrate, being more soluble salts, if added in sufficient amounts to solutions of sodium carbonate, will carry the reaction to an end, and will force all of the hydroxyl ions out of solution.

CONCLUSIONS

1. Under western conditions, the presence of black alkali, (sodium carbonate) is usually indicated by the deflocculated condition of the soil or subsoil carrying it.

2. A very small amount of sodium carbonate or black alkali is sufficient to deflocculate a soil that contains appreciable amounts of colloidal material.

3. Sodium carbonate and calcium sulphate may exist together in the same soil solution up to approximately 25 parts per million of the former.

4. In applying gypsum as a corrective for black alkali to soils that contain no free carbon dioxide, the amount of black alkali may be reduced to about 25 parts per million in the soil solution, *but no lower*.

5. Soils that contain black alkali contain no free carbon dioxide.

6. After an application of gypsum as a corrective for black alkali, it is advisable to leach the soil in order to remove the soluble salts. It is also advisable to apply organic matter and to aerate the soil by good cultivation, so that aerobic soil bacteria may produce the carbon dioxide necessary to transform the small amounts of sodium carbonate remaining into the innocuous sodium bi-carbonate.

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