University of Arizona
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METHODS FOR DETERMINING THE RE-
PLACEABLE BASES OF SOILS, EITHER
IN THE PRESENCE OR ABSENCE
OF ALKALI SALTS

By P. S BURGESS and J F BREAZEALE

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METHODS FOR DETERMINING THE RE-PLACEABLE BASES OF SOILS, EITHER IN THE PRESENCE OR ABSENCE OF ALKALI SALTS

By P. S. BURGESS and J. F. BREAZEALE

INTRODUCTION

The subject of base replacement in soils has received extensive attention over a long period of years by some of the world's most distinguished agricultural chemists. Its importance in soil economy is unquestionably great, for by such replacements are the bases used by plants largely rendered available. By the same reactions, fertilizer salts are retained against wasteful leaching and loss, and Gedroiz and Kelley each has shown recently that the formation of black alkali in arid and semi-arid soils may also be accounted for, in part at least, by such base exchanges, with subsequent hydrolysis. Just as black alkali may be formed in soils by base exchanges (usually Na for Ca), so must it be reclaimed in similar manner, but by the reverse reaction (Ca for Na). The reclamation of alkali lands will ever be a most important factor in the agriculture of the Southwest, hence any information which may help—either in its understanding or practice—should receive careful consideration.

It has long been known that one base may replace another in the soil hydrated aluminum silicates or "zeolites." Calcium for example may replace sodium, and sodium in turn may replace calcium, depending upon the concentration of the ions in solution. If, therefore, a normal, arable soil that contains a considerable amount of replaceable calcium and no replaceable sodium, is percolated with a solution of sodium chloride of sufficient concentration, the sodium will replace the calcium and become "fixed" in the soil, while the calcium will go into solution and come through with the percolate as calcium chloride. Such replacements as the one just described will bring about a very decided physical change in soil texture. The normal soil doubtless was originally flocculated and permeable to water, while the same soil, after it has been leached with a sodium chloride solution, and subsequently with pure water until free from salt will be dispersed and impermeable. If the dispersed soil is now percolated with a solution of calcium chloride, the calcium will replace the absorbed sodium, and the soil will become again flocculated and freely permeable to water.

THE CALCIUM : SODIUM RATIO

Irrigation agriculture and the reclamation of alkali lands, depend to a great extent upon soil permeability, or the ability of a soil to "take water," and this is determined largely by its degree of dispersion. In a study of the replaceable bases of the soil, it has been the hope of many investigators to obtain a mathematical expression for permeability in terms of replaceable sodium or replaceable calcium, or in terms of a ratio between these two bases. The value of such an expression is evident. It would enable the farmer, from an analysis, to predict the approximate speed of water penetration and he could thus be governed in his irrigation practices. Efforts to obtain such mathematical expressions, however, thus far have been disappointing.

In working with dispersed, calcareous soils, such as occur in the vicinity of Tucson, it has been our experience that the ratio of replaceable sodium to replaceable calcium has little or no meaning when applied to permeability, that is, one cannot expect a soil that runs 10 replaceable sodium to 1 of replaceable calcium, to be more impermeable than a soil that runs 1 replaceable sodium to 10 replaceable calcium. In fact it seems that the lower the percentage of sodium, often the more highly dispersed the soil, regardless of the calcium content.

The ratio of replaceable sodium to replaceable calcium depends upon a variety of conditions, one of which is the moisture content of the soil. If a moist soil that contains sodium zeolite, calcium zeolite, and calcium carbonate, is dried out, as for example between irrigations, the percentage of replaceable sodium is gradually increased while that of replaceable calcium is proportionately decreased. A perfectly dry, calcareous soil is likely to be hard and highly dispersed. Upon the addition of water the replaceable sodium is gradually decreased and the replaceable calcium is proportionately increased. If the addition of water is carried on indefinitely, or if the soil is thoroughly leached, practically all of the sodium zeolite will be converted into calcium zeolite. In other words, upon dilution, the sodium zeolite is hydrolyzed and the sodium is replaced by the calcium that formerly was in combination as calcium carbonate. Calcium seems to possess the ability to change from the carbonate into the zeolite, and back again into the carbonate as moisture conditions change. It is thus a reversible reaction.

In practice, if a dispersed, calcareous soil is irrigated, and leached with fairly pure water, the sodium zeolite will gradually hydrolyze and be removed in the drainage. At the same time, although the calcium is gradually entering into combination with the zeolite, the soil becomes more and more impermeable to water. Finally, when but a trace of sodium

remains, the soil often becomes so dispersed that it is almost impossible to get water through it. This conditon has put an end to many attempts at reclamation.

Water penetration is absolutely essential in the reclamation of alkali land, and the final state of dispersion does not take place until nearly all of the alkali has been removed. The soil that is thus almost free from alkali would probably be good for agricultural purposes, if it were not so dispersed. The difficulty at this stage seems to be a purely mechanical one, and the application of gypsum, or other soluble calcium salt, will accomplish much good. Occasionally, however, the application of gypsum is not economical, so if a practical method of obviating the difficulty caused by this final state of dispersion could be found, it would solve an important problem of alkali reclamation.

In some sections of Arizona the farmers are successfully reclaiming dispersed or "slick" spots in their fields by raising borders around these spots, bringing the soil to a perfect level, and keeping a good head of water on the spots for a long period of time. The downward movement of the water may eventually become very slow. This takes place when the percentage of sodium zeolite in the soil is probably near the minimum. With a little perseverance, if the head of water is maintained, the soil often begins to improve slowly in permeability. The soil may thus be reclaimed without the addition of gypsum or other flocculating agents. We have demonstrated this to be a fact in the laboratory and in the field. The plan seems to work best when the plots are leached, then dried out, leached again, and so on.

It is a relatively easy matter, under laboratory conditions, to obviate this final dispersion of the soil which has just been described. One of the soil types on the University of Arizona Farm contains a little black alkali, is highly dispersed, and only slightly permeable to water. If a sample of this soil is placed in a percolating tube and distilled water added at the top of the column, the water will percolate slowly for probably twenty-four hours, then percolation will practically cease.

A 500-gram sample of this soil was placed in a jar and 2 liters of distilled water added to it. The mixture was shaken, allowed to stand overnight, and the solution decanted and filtered under pressure through a porous, porcelain filter. The filtrate was saved, while the soil that adhered to the filter candle was washed back into the jar with the rest of the soil, and 2 liters more of water added. This was shaken and filtered as before. This operation was continued until 11 large bottles, holding 2,500 c. c. each, had been progressively filled with the percolate. Five hundred grams of soil had, therefore, been leached with 27,500 c. c. of

water. The solutions were now analyzed and the analyses are given in Table I.

TABLE I.—GRAMS OF SOLUTES REMOVED BY PERCOLATE FROM EACH 100 GRAMS OF SOIL.

No.	Total solids	Calcium	Magnesium	CO_3	HCO_3	Cl	SO_4
1.	0 371	Trace*	Trace	0.030	0 072	0 070	0.113
2.	0.122	Trace*	0	0.036	0 036	0.010	Trace
3.	0 082	Trace*	0	0 024	0.036	0	0
4.	0 069	Trace*	0	0.018	0.030	0	0
5.	0 047	Trace*	0	0.018	0.006	0	0
6.	0.029	Trace*	0	Trace	0 030	0	0
7.	0 028	Trace*	0	Trace	0.030	0	0
8.	0 026	Tiace*	0	Trace	0.030	0	0
9.	0.018	Trace*	0	Trace	0 024	0	0
10.	0.015	Trace*	0	Trace	0 021	0	0
11.	0 025	Tiace*	0	Trace	0 024	0	0

*Due to slight solution of $CaCO_3$.

The percolates showed little or no calcium or magnesium. The carbonates decreased gradually as the leaching proceeded. The soil was calcareous, so the final traces of alkalinity were probably due to the solubility of calcium carbonate.

After leaching, the soil was dried, placed in a tube and percolated with pure water. It took water freely and showed no signs of being dispersed. The physical properties of the soil had been changed, it was no longer gummy, but seemed to be in good, mechanical condition.

The replaceable sodium and replaceable calcium were determined in the leached soil by the method that will be described and these results are shown in Table II, in comparison with the results obtained from a sample of untreated soil.

TABLE II.—REPLACEABLE Ca AND Na IN 100 GRAMS OF SOIL.

	Replaceable calcium	Replaceable sodium
Untreated soil	0.0370 gm	0.1771 gm.
Leached soil	0 1320 gm.	0

It will thus be seen that the sodium carbonate and zeolite had been hydrolyzed and removed completely from the soil during the leaching process, and that the sodium had been replaced by the calcium that originally existed as calcium carbonate, even though $CaCO_3$ is soluble to the extent of only 6 or 8 parts per million of solution.

The phenomenon above described has been demonstrated in other ways. The gradual replacement of the sodium by calcium during the leaching process has been followed. At the point where percolation almost

stops, the amount of replaceable sodium in the soil is usually very low. A trace of replaceable sodium may, therefore, cause a decided dispersion in a heavy soil.

It thus may be safe to assume that a high percentage of replaceable sodium in a soil cannot be correlated with a high degree of dispersion and impermeability, and that little or no idea of the degree of dispersion of a soil can be gained from the study of the Ca:Na ratio. As long as there is an appreciable amount of replaceable sodium present (which gives up OH ions to the soil solution) the soil is almost sure to be dispersed, regardless of the amount of replaceable calcium present.

NEED FOR IMPROVED METHODS

The object of this bulletin is to advance methods whereby replaceable bases may be determined quantitatively and with a minimum expenditure of time and effort in soils ranging in reaction from extreme acidity to high alkalinity, and where alkali salts may or may not be present. So far as the writers have been able to find, no satisfactory methods exist, although much work has been done along this line. Adsorptions, solutions, and side-reactions have crept in, and tended to vitiate many results published heretofore. The bases present in slightly acid and neutral soils are comparatively easy to replace quantitatively, but soils carrying $CaCO_3$ and $MgCO_3$ in considerable quantities, as well as soils high in organic matter and in alkali salts, have presented difficulties which so far have been largely insurmountable.

The displacing solutions most commonly employed heretofore have been those of NH_4Cl, KCl, and $NaCl$, but, as it is often desirable to determine replaced K and Na, the latter two salts are not always applicable. We thus have NH_4Cl left as the salt at present almost universally used for this purpose. It is unsatisfactory in three important respects. First, where sufficiently large samples of soil are extracted to give proper amounts of Ca, Mg, Na, and K for accurate gravimetric or volumetric determination, and where tenth-normal (or stronger) solutions of NH_4Cl are employed, there remains upon evaporation an enormous amount of NH_4Cl which must be gotten rid of before these determinations can be made. This is often accomplished by volatilization, and, as is well known, where the amounts of NH_4Cl are large, (many grams) and the amounts of Ca, Mg, Na, and K small (often but a few milligrams) the possibilities of error due to mechanical loss are great. Furthermore, such a procedure is time-consuming and requires constant attention. Repeated evaporation with HNO_3, as used in some laboratories for this purpose, is also wasteful of time and disagreeable. The second, and, to us in the arid Southwest a very important reason for condemning NH_4Cl is that $CaCO_3$ is

appreciably soluble in its solutions (280 p. p. m. in tenth-normal NH_4Cl). The soils of this section are almost without exception calcareous, varying from 1 to over 50 percent $CaCO_3$, hence any solution which appreciably dissolves this salt is of questionable value where replaceable Ca is to be determined. Magnesium carbonate is also soluble in solutions of NH_4Cl, but to a lesser degree.* The third reason for condemning the use of NH_4Cl as a replacing agent is that it dissolves and removes from the soil large amounts of organic matter (especially from alkaline soils) which, as a soil colloid, may have a bearing on the replacement reaction.

The attention of the writers was first called to the possibility of using solutions of $BaCl_2$ as agents for the quantitative determination of replaceable bases in soils, by C. S. Scofield. It was found, however, that the use of $BaCl_2$ presented serious difficulty in that the several replaced bases could not be quantitatively separated from the excess of Ba by the ordinary methods. The total replacing power of Ba, as compared with mono and trivalent ions had previously been studied by Gedroiz and others, but, so far as the writers know, none had proposed the use of $BaCl_2$ in a method for determining the *amounts* of the several bases replaced. We are thus laying no claim to priority in the use of barium chloride as a replacing agent. We are, however, advancing the method which follows as a means whereby the calcium, magnesium, sodium, and potassium may be quantitatively separated and determined in the barium chloride percolate, thus rendering barium chloride a replacing agent of decided value from both the qualitative and quantitative standpoints. The carbonates of calcium and magnesium are but slightly soluble in tenth-normal solutions of $BaCl_2$, as results soon to be presented will show; it does not dissolve appreciable amounts of soil organic matter, and it is very active as a replacing agent, less prolonged treatment being required than with the salts of the monovalent bases in solutions of equivalent strengths.

THE SOLUBILITIES OF $CaCO_3$ AND $MgCO_3$ IN TENTH-NORMAL NH_4Cl, TENTH-NORMAL $BaCl_2$, AND DISTILLED WATER

When an excess of pure $CaCO_3$ or $MgCO_3$ is shaken with carbon-dioxide-free water until equilibrium is reached, a definite amount of the salt is dissolved, depending upon the temperature. This is a solution phenomenon, pure and simple. When, however, these substances are shaken with solutions of salts, besides true solution, a certain reaction-product results, depending upon the masses of the reacting compounds and their

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*Gedroiz states that magnesium carbonate is more soluble in solutions of NH_4Cl than is calcium carbonate. Our work, using finely ground magnesite, is not in agreement with this statement.

solubilities. For instance, if we shake $CaCO_3$ with a $BaCl_2$ solution we have the following reaction slowly taking place:

$$CaCO_3 + BaCl_2 \rightleftarrows BaCO_3 + CaCl_2 \qquad (1)$$

Thus, depending upon the masses and solubilities involved, more or less $CaCl_2$ is formed which is a soluble salt, and which is the *result of this reaction* rather than a simple solution phenomenon. The same is true where we use NH_4Cl:

$$CaCO_3 + 2NH_4Cl \rightleftarrows (NH_4)_2CO_3 + CaCl_2 \qquad (2)$$
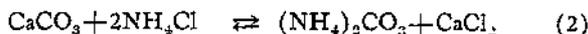
Now, as both compounds on the right side of equation (2) are readily soluble this reaction will proceed fairly rapidly from left to right until little solid $CaCO_3$ remains; but, as $BaCO_3$ is but slightly more soluble than $CaCO_3$, equilibrium is soon reached in equation (1). It will thus readily be seen that much more calcium will be present in solution where a tenth-normal solution of NH_4Cl is used than where a $BaCl_2$ solution of like normality is employed.
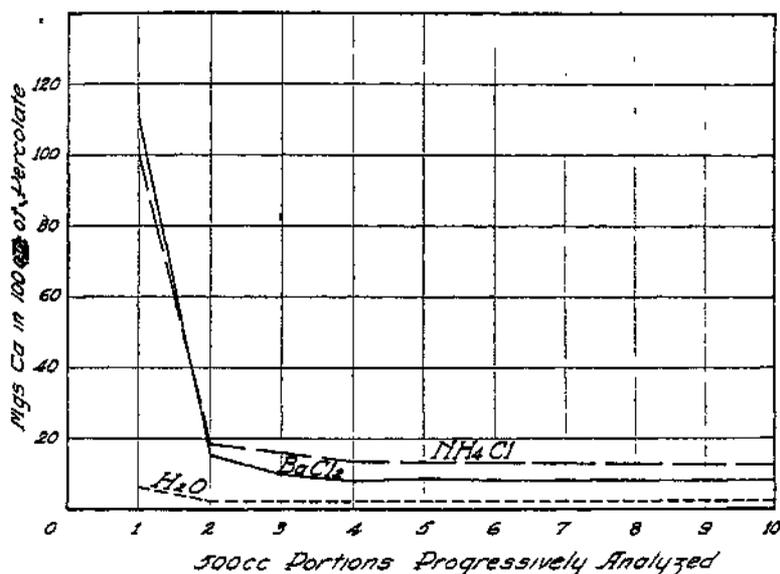

Fig. 1.—Yuma fine sand.

Our first attempts at determining the amounts of $CaCO_3$ and $MgCO_3$ which were dissolved by tenth-normal solutions of NH_4Cl and $BaCl_2$ were made as follows: One-half gram of Kahlbaum's C. P. $CaCO_3$ (or

MgCO$_3$), which had been washed several times by decantation with carbon-dioxide-free distilled water and subsequently dried, was placed in a hard glass bottle and shaken in a machine for 1 day with 250 c. c. of the salt solution to be tested. At the end of this time it was allowed to stand 1 day (until perfectly clear) when a proper aliquot (10 to 25 c. c.) was withdrawn for analysis. The original solution was then shaken for another day and analyzed again. This was continued several times, and in all cases, except where pure water was used, there was a progressive increase in solubility with each successive period of shaking. This was especially marked in the case of CaCO$_3$ in BaCl$_2$ solution and MgCO$_3$ in NH$_4$Cl solution.

It was soon realized that data thus secured could not be applied to our method, which was one of percolation rather than shaking. Three glass percolating tubes were, therefore, filled with Yuma fine sand* and
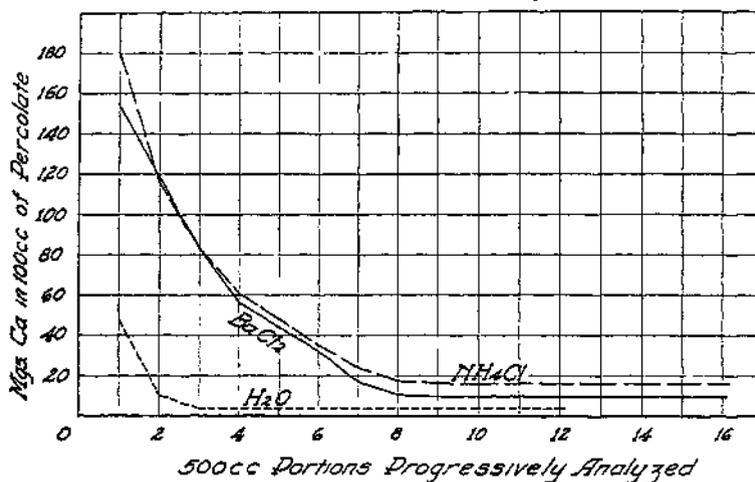

Fig. 2 —Yuma silty clay.

three others with Yuma silty clay.* One tube of each soil was constantly leached with water, one with tenth-normal NH$_4$Cl, and one with tenth-normal BaCl$_2$. As soon as 500 c. c. of percolate had come through, it was removed and analyzed for soluble calcium in each case. This was continued until ten 500 c. c. portions of each of the three solutions had been analyzed from the sandy soil and sixteen each from the silt.† The

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*These soils were purposely chosen because they are both calcareous (the sand carried 3.0 percent CaCO$_3$ and the clay 6 2 percent), and they represent physically two extreme cases, a very light sand and a very heavy, silty clay.

†Only eight 500 c.c. portions of the pure-water percolates from the silt soil were analyzed as here percolation was very slow.

data thus secured were plotted and appear in figures 1 and 2. As neither of these soils contained appreciable amounts of $MgCO_3$, and as this compound is seldom present in soils unaccompanied by $CaCO_3$, it was decided to set up another similar percolation experiment, using fine, washed, quartz sand impregnated with $MgCO_3$, to obtain similar solubility data for this salt. As it seemed desirable to use a naturally occurring product rather than precipitated $MgCO_3$, a sample of magnesite was secured from the University of Arizona College of Mines and Engineering, having the following composition: MgO 46.26 percent, CaO 1.74 percent, Fe_2O_3 1.27 percent, CO_2 50.48 percent, H_2O nil, insoluble nil, total 99.75 percent. As will be seen, this material analyzed over 96 percent $MgCO_3$. It was finely ground in a ball mill and thoroughly incorporated with the quartz sand at the rate of 2 percent by weight. Three portions of 125 gm. each were placed in small glass percolators and treated with water, tenth-normal NH_4Cl and tenth-normal $BaCl_2$ as above, each 100 c. c. of percolate being progressively analyzed for soluble magnesium. The rate of flow was regulated (by rubber tubing and clamps at the lower apertures of the percolating tubes) to permit 100 c. c. to pass through in approximately two hours. The results secured have been plotted and appear in figure 3.

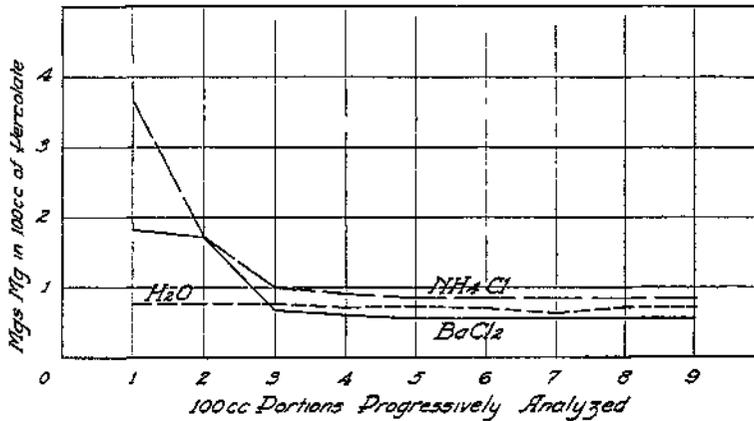Fig 3.—Finely ground magnesite in quartz sand.

In none of the percolation tests was carbon-dioxide-free water used. Ordinary distilled water was employed throughout, and conditions maintained as nearly like those where replaceable bases were to be determined by our methods, as possible. It was our aim here to determine the errors due to solubilities and side-reactions incurred by the presence of the earthy

carbonates. The Yuma soils carried traces of gypsum which accounts for the relatively larger amounts of water-soluble calcium shown in the first two extractions (see Figs. 1 and 2). Thereafter the curves for distilled water ran practically parallel with the base line, showing that the resulting small amounts of calcium were being progressively dissolved from the solid $CaCO_3$ present in the soils. This amounted to approximately 10 p. p. m. of solution (doubtless present in part as calcium bicarbonate) in the case of the sandy soil, and 25 p. p. m. where the clay soil was employed. After the curves for NH_4Cl and $BaCl_2$ had flattened out, i. e., when all of the readily soluble and replaceable calcium had been removed, we found, in the case of both soils, that the tenth-normal $BaCl_2$ extracts much less calcium from the residual $CaCO_3$ than does the tenth-normal NH_4Cl. In the case of the sandy soil (Fig. 1), where percolation is fairly rapid, the NH_4Cl removes in solution approximately 110 p. p. m. of calcium, while the $BaCl_2$ removes 70 p. p. m. In the case of the heavy soil (Fig. 2) an average of 135 p. p. m. of calcium is removed by the NH_4Cl, while less than 60 p. p. m. is leached out by the $BaCl_2$. Expressed in percentages of soil employed, where, let us say, 2 liters of percolate are secured and
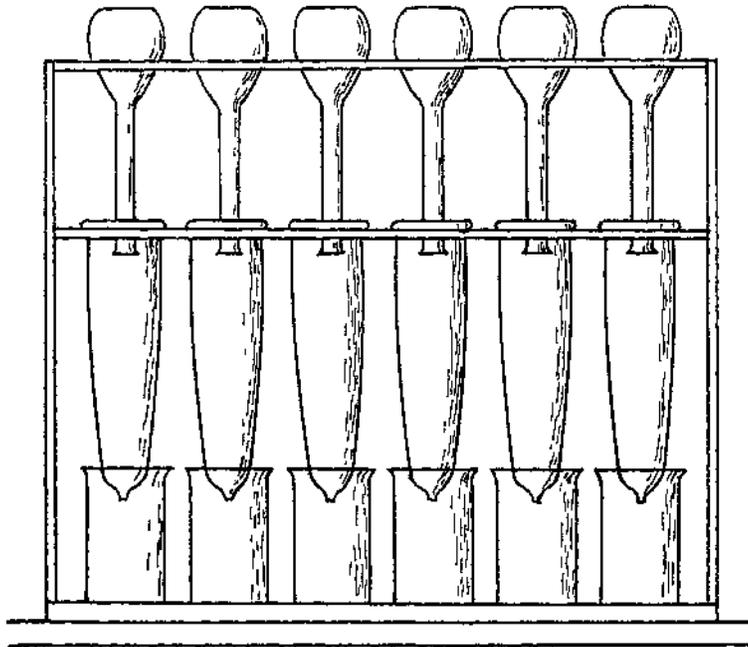

Fig. 4.—Wooden rack carrying percolators and flasks used in leaching soils.

analyzed, the errors, especially with the $BaCl_2$ solution, are relatively small. For example, 800 grams of soil were used in each of the above tests, and 2 liters of percolate secured, which would carry *in solution* approximately 120 mgs. of calcium, which would represent a positive error of 0.015 percent. If great accuracy is desired, this percentage may be subtracted from the figure found for replaceable calcium in calcareous soils where 2 liters of percolate are secured.

Figure 3 shows the amounts of magnesium dissolved by the two salt solutions and by distilled water from the magnesite-impregnated sand. After the first two 100 c. c. portions had passed through the percolators, the amounts of magnesium dissolved were thereafter fairly constant for each solution used, and in no case were they of sufficient magnitude to cause trouble. It will be noticed that the amounts removed in tenth-normal $BaCl_2$ are often less than are those dissolved in distilled water, while the opposite is always true for tenth-normal NH_4Cl.

METHOD FOR DETERMINING REPLACEABLE BASES IN CALCAREOUS SOILS FREE FROM BLACK ALKALI

The method finally adopted for the determination of replaceable bases in calcareous soils free from black alkali (white alkali does not interfere unless large amounts of gypsum are present) is as follows:

Five hundred grams (or 100 grams if high in clay) of air-dry soil are placed in a glass percolating tube (see Fig. 4) and leached with tenth-normal $BaCl_2$ solution until free from replaceable Ca (700 c. c. to 2,000 c. c. depending upon soil texture). The percolate is then made up to a definite volume (1 or 2 liters) with distilled water, and if at all turbid (which is not usual) filtered through a porcelain pressure filter. Two hundred c. c. are placed in a 250 c. c. graduated flask, 4 or 5 drops of con. acetic acid, and 20 c. c. of sodium chromate solution (175 gm. $Na_2CrO_4 : 10 \ H_2O$ per liter) are added in the cold to precipitate the barium. The whole is made up to 250 c. c., thoroughly agitated, and allowed to stand overnight to clear. Careful examination has shown no absorption of either Ca or Mg by the $BaCrO_4$ precipitate. Two methods of procedure are here possible. The Ca and Mg may be determined by the soap-titration methods, or by the standard methods, after separating them from the chromate solution. Both are often used in this laboratory as checks.

SOAP-TITRATION METHODS FOR Ca AND Mg

These methods which are modifications of the old Clarke method are extremely accurate where small amounts of Ca and Mg (7 mgs. or less) are present in the aliquot taken, and where Ca is in excess of Mg, or where

either is present alone. These conditions, incidentally, usually prevail in the salt solutions carrying replaced Ca and Mg from soils.

For the Ca determination take an aliquot of the clear, yellow, supernatant liquid carrying not over 6 or 7 mgs. Ca (5 to 25 c. c.), place it in a 250 c. c. bottle, make up to approximately 50 c. c. with distilled water, add 2 or 3 drops of concentrated NH_4OH and 5 c. c. of the alkaline tartrate solution.* Titrate, with shaking, against the standard soap solution* until a permanent froth remains after 2 minutes' standing. This reading, minus 0.3 c. c., multiplied by 0.00075 gives grams of Ca in the aliquot taken.

For the Mg determination take another aliquot carrying not over 6 or 7 mgs. of combined Ca and Mg, place in a 250 c. c. bottle, make up to approximately 50 c. c. with distilled water, add 2-3 drops of con. NH_4OH and 5 c. c. of the alkaline-ammonium-chloride solution.† Titrate as above to a permanent froth, being careful not to be misled by the "false foam" which often occurs at the Ca "end point." Subtract 0.3 c. c. from the final reading, which is the sum of the Ca and Mg present in the aliquot taken. Subtract the Ca reading already obtained from this total and multiply the remainder by 0.00039, this gives grams of Mg in the aliquot taken.

STANDARD METHODS

Pipette off an aliquot of the clear, yellow, supernatant liquid (100 or 150 c. c.). Make alkaline with NH_4OH and add, with stirring, sufficient 2 percent amonium-acid-phosphate solution, in the cold, to precipitate completely the Ca and Mg as phosphates,‡ as in the ordinary precipitation of magnesium. Let stand overnight, filter, wash with 2 percent NH_4OH, dissolve the precipitate in a small amount of hot, dil. HCl, make up to a volume of about 100 c. c. with distilled water and bring to boiling point. Add *just enough* NH_4OH to make slightly alkaline and throw out the phosphates, then with stirring, add 10 c. c. of a 5 percent solution of oxalic acid and boil. The solution now should be distinctly acid, while the Ca will be precipitated completely as the oxalate. Filter and determine the Ca by titrating with a standard solution of $KMnO_4$.

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*The reagents are made up as follows:

Standard Soap Solution: A little over 13 gm. of C. P. sodium oleate (Merck's) are dissolved in 1 liter of 50 percent ethyl alcohol and standardized against a Ca solution of known strength (a saturated solution of C. P. gypsum contains 0.210 percent $CaSO_4$ and is usually used in this laboratory) so that each c.c. equals 0.00075 gm. of calcium. *Alkaline Tartrate Solution*: Dissolve 12 gm. of potassium hydroxide and 200 gm. of sodium-potassium-tartrate in 1 liter water.

†*Alkaline-Ammonium-Chloride Solution*: Dissolve 20 gm. ammonium chloride in 1 liter water carrying 70 c.c. of concentrated C. P. ammonium hydroxide.

‡See, "The Determination of Calcium in the Presence of Phosphates," by Breazeale in Jour. A. O. A. C., V. 4, p. 124.

Evaporate the filtrate to a bulk of about 50 c. c., cool, add 2 or 3 c. c. of the amonium-acid-phosphate solution and precipitate the Mg as $MgNH_4$-PO_4 by making alkaline with NH_4OH in the usual way, igniting, and finally weighing as $Mg_2P_2O_7$.

Sodium and potassium are determined in the original $BaCl_2$ percolate as follows: An aliquot (usually 100 c. c.) is placed in a porcelain evaporating dish, slightly acidified with HCl and 5 c. c. (or more) of a 14-percent solution of $(NH_4)_2$ SO_4 added. Evaporate to dryness on the water bath, dry in the oven, and drive off slight excess of ammonium salts in the electric muffle at low heat, finally heating to *dull* redness. Take up in 2 percent HCl, digest on the water bath for an hour or more, filter, and determine Na and K by Hilgard's Method or by the Official Methods of the A. O. A. C. The $BaSO_4$, *after heating*, has little or no tendency to absorb sodium and potassium. This, however, is not true in the cases of calcium and magnesium. If replaceable K only is desired, the procedure is greatly simplified. After digesting the residue in dil. HCl, filter into a porcelain evaporating dish, add the proper amount of platinic chloride solution and gravimetrically determine K in the usual way.*

Where the soils carry white alkali (sulphates and chlorides of sodium) the soil in the percolator must first be leached free from these salts with pure water before being subjected to the $BaCl_2$ treatment,† or, where percolation with water is slow as in the case of heavy soils, a separate analysis may be made for water-soluble bases and these subsequently subtracted from those found in the $BaCl_2$ percolate.

In the case of acid soils (unsaturated with respect to bases), the amounts of replaceable H-ion may be determined in the $BaCl_2$ percolate by means of titrations as recently recommended by Gedroiz,‡ and modified by Joffe and McLean.§

TESTS OF THE PROPOSED METHOD WHERE BLACK ALKALI IS ABSENT

On several occasions during the past year in which this method has developed in our laboratory, standard stock solutions of the chlorides of

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*See, Official Methods of Analysis of the A. O. A. C. (2nd Edition) p. 14, Sec. 45a.

†Where gypsum (which is but slightly soluble and slowly leached out of soils) is present in considerable quantities, the method here proposed cannot be used, for, after the more readily soluble sodium salts have been removed, the calcium, slowly coming into solution as leaching is continued, will replace zeolitic sodium. Low results will thus be obtained for replaceable sodium (and potassium) and too high results for replaceable calcium. Gypsum, however, is seldom present in such large quantities.

‡"A Method of Determining the H-Ion Absorbed in the Soil, etc.," by K. K. Gedroiz, In Zhur. Opit. Agr. (Jour. Expt. Agr.) Vol. 22. pp. 1-28.

§"Colloidal Behavior of Soils and Soil Fertility: II The Soil Complex Capable of Base Exchange and Soil Acidity," by J. S. Joffe and H. C. McLean, Soil Science, Vol. 21, No. 3, pp. 181-195, (1926).

Ba, Ca, Mg, Na, and K have been prepared, from which both "known" and "unknown" solutions have been made up and subjected to analysis by one or the other of the authors. It is not our intention to give all of the data secured. It was thought, however, that a certain amount of it should be included to substantiate our claims as to the accuracy of the separations.

Fairly concentrated solutions of the chlorides of Ca, Mg, Na, and K were prepared so that 5, 10, or 15 c.c. only were required to furnish all of each base added, while tenth-normal $BaCl_2$ was used in all cases to bring the solutions up to a volume of 250 or 500 c.c., as the case might be. A majority of the work has been done intentionally with the elements Ca and Mg for the reasons that these elements are more subject to adsorptions during separations, and furthermore, the accurate determination of the amounts of these elements *in replaceable forms* is of considerable importance in the study of alkali soils carrying large amounts of their carbonates. Table III presents the very first of these data secured.

TABLE III — AMOUNTS OF Ca AND Mg ADDED AND RECOVERED FROM MIXED SOLUTIONS OF THEIR CHLORIDES IN THE PRESENCE OF AN EXCESS OF $BaCl_2$

No.	Mgs. added		Mgs recovered by soap-titration methods		Mgs. recovered by standard methods	
	Ca	Mg	Ca	Mg	Ca	Mg
1	20	12	20 0	11.0	20 4	10.7
2	40	12	40 2	10 4	40 4	12 5
3	20	24	22 4	24 4	20 8	19 0
4	10	6	11 6	5 7	10.6	7 0
5	30	6	30.0	4.1	30.7	5 3
6	10	36		31 0	11 0	32 0

In all but two or three cases these figures are in very fair agreement, and showed at the outset that the method had promise of possibly somewhat greater exactitude after more care and time had been expended upon it.

The accuracy of the potassium determination was next tested with the results appearing in Table IV.

The agreement in Table IV appears to be all that one could desire. No adsorption of K by the $BaSO_4$ precipitate is indicated. Calcium and magnesium also were present here in small quantities to find whether or no they interfered with the potassium determination. Calcium and magnesium were not determined.

The sodium determination in the presence of tenth-normal $BaCl_2$ by the method above outlined was tried, with the results set forth in Table V. The solutions were made up with pure NaCl and $BaCl_2$. No other salts were present.

TABLE IV.—AMOUNTS OF K ADDED AND RECOVERED FROM SOLUTIONS OF KCl IN TENTH-NORMAL BaCl₂ IN THE PRESENCE OF SMALL AMOUNTS OF CaCl₂ AND MgCl₂.

No.	Mgs. K added as the chloride	Amounts recovered	
		Wts. K_2PtCl_6	Mgs K
1	4	0 0310 gm.	4 90
2	8	0 0500	8 04
3	12	0.0770	12 30
4	16	0.1025	16 30
5	20	0.1170	18.90
6	24	0.1560	25 00
7	28	0.1695	2⁷ 40
8	40	0.2435	39 20

These results show little or no adsorption of Na by the ignited $BaSO_4$ precipitate.

TABLE V —AMOUNTS OF Na ADDED AND RECOVERED FROM SOLUTIONS OF NaCl IN TENTH-NORMAL BaCl₂.

No	Mgs. Na added as the chloride	Amounts recovered	
		Wts. Na_2SO_4	Mgs. Na
1	20	0.0644 gm.	20 8
2	30	0 0921	29 8
3	40	0 1180	38 5
4	50	0.1460	47 3

Four solutions of 250 c.c. each were made up to contain the following amounts of Ca, Mg, K, and Na as chlorides, dissolved in tenth-normal $BaCl_2$:

TABLE VI.—COMPOSITION OF TEST SOLUTIONS

No.	Mgs Ca	Mgs Mg	Mgs K	Mgs. Na
1	100	60	100	25
2	150	30	80	50
3	40	90	60	75
4	60	120	40	100

From time to time, as opportunity permitted, these solutions, or solutions of the same concentrations, were analyzed, different aliquots often being taken. The results secured appear in Table VII.

These analyses were made later on, after considerable experience had been gained with the method. In all cases very good agreement is shown between the weights of the several elements contained in the aliquots taken, and those recovered upon analysis. No adsorption of Ca and Mg by the $BaCrO_4$ precipitates, or of Na and K by the ignited $BaSO_4$ precipitates is indicated.

TABLE VII.—MILLIGRAMS OF Ca, Mg, K, AND Na ADDED AND RECOVERED FROM SOLUTIONS OF THEIR CHLORIDES, IN THE PRESENCE OF TENTH-NORMAL $BaCl_2$

No.	Calcium						Magnesium						Potassium		Sodium	
	Aliquot contained	Recovered*	Aliquot contained	Recovered	Aliquot contained	Recovered	Aliquot contained	Recovered	Aliquot contained	Recovered	Aliquot contained	Recovered*	Aliquot contained	Recovered	Aliquot contained	Recovered
1	4	3.8	20	20.4	15	14.6	24	22.6	9	9.0	2.8	2.4	40	38.2	10	10.1
2	6	6.0	30	30.4	22.5	22.0	12	11.5	4.5	4.8	1.4	1.4	32	29.1	20	20.5
3	1.6	1.8	8	8.4	6	6.4	36	34.8	13.5	13.0	4.2	4.5	24	22.6	30	29.9
4	2.4	2.3	12	12.0	9	9.0	48	—	18	17.4	5.6	5.4	16	16.5	40	39.3

*Soap-titration method used.

Four solutions were prepared by one of the writers and analyzed as "unknowns" by the other. They contained Ca and Mg only. The results secured are recorded in Table VIII.

TABLE VIII.—AMOUNTS OF Ca AND Mg RECOVERED FROM "UNKNOWN" SOLUTIONS OF THEIR CHLORIDES IN THE PRESENCE OF AN EXCESS OF BaCl₂.

No.	Mgs. added		Mgs. recovered by soap-titration methods		Mgs recovered by standard methods	
	Ca	Mg	Ca	Mg	Ca	Mg
1	20	12	20 0	7.8	20.0	12.0
2	50	30	52.5	31.0	50.0	30.6
3	70	42	70.0	44.0	70.0	40.2
4	120	60	122 5	56 5	118.0	60.4

Where the standard methods (titration of Ca with KMnO₄ and gravimetric determination of Mg as Mg₂P₂O₇) were employed, the methods here advocated are as accurate as needful. While the soap-titration methods are subject to slightly greater variations where large amounts of Ca and Mg are present (due to multiplication of error from aliquot taken), the extreme rapidity of operation is here a factor to be considered where large numbers of such determinations are to be made.

METHOD FOR DETERMINING REPLACEABLE BASES IN CALCAREOUS SOILS WHERE BLACK ALKALI IS PRESENT

In the West, many soils contain black alkali, or sodium carbonate, and this salt is always associated with dispersion if the soil carries much clay and silt. Dispersed soils aways contain a certain amount of sodium that is combined as zeolite (basic-hydrated-aluminum silicate), and such soils are nearly always calcareous. We thus have sodium existing as the carbonate, the bicarbonate, and the zeolite, in the presence of an excess of calcium carbonate. In reclamation work and in our percolation studies we are concerned with sodium zeolite fully as much as with sodium carbonate. Sodium carbonate is but slightly hydrolyzed and does not completely retard percolation, as it is readily soluble and may be slowly leached from soils. On the other hand, sodium zeolite is only slightly soluble, and cannot be washed out readily from soils, due to almost complete hydrolysis of the dissolved portion.

In the methods for the determination of replaceable bases in alkali soils that have so far been proposed no attention has been given, and no attempt has been made to separate the sodium that may be combined in the hydrated silicate molecule from that which may be combined with

the CO_3 radical. The sodium is either reported as replaceable sodium, or as sodium carbonate (black alkali). In ordinary alkali-soil analyses where an excess of water is used, the sodium, whether it is derived originally from the carbonate or the zeolite, is reported as sodium carbonate. If a soil is digested with an equal weight of water, all of the sodium carbonate and a very small part of the sodium zeolite will go into solution, but if the ratio of water to soil is increased to say 5 to 1 or 10 to 1, as is often the case, the sodium zeolite is hydrolyzed further, or possibly completely, and we titrate it as hydrolyzed sodium carbonate in the resulting solution. Ordinary analyses are, therefore, only arbitrary, unless sufficient amounts of water are used to bring about complete hydrolysis of the sodium zeolite, and in this way bring all of the sodium into solution. Even then the sodium determination would represent the total soluble sodium and there would be no distinction made between that originally existing as carbonate, and the zeolite. A method which will distinguish between the sodium that is combined with the CO_3 ion and that existing as zeolite should be, therefore, of considerable value.

THE TWO-TUBE PERCOLATION METHOD

Two samples of dry soil of 500 gm. each (or 100 gm. if high in clay) are placed in two percolating tubes and treated as follows:

Tube No. 1. Percolated with n/10 $BaCl_2$ until soil bases are all replaced (shown by qualitative test in percolate for Ca). Solution A.

Tube No. 2. Percolated with n/10 $CaCl_2$ until Mg, Na, and K are all replaced—until no more Ca is being fixed by the soil. Determined by titrating the percolate and the original solution for Ca. Solution B.

Tube No. 2 is now leached with pure water until all the $CaCl_2$ solution is removed. This leaching water is discarded. The soil column is now leached with n/10 $BaCl_2$ until all the Ca has been replaced by the Ba. Solution C.

Solutions A, B, and C are now titrated for combined Ca and Mg by the soap-solution method, as these two bases act very similarly in soils, or they may be determined gravimetrically. In this discussion for the present they will be considered together, the term Ca being assumed to mean both Ca and Mg.*

The Ca content of Solution A is the total replaceable Ca in the soil.

The Ca content of Solution B is determined, and the difference in the Ca content of this percolate and that of the original n/10 $CaCl_2$ used, represents the Ca equivalent of both the sodium carbonate and sodium zeolite originally present in the soil. The Ca of the n/10 $CaCl_2$

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*Incidentally, replaceable Mg is usually *very low* in calcareous soils carrying black alkali.

solution has liberated the Na in the sodium zeolite and is now present as calcium zeolite in the soil. The Ca in the $CaCl_2$ solution has also combined with the CO_3 radical formerly present as Na_2CO_3, and been precipitated in the soil as $CaCO_3$, which is insoluble. Thus, the total amount of Ca fixed by the soil is equivalent to the Na originally existing both as the carbonate and as zeolite. A little Na_2CO_3 may be brought into the percolate during the first stages of the leaching process and should be poured back through the soil, in order to be sure that all of the Na_2CO_3 has reacted, with the formation of the insoluble $CaCO_3$. The $NaHCO_3$ which may be present in the soil in small amounts, causes no trouble whatever, as the soluble calcium bicarbonate (if formed at all) comes through with the the excess $CaCl_2$ present, and it is the difference between the amounts of Ca in the original solution and in the percolate, which is fixed, and which is of interest.

Solution C contains both the Ca which was originally present in the soil as calcium zeolite, and the Ca from the calcium zeolite formed from the sodium zeolite by the preceding percolation with $CaCl_2$ solution. This total amount of replaceable Ca was replaced by the Ba, and came through into the percolate as $CaCl_2$. *It should be remembered here that the Ca that reacted with the Na_2CO_3 was precipitated in the soil as $CaCO_3$, and does not enter into this reaction.* Calcareous soils already contain an excess of $CaCO_3$, and this precipitation adds but a very small amount in addition. Thus, the Ca in Solution C represents the replaceable Ca of the soil together with the Ca equivalent of the Na derived from the sodium zeolite originally present in the soil.

In calculating the results of the analyses of the three percolates for Ca, an outline of the analysis of the University Farm Soil may be helpful. The results are expressed as percent of dry soil.

ANALYSIS OF SOLUTIONS

Sol.	Ca	Ca equivalent of:
A	0.0350	Calcium zeolite present in soil
B	0.1790	Sodium zeolite plus Na_2CO_3 present in soil
C	0.1650	Calcium zeolite plus sodium zeolite present in soil

Now C minus A equals sodium zeolite.

B minus sodium zeolite equals Na_2CO_3.

Or:
$$
\begin{array}{l}
0.1650\text{—CaZ plus NaZ} \\
0.0350\text{—CaZ} \\
\hline
0.1300\text{—NaZ}
\end{array}
\left.\vphantom{\begin{array}{l}0\\0\\0\end{array}}\right\} \text{All in Ca equivalents.}
$$

$$0.1790 — NaZ \text{ plus } Na_2CO_3$$
$$0.1300 — NaZ$$

\left.\right\} \text{All in Ca equivalents.}

$$0.0490 — Na_2CO_3$$

We thus have, in terms of Ca, for the soil in question:

Replaceable Ca .... 0.0350 percent
Ca equivalent to replaceable Na................ 0.1300 percent
Ca equivalent to Na_2CO_3 .... 0.0490 percent

As Ca is bivalent, and Na monovalent, 20 of Ca is equivalent to 23 of Na, thus calculating Na from Ca equivalent, we have:

Replaceable Ca .... 0.0350 percent
Replaceable Na.. 0.1495 percent
Na as Na_2CO_3.. 0.0563 percent

In the case of soils carrying water-soluble Ca, the amount of this base must be determined by leaching another similar column with distilled water and subtracting the results obtained from the data secured by the replacing solutions noted above.

It will be noticed that this method involves the determination of Ca only, in so far as the replaceable Na is concerned. This is a decided advantage, as all analysts know, for the Na determination is tedious and subject to many chances for error.

If we are desirous of determining the exact amounts of replaceable Ca, Mg, Na, and K, as well as black alkali (Na_2CO_3), it may be done as follows:

Another aliquot of Solution A is taken and the separation of Ca and Mg here made by means of sodium chromate, as in the method above described.

K also may be readily separated and determined in another aliquot of Solution A, as in the first method. Its Na equivalent is calculated and subtracted from the percentage of replaceable Na found.

CONCLUSIONS

The quantitative determination of replaceable bases (Ca, Mg, Na, and K) in soils is often desirable, as such exchangeable bases play an important part in plant nutrition and in black alkali formation in many arid western soils.

Methods are here advanced for making such quantitative determin-

ations in acid, neutral, or calcareous soils. The methods are also modified to minimize, or entirely do away with complications arising from the presence of soluble alkali salts which are often present in considerable quantities in the soils of the West.

Tenth-normal barium chloride is employed as the replacing agent, the Ba being later removed from solution as $BaCrO_4$ where Ca and Mg are to be determined, or $BaSO_4$ (ignited) where Na and K are sought. Solutions of $BaCl_2$ have often been used as base replacing agents, but, so far as the authors are aware, no quantitative method using such solutions, has been heretofore advocated. This has doubtless been due to difficulties encountered in quantitatively separating Ca and Mg from the excess of the Ba present in the solutions where the ordinary methods of precipitation are followed.

In the case of black alkali soils (soils carrying Na_2CO_3), a method for the determination of replaceable bases is proposed, which involves analyses for calcium only, thus doing away with the tedious sodium determination.