Determining Cation Exchange Capacity: A New Procedure for Calcareous and Gypsiferous Soils[1]

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ABSTRACT

A new, two-step procedure is presented for determining the cation exchange capacity (CEC) of calcareous and gypsiferous soils. The method eliminates most of the errors inherent in conventional methods. The cation exchange sites are saturated with sodium by four successive "equilibrations" of the soil (4-5 g) with 33-ml increments of a pH 8.2, 60% ethanol solution of 0.4N NaO Ac - 0.1N NaCl (saturating solution). The saturated sample then is extracted with three 33-ml increments of 1.0N, pH 7 magnesium nitrate. Total sodium (Na_t) and chloride (Cl_t) are subsequently determined in the extracted solution. Chloride (Cl_t) is determined so that the soluble sodium (Na_{sol}), from the excess saturating solution carried over from the saturation step to the extraction step, may be deducted from the total sodium (Na_t) to obtain exchangeable sodium (Na_{exch}), which is equivalent to the CEC. Thus,

$$\mathrm{CEC} = \mathrm{Na_{exch}} = (\mathrm{Na}_t - \mathrm{Na_{sol}}) = \mathrm{Na}_t - [\mathrm{Cl}_t(\mathrm{Na/Cl})_{\text{saturating solution}}]$$

where $(Na/Cl)_{\text{saturating solution}}$ is the ratio of Na to Cl in the saturating solution.

Additional Index Words: **cation exchange capacity, calcareous soils, gypsiferous soils.**

Methods of determining cation exchange capacities (CEC) of soils generally consist of saturating the soil with saline solutions of an index cation, eliminating the excess saturating solution, and then determining the amount of extracted index cation per unit dry weight of soil. The results obtained are often different with different methods. Variations in results are not surprising in view of the many possible complicating interactions between saturating, washing, and extracting solutions and soil constituents during the analytical operations and the fact that CEC is not a conservative property of the soil (Frink, 1964; Okazaki et al., 1962, 1963, 1964; Rich, 1962; Smith et al., 1966). The complications arising from the dissolution of calcium carbonate and gypsum in the soil during CEC determinations are particularly troublesome. Although methods have been proposed for calcareous and gypsiferous soils (Carpena et al., 1972; Garman and Hesse, 1975; Papanicolaou, 1976; Yaalon et al., 1962), they either are not generally applicable to soils containing both calcium carbonate and gypsum or they are too cumbersome and demanding for routine determinations. For this reason we evaluated the sources of error inherent in conventional methods of CEC determinations and developed a new method for calcareous and gypsiferous soils that eliminates most of these errors while retaining the advantages of accuracy and simplicity.

The new method presented and the errors it minimizes are discussed by contrasting it with the CEC method probably used most frequently for salt-affected soils, the method of Bower et al., (1952).

SOURCES OF ERROR IN CONVENTIONAL CEC METHODS

Each of the three steps commonly used in the conventional methods of determining the CEC of soils can introduce errors. Some of these errors are enhanced if the soils contain calcium carbonate and/or gypsum. While the method of Bower et al. (1952) is the standard used in many laboratories, it cannot be used with gypsiferous soils without first removing the gypsum. The basic error sources in most conventional methods can be pointed out in discussing the Bower method. This discussion also serves to contrast our method with that of Bower.

The steps of the "Bower" method are:

1) Saturation of the cation exchange sites by four successive "equilibrations" of the soil with normal, NaOAc of pH 8.2.

2) Removal of excess saturating solution by three washings with 95% ethanol; each washing solution is decanted after centrifugation.

3) Replacement of the adsorbed Na by three extractions with neutral, normal NH_4OAc for subsequent quantitative determination.

Possible sources of error in this method are:

1) In the saturation step, the exchange sites may not be completely saturated with Na because other cations in the "saturating solution" compete with Na for adsorption sites. These other cations derive from the dissolution of $CaCO_3$, gypsum, and silicate minerals in the saturating solution. Gypsum is quite soluble in the NaOAc solution (31 meq/liter)[3]; $CaCO_3$ is less soluble (1.5 meq/liter)[3]; only a few silicates are sufficiently "soluble" to produce significant errors with this method (Rhoades and Krueger, 1968). This error would result in an underestimate of CEC.

2) In the washing step there are four potential sources of error:

a) Adsorbed Na may be removed by hydrolysis;

b) Adsorbed Na may be replaced by cations—especially Ca—brought into solution in the washing solvent from the dissolution of $CaCO_3$, gypsum, and silicates;

c) Cation exchangers—especially fine-clay particles and organic matter—may be lost during decantation because they tend to disperse as the excess electrolyte is removed during washing;

d) Some of the original saturating cation may be retained in the sediment, and subsequently extracted as an exchangeable cation if the washing is incomplete or salt is retained.

All but (d) result in underestimates of CEC.

3) In the replacement step there are two potential sources of error:

a) Adsorbed Na may be trapped between interlayers by contraction of expandable 2:1 layer silicates, especially

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[3] Experimentally determined values.

vermiculites and weathered micas, due to ammonium fixation and not removed during extraction. This is a common problem in many arid-land soils (Bower, 1950). This adsorption would result in an underestimate of CEC.

b) Nonexchangeable Na may be extracted from zeolitic- and feldspathoid-minerals by the ammonium ion (Rhoades and Krueger, 1968). This would result in high CEC values.

Soils containing appreciable gypsum cannot be used with this method because Ca would be brought into solution during saturation and washing.

LIMITATIONS OF PRESENT METHODS FOR CALCAREOUS AND GYPSIFEROUS SOILS

Two CEC methods have been proposed for gypsiferous soils (Tucker, 1974; Garman and Hesse, 1975), but each suffers some limitations. The method of Tucker (1974) uses NH_4^+ in 60% ethanol as the saturating cation and KNO_3–$Ca(NO_3)_2$ as the replacing solution. As shown by Bower (1950), many arid-land soils contain mica-type minerals that fix NH_4 and K within interlayers. Such reactions preclude complete saturation and extraction of the saturating cation and, hence, result in decreased CEC values. In addition to this limitation, exchangers may disperse and be lost during the final saturation step in which 0.05*M* NH_4Cl is used. With the method of Garman and Hesse (1975), $BaCl_2$ is used as the saturating solution to coat gypsum with $BaSO_4$ to prevent gypsum from dissolving during saturation of the exchange sites with Ba. Magnesium sulfate (0.05*N*) is used as the replacing solution (100 ml); the Mg lost from this solution, per unit weight of soil, is taken as the CEC. However, appreciable soluble Ca was also observed in the replacing solution and we conclude that gypsum dissolves in the replacing solution. Under such conditions, Ca would be competing with Mg for exchange sites; to this extent, Mg loss from the replacing solution would be reduced and, hence, calculation of CEC with this method would be low. Additional weaknesses of the method lie in the uncertainty of the extent to which $BaCl_2$ prevents gypsum dissolution in the saturating step and how much exchangeable barium is lost in the washing step (200 ml of distilled water). The reliability of this method seems questionable.

Several methods have been proposed for calcareous soils (Mehlich, 1938, 1942; Bower, et al., 1952; Yaalon, et al., 1962; Bascomb, 1964; Tucker, 1974; Papanicolaou, 1976). The limitations of the Bower method have been discussed and, as will be shown later, $CaCO_3$ does produce appreciable errors in CEC determinations with this method.

Mehlich (1938, 1942) used aqueous solutions of buffered (pH 8.2) $BaCl_2$ -triethanolamine (TEA) to saturate the exchange complex of calcareous soils, taking advantage of the ability of Ba to be adsorbed on $CaCO_3$ to minimize its subsequent dissolution during exchange saturation. Others have used this method, with slight modifications, for calcareous soils with variable success (Hanna and Reed, 1948; Pratt and Holowaychuk, 1954; Bascomb, 1964; and Carpena et al., 1972). Most of these methods have the limitation that Ba loss from the saturating solution is taken as equivalent to the CEC; this ignores the loss of Ba by adsorption on $CaCO_3$ and includes the errors inherent in "differences" methods. Extensive leaching to remove soluble sulfate and carbonate before determining CEC was recommended by Mehlich (1942) when the method is to be used for gypsiferous and calcareous soils. Such leaching is not generally advisable, however, because exchangers tend to be lost concurrently through dispersion, which is enhanced by the lowered electrolyte level produced with leaching.

In the methods of Yaalon et al. (1962), Okazaki et al. (1962), and Papanicolaou (1976), the errors involved in the washing step are avoided by eliminating this step. Okazaki et al. did not recommend their method for calcareous or gypsiferous soils; we conclude that it cannot be used because NH_4OAc extracts not only adsorbed Ba but also Ba precipitated as $BaCO_3$ and $BaSO_4$. In the Yaalon et al. method, the exchange complex is saturated with pH 8.2, LiOAc-LiCl solution, then adsorbed and soluble Li are replaced with pH 8.2, $Ca(OAc)_2$ solution. The necessity of washing the soil is eliminated by assaying for Cl to determine the remaining excess saturating salts in the replacing solution and deducting this amount from the total Li found in the used replacing solution. Errors due to incomplete saturation because of $CaCO_3$ dissolution are minimized by keping the pH at 8.2; however, gypsum dissolution would not be prevented. A potential error exists in the method even for calcareous soils, though discounted by Yaalon, et al. Cation exchangers have very low affinity for Li adsorption; hence, during saturation even small amounts of Ca in solution will preclude complete saturation. For example, Papanicolaou (1976) showed that 12 leachings with 1*N* LiCl solution were insufficient to remove all adsorbed cations from soils. In the Papanicolaou CEC method, 1*N* $CaCl_2$ (pH 7.0) is used as the saturating solution; adsorbed Ca is replaced by extraction with 1*N* $NaNO_3$ (pH 7.0). Total (Ca^{2+} + Mg^{2+}), Cl^- and (CO_3^{2-} + HCO_3^-), are determined in the combined extract. The CEC is calculated as (Ca + Mg) − (Cl^- + CO_3^{2-} + HCO_3^-). This method could be used for soils containing gypsum if SO_4 were determined. The method, however, requires numerous analyses.

For the preceding reasons it is apparent that still lacking is a reliable, generally applicable, and simple method for routinely determining CEC of calcareous and gypsiferous soils, especially the latter.

PROPOSED METHOD

The following two-step procedure for CEC was developed to help meet this need:

1) Saturation of the cation-exchange sites of the soil (4-5 g) by four successive "equilibrations" with 33-ml increments of a pH 8.2, 60% ethanol solution of 0.4*N* NaOAc-0.1*N* NaCl. Equilibrations are achieved by shaking the soil-solution mixtures for 5 min. The "exhausted" solutions are decanted after centrifugation. If the soil is initially high in salts (EC_e > 2 mmhos/cm), wash the soil with one 33-ml increment of water before saturation. Excessive washing should be avoided to prevent loss of particles during decantation.

2) Extraction of the saturated sample with three 33-ml increments of 1.0*N*, pH 7 solution of $MgNO_3$. Both sodium (Na_t) and chloride (Cl_t) are subsequently determined in this solution. Chloride is determined so that the soluble sodium (Na_{sol}) from the excess saturating solution carried over from the saturation step to the extraction step may be deducted from the total sodium to obtain exchangeable sodium (Na_{exch}). Thus,

$$CEC = (Na_t - Na_{sol}) = Na_t - [Cl_t(Na/Cl)_{\text{saturating solution}}]$$

Table 1—CEC of Pachappa soil to which various increments of calcium carbonate and gypsum were added, as determined by the Bower et al. (1952) method *(A)* and newly developed method *(B)*.

Sample	Amount of minerals added†		CEC by method		Difference
	$CaCO_3$	$CaSO_4$	A	B	(A - B)
	——— % ———		meq/100 g		meq/100 g
1	--	--	9.7	9.7	--
2	0.5	--	9.4	9.7	-0.3
3	1	–	9.4	9.7	-0.3
4	2	--	9.3	9.7	-0.4
5	4	–	9.2	9.7	-0.5
6	8	--	8.8	9.7	-0.8
7	12	–	8.7	9.7	-1.0
8	16	–	8.6	9.6	-1.0
11	--	0.5	9.3	9.7	-0.4
12	--	1	9.3	9.7	-0.4
13	--	2	9.2	9.7	-0.5
14	--	4	9.1	9.7	-0.6
15	--	8	8.5	9.5	-1.0
16	--	12	8.4	9.6	-1.2
17	--	16	8.2	9.6	-1.4
18	0.5	0.5	9.4	9.7	-0.3
19	1	1	9.4	9.7	-0.3
20	2	2	9.2	9.6	-0.4
21	4	4	8.9	9.7	-0.8
22	8	8	8.8	9.4	-0.6
23	12	12	8.7	9.5	-0.8
24	16	16	8.5	9.4	-0.9

† As added to 4 g of soil.

where $(Na/Cl)_{\text{saturating solution}}$ is the ratio of Na to Cl in the saturating solution.

The solubilities of gypsum and $CaCO_3$ in the saturating solution are sufficiently low (5.8 and 4.0 meq/liter for gypsum and calcite, respectively)[3] and the exchange affinity for Na vs. Ca is sufficiently high to allow essentially complete saturation of the CEC with Na. All the errors associated with washing are avoided by omitting this step. The errors associated with the extraction step are minimized by replacing NH_4OAc with $MgNO_3$, since Mg is not fixed in soils nor does it extract many nonexchangeable cations (Rhoades and Krueger, 1968).

EXPERIMENTAL PROCEDURE

To test the developed method, we conducted two kinds of experiments. In the first experiment various increments of $CaCO_3$ and/or gypsum were added to 4 g of Pachappa soil, which is free of these minerals in its natural state. The CEC's of these mixtures were then determined using the newly developed method and that of Bower et al. (1952). In the second experiment, the CEC's of soils with different $CaCO_3$ and gypsum contents and other properties were determined with the two methods.

Sodium and chloride in the extracted solutions were determined by atomic absorption spectrophotometry and potentiometric titration, respectively. Calcium carbonate in the soils was determined by the manometric method of Williams (1949). Gypsum, saturation percentage (SP), saturation extract electrical conductivity (EC_e), air-dry water content *(Pw)*, and saturation paste pH (pH_s) were determined by methods described by U.S. Salinity Laboratory Staff (1954).

RESULTS AND DISCUSSION

The CEC's of Pachappa soil to which various amounts of $CaCO_3$ and gypsum were added as determined by the newly developed method (B) and the Bower et al. (1952) method (A) are given in Table 1. Each value is the average of two replicates. In all cases, increasing increments of $CaCO_3$ and/or gypsum resulted in reduced CEC values with the "Bower" method, whereas nearly constant CEC values, or negligible reductions, were obtained with the newly developed method.

Table 2—Properties of soils and CEC's as determined by the Bower et al. (1952) *(A)* and newly developed *(B)* methods.

Soil no.	SP†	pH_S‡	EC_e§	Pw¶	$CaCO_3$	$CaSO_4 \cdot 2H_2O$	CEC by method A	CEC by method B
	%		mmhos/cm	——— %		———	meq/100	g
3565	29	7.6	2.37	1.53	2.2	--	15.0	16.0
3571	38	7.4	1.09	2.08	3.2	--	18.2	19.0
3582	29	9.2	4.96	1.06	5.6	--	18.0	13.7
3576	82	8.1	7.88	4.14	1.4	0.15	33.5	36.5
3564	40	7.6	79.5	4.30	7.7	0.84	31.3	20.8
3572	53	8.3	12.0	1.73	12.9	0.06	20.5	19.5
3580	46	7.6	5.13	2.33	3.8	1.46	22.0	24.4
3581	48	7.0	7.28	2.93	0.05	–	25.5	27.9
C3/575	54	7.8	12.9	7.40	25.0	26.5	15.6	16.2
C4/142	49	7.2	3.1	4.51	24.0	14.4	19.9	21.1
C4/155	45	7.7	2.9	2.52	28.0	7.3	12.7	12.7

† Saturation paste water content as percentage.
‡ pH of soil saturation paste.
§ Electrical conductivity of saturation extract.
¶ Air-dry water content (hygroscopic water).

Table 2 shows the CEC's of 11 different soils, which contain various amounts of $CaCO_3$, gypsum and salinity. With two exceptions, which are explained later, the CEC's were higher when determined with the newly developed method; this was as expected since the major errors in the Bower method result in reduced CEC values. Papanicolaou (1976) also found low CEC values for calcareous soils when he used the Bower method.

Lower CEC values were obtained with the newly developed method compared to the Bower method for two soils. To decide which method was the more accurate, especially for these two soils, we made an indirect test, since there exists no absolute reference method for CEC. CEC values were correlated with saturation percentage and air-dry (hygroscopic) water content, two soil properties known to be proportional to CEC (Banin and Amiel, 1969). In correlations involving saturation percentage, soils with > 10% $CaCO_3$ were excluded because their relation between SP and CEC would be expected to differ from that of noncalcareous soils. Similarly, in correlations involving hygroscopic water content, soils with > 5% gypsum and very high salinity (Soil 3564) were excluded because the method used to determine air-dry water content (loss of weight upon heating to 105°C) would be inaccurate due to loss of water of crystallization and hydration, respectively.

The coefficients of linear correlation *(r)* between CEC and SP were 0.78 and 0.96 where CEC was determined with the Bower and newly developed methods, respectively. When the CEC values of the two problem soils, as determined by the Bower method, were excluded from the regression, *r* was increased to 0.97. Thus, the problem soil CEC values determined by the Bower method seem questionable, rather than those determined by the newly developed method. The *r* values determined between CEC and hygroscopic water were 0.93 and 0.99 where CEC was determined with Bower and newly developed methods, respectively. The relations between hygroscopic water content and CEC, as determined with the new method, is shown in Fig. 1. The better correspondence between CEC and hygroscopic water content when the CEC values obtained with the new method are used, while not proof in it-

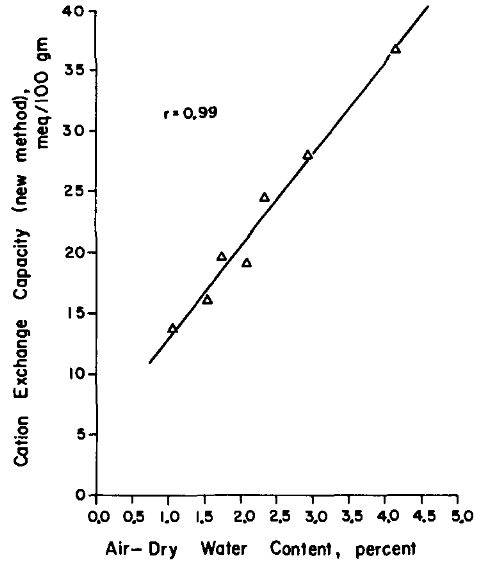

Fig. 1—Relations between cation exchange capacity and air-dry water content of soils.

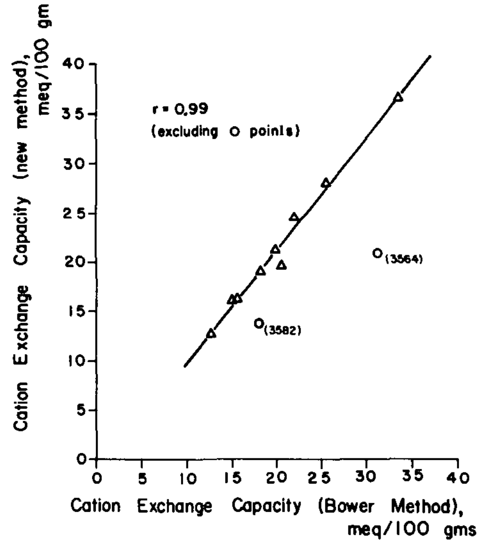

Fig. 2—Comparison of cation exchange capacities of soils as determined by the new and Bower methods.

self, gives credence to our conclusion that it is the Bower method CEC values that are questionable.

As mentioned earlier, high CEC values may be obtained in two ways in the Bower method. Some of the Na in the saturating solution may be carried over and subsequently extracted if the washing is incomplete. Or, nonexchangeable Na may be brought into solution during the extraction with NH_4 if the soils contain zeolitic or feldspathoidic minerals (Rhoades and Krueger, 1968). It seemed that the latter case was more likely since one of the problem soils (3582) has a high pH (9.2) and is high in bicarbonate content, the two conditions required for zeolites to exist in soils (Baldar and Whittig, 1968). The other problem soil (3564) was dominated by Na salts. To ascertain if these soils did indeed contain nonexchangeable Na which was extracted with NH_4OAc but not $MgNO_3$, as speculated, we extracted these soils using the extraction procedures of each method. Soil 3564 was washed once with water before extraction to remove most of the soluble sodium salts. No other pretreatments (saturation, etc.) were made. Soil 3582 released 9.5 and 8.0 meq Na/100 g upon extraction with NH_4OAc and $MgNO_3$, respectively. The analogous values for Soil 3564 were 16.6 and 8.0 meq/100 g, respectively. This evidence supports our assumption that these soils release nonexchangeable Na when extracted with ammonium acetate in the Bower method.

The CEC values obtained with the two methods are compared in Fig. 2. Linear correlation is excellent ($r = 0.99$), if the two CEC values concluded to be incorrectly determined using the Bower method are excluded. The CEC values determined with the new method are higher for the rest of the soils, as expected, because steps are eliminated that produce errors in conventional methods.

We conclude that the new method presented here is practical, simple, and reliable for determining CEC. We recommend its adoption, especially under arid-land conditions for calcareous and gypsiferous soils and for soils containing zeolites or feldspathoids. The method is not intended for acidic soils or other soils having appreciable anion exchange capacities.

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