Procedure for Determining Sodium–Calcium Selectivity in Calcareous and Gypsiferous Soils

C. Amrhein* and D. L. Suarez

ABSTRACT

A procedure to determine the exchanger-phase composition (and thus the Na/Ca selectivity) of calcareous and gypsiferous soils was developed and tested on three soils and three phyllosilicate minerals. The procedure corrects for anion exclusion and mineral weathering by measuring the Cl, SO$_4$, and HCO$_3$ in the soil solution and in the extracting solution. Anion exclusion was found to be significant in the montmorillonite system, but generally less than 10% of the cation-exchange capacity in the soil, illite, and vermiculite systems. Mineral weathering contributed significantly to the total extracted Ca. Thus, exchangeable-Ca values were overestimated by 30 to 500% in the gypsiferous soils and 3 to 20% in the calcareous soils when weathering was neglected. The proposed method allows the determination of cation-exchange capacity, exchangeable-cation composition, and anion exclusion at any solution composition, concentration, and pH.

SEVERAL PROBLEMS have been identified in the determination of exchangeable cations and cation-exchange capacity (CEC) of arid-zone soils (Rhoades, 1982; Thomas, 1982). Thomas (1982) states that, for soils containing CaCO$_3$ or gypsum, the traditional NH$_4$OAc extraction procedure should not be used to determine exchangeable Ca and that no satisfactory substitute exists. The high solubility of CaCO$_3$ and gypsum in 1.0 M NH$_4$OAc precludes the accurate estimation of exchangeable Ca. The preferred method to date has been to determine exchangeable sodium percentage (ESP) or exchangeable sodium ratio (ESR) by difference; that is, the CEC is determined separately and the exchangeable Ca or Ca + Mg is calculated as the difference between the CEC and the exchangeable Na + K (U.S. Salinity Laboratory Staff, 1954). Assuming exchangeable K to be negligible, the following relationship is often used (Nadler and Magaritz, 1981; Jurinak et al., 1984):

$$\text{ESR} = \text{NaX} / (\text{CEC} - \text{NaX})$$

where NaX is exchangeable Na.

For sodic, saline soils, the relationship between soluble Na and exchangeable Na is most commonly assumed to follow the relationship developed by the U.S. Salinity Laboratory Staff (1954):

$$\text{ESR} = -0.0126 + 0.01475\text{SAR}$$

where SAR is the sodium adsorption ratio, Na/(Ca + Mg)$^{1/2}$, with concentrations in mmol L^{-1} and the Gapon selectivity coefficient (K_G) is assigned an average value of 0.01475. Evaluation of the quantity of amendment needed to reclaim a sodic soil or the effect of a particular irrigation water on the ESP requires knowledge of K_G under the pertinent conditions.

C. Amrhein, Dep. of Soil and Environmental Science, Univ. of California, Riverside, CA 92521; and D.L. Suarez, U.S. Salinity Lab., 4500 Glenwood Dr., Riverside, CA 92501. Contribution from the U.S. Salinity Lab., Riverside, CA. Received 7 June 1989. *Corresponding author.

Exchangeable Na can be determined by several different methods. The traditional procedure (Bower et al., 1952) involves subtracting soluble Na (determined from a saturation extract) from the amount of Na extracted with 1.0 M NH$_4$OAc. However, Bower and Hatcher (1962) cautioned that, for highly saline soils (electrical conductivity of the saturation extract >10 dS/m), the traditional method for determining exchangeable Na may underestimate the true value due to anion exclusion (negative adsorption).

In an attempt to minimize the anion-exclusion problem, Nadler and Magaritz (1981) measured ESP values by first removing all soluble salts with ethanol washings prior to an NH$_4$OAc extraction. This procedure resulted in extraordinarily high ESP values when compared with those estimated from the SAR values of corresponding saturation extracts. The authors maintained that the ESP values represented true field conditions and that the measured SAR values were artificially low due to CaCO$_3$ dissolution into the saturation extract. However, the removal of soluble salts by washing prior to extraction of exchangeable cations should, in theory, reduce the measured ESP values as Ca from dissolving solid phases replaces some of the Na on soil exchange sites.

High exchangeable-Na values were also reported by Gupta et al. (1985) when high pH, sodic soils were first washed with 90% ethanol to remove soluble salts prior to extraction. They attributed these high values to Na release from zeolitic and feldspathoidic minerals that may have been present in the strongly alkali soils.

In addition to uncertainties in the determination of exchangeable Na, there are differences of opinion regarding the best method for determining CEC (Okazaki et al., 1963; Rhoades, 1982). Various procedures for CEC have been developed that have attempted to reduce the effects of Ca-mineral dissolution by: (i) suppressing the solubility of CaCO$_3$ and gypsum through the use of water/alcohol mixtures, high pH, or both (Bower et al., 1952; Polemio and Rhoades, 1977; Misopolinos and Kalovoulos, 1984; Tucker, 1985; Gupta et al., 1985; Begheyn, 1987); (ii) removing the CaCO$_3$ and gypsum by repeated washings or reaction with selective-exchange resins (Frenkel et al., 1986; Cruanas and Cardus, 1987); or (iii) dissolving and reprecipitating the CaCO$_3$ and gypsum as a less soluble phase (Begheyn, 1987). Rhoades (1982) recommends the CEC procedure developed by Polemio and Rhoades (1977) for such soils. However, there has been some concern that the use of alcohol-based solutions may alter the solvation of cations and the dielectric constant of the solution, thereby affecting the double-layer environment of the exchanger (Gupta et al., 1985).

In addition, Gupta et al. (1984) observed both an increase in CEC and an increase in Ca selectivity when CaCO$_3$ was removed from soils. This is consistent with the problem of incomplete Na saturation during the CEC determination in the presence of CaCO$_3$, resulting in higher apparent ESP values.

Since the CEC of many soils is sensitive to ionic strength and pH (Pratt, 1961; Pratt et al., 1962; Chan et al., 1979; Gillman, 1981; Kalisz, 1986), it would be preferred if the exchangeable cations and the cation selectivity could be determined under conditions somewhat representative of the field. In addition to the problems with variations in CEC and exchangeable Na (and, thus, errors in calculated SAR–ESR relations), the present procedures do not allow investigation of the variation in Na–Ca selectivity of calcareous and gypsiferous soils as a function of pH and ionic strength.

The procedure described here was developed to determine the composition of the exchangeable cations (and, thus, Na–Ca selectivity) in calcareous and gypsiferous soils, taking into account the weathering of $CaCO_3$ and gypsum during the equilibration and extracting steps and accounting as well for anion exclusion.

Rather than try to suppress Ca-mineral dissolution or to selectively remove these minerals, the procedure corrects for mineral dissolution by measuring SO_4 and $CO_3 + HCO_3$, both in the bulk solution and in the extracting solutions. The dissolution of gypsum and calcite during the extraction step is accounted for by assuming that the SO_4 in the extracting solution is due to gypsum dissolution and that the HCO_3 is from calcite dissolution. Correction is made for HCO_3 and SO_4 in the soil solution or as soluble salts in the soil prior to extraction. The idea of correcting for weathering by measuring the resultant $CO_3 + HCO_3$ has been proposed by Carpena et al. (1972) and Papanicolaou (1976) for calcareous soils; however, there are important differences between their procedures and our method. Also, Rhoades (1982) suggested that measurement of SO_4 could be used to correct for gypsum dissolution in gypsiferous soils. Correction for primary mineral weathering is not included in this procedure and is assumed to be insignificant compared with calcite and gypsum dissolution.

In contrast to earlier methods, the proposed procedure can be used to simultaneously determine the composition of the exchanger, the CEC, and the selectivity coefficient at any solution composition, concentration, and pH. In addition, this procedure allows the determination of anion exclusion, which can be significant under saline conditions. The method also avoids the use of Ba salts, which cause enhanced $CaCO_3$ dissolution due to $BaCO_3$ precipitation.

This procedure was tested on three soils and three specimen phyllosilicate minerals at concentrations ranging from 25 to 1000 $mmol_c$ L^{-1} and at SAR values ranging from 0 to 50 $(mmol/L^{-1})^{1/2}$.

In addition, we present some data on mineral solubility in various solutions. These data explain many of the anomalous SAR–ESP relationships found in the literature.

MATERIALS AND METHODS

The solubility of $CaCO_3$ and gypsum in various solutions was determined by batch equilibration and determination of Ca in the supernatant solutions. The solubility of Na salts in ethanol/water mixtures was determined by batch equilibration and electrical-conductivity measurement of the supernatant.

Table 1 lists some general characteristics of the three soils studied. The soils differ mainly in mineralogy and gypsum content. The Imperial Valley clay was sampled in the Imperial Valley, California, from an area mapped as the Imperial clay series, which is classified as a fine, montmorillonitic (calcareous) hyperthermic Vertic Torrifluvent. The Shiprock and Many Farms soils were sampled on the Navajo Indian Reservation near the locations of the same names. The Shiprock soil has not been mapped, but appears to be a mesic Torriorthent (possibly Shalet or Fruitland series). The Many Farms soil is also unmapped but appears to be a mesic Torrifluvent (possibly Tours or Navajo series). The surface soils (0–15 cm) were used in these studies.

The phyllosilicate minerals included Wyoming bentonite (SWy-1; Source Clays Repository, Columbia, MO), Silver Hill illite (Source Clays Repository), ground and sieved to <250 μm; and a specimen of Utah vermiculite, ground to <250 μm (described by and obtained from Rhoades [1967]). These three minerals represent predominant clay minerals contributing to the CEC of arid-land soils.

A weighed amount of soil (5 g) or clay (1 g) was added to a tared 50-mL centrifuge tube an equilibrated with a solution of known pH and chemical composition by repeated shaking, centrifuging, and decanting. This equilibrium step was repeated four times for each sample. For dilute solutions, we preferred to first rinse the soil with a solution of high concentration and then subsequently step down to a low concentration, keeping the SAR and pH constant. In this study, we used solutions made with Na, Ca, Cl, SO_4, and HCO_3 at SAR values from 0 to 50 $(mmol$ $L^{-1})^{1/2}$. Magnesium was not added to the solution, and analysis for Mg in the equilibrating and extracting solution showed negligible amounts.

Following the fourth equilibration, the suspension was centrifuged and the supernatant saved for analysis.

The mass of equilibrating solution entrained in the centrifuged soil was determined by weighing the centrifuge tube plus wet soil. This is the *carryover solution*. The volume of carryover solution was determined using the solution density of the final decantation, which was measured by weighing a pipetted volume. A density of 1.0 can be assumed if the salt concentration is <0.2 M.

The wet soil was extracted with a solution made from a salt that had a cation and anion that were not found in the equilibrating solution. Ammonium acetate is traditionally used for this step, but is not recommended. Not only does NH_4OAc solubilize large quantities of $CaCO_3$ (as further demonstrated below), but titrating HCO_3 in the 1.0 M OAc solution requires an additional step (Amrhein and Suarez, 1987). To eliminate these problems, we used 0.25 M $Mg(NO_3)_2$, as also used in the Polemio and Rhoades (1977) CEC procedure. If the original equilibrating solution contained Mg or NO_3, however, this extractant would not be suitable.

Analyses of the equilibrating and extracting solutions for Ca, Mg, K, Na, and SO_4 were done by inductively coupled argon plasma spectrometry. Alkalinity was determined by titration to pH 4.40 using 0.010 M $KH(IO_3)_2$ (National Bureau of Standards primary acid standard). Chloride was determined by argentiometric titration on an automated Cl titrator.

This procedure requires more analyses than other CEC and cation-selectivity methods, since HCO_3 and SO_4 need to be determined on both the equilibrating and extracting solutions. However, the procedure also can be used in situations where simultaneous determination of exchangeable cations, CEC, and anion exclusion is desired.

The calculations partition the total extracted cations and anions into several possible phases. Calcium in the $Mg(NO_3)_2$ extracting solution could have come from the exchange phase (CaX), the solution phase (carryover solution),

Table 1. Characteristics of the soils and minerals on which the procedure was tested.

Soil/mineral	Dominant clay mineralogy†	CaCO₃ equivalent	Gypsum	Texture			Surface area	Surface charge density
				Clay	Silt	Sand		
		g kg⁻¹					m² g⁻¹	μmol_c m⁻²
Imperial Valley clay	S,V,M,K	109	trace	560	430	10	295	1.02
Shiprock soil, A horizon	V,K,M,C	113	93	240	530	230	115	1.05
Many Farms soil, A horizon	M,V,S,K	139	0	200	420	380	121	1.12
Wyoming bentonite (SWy-1)	S	trace	ND‡		ND		753	0.91
Silver Hill illite (IMt-1)	M	0	ND		ND		119	1.14
Utah vermiculite	V	0	ND		ND		173	4.15

† Mineralogy key (based on relative x-ray diffraction peak intensities): S, smectite; V, vermiculite; M, mica (illite); K, kaolinite; C, chlorite.
‡ Not determined

or from dissolving carbonates or gypsum. Sodium in the extracting solution is partitioned into exchanger and solution phases. Sodium from the dissolution of zeolites or feldspathoid minerals (Rhoades and Krueger, 1968; El-Nahal and Whittig, 1973) is not considered in the procedure; however, the use of Mg as an extractant should suppress the removal of lattice Na from zeolite (El-Nahal and Whittig, 1973). Chloride in the extracting solution is partitioned wholly into the solution phase. Anion adsorption is not specifically accounted for, but, instead, determined as the net results of concurrent anion adsorption and anion exclusion. In many soils, anion exclusion is nearly balanced by anion adsorption. Sulfate and HCO₃ are partitioned into both the solution phase and dissolved-mineral phase (gypsum and CaCO₃).

The composition of the exchanger phase was determined using modifications of the different methods originally outlined by Bolt et al. (1978). The following terms are defined:

i = ions participating in the reaction,

T_i = total ions found in the $Mg(NO_3)_2$ extract (mmol_c kg⁻¹),

C_i = concentration of ions in the carryover solution (mmol_c kg⁻¹),

$[i]$ = ion concentration in the final-rinse decantation (mmol_c L⁻¹),

iX = ions associated with the exchanger phase (mmol_c kg⁻¹),

θ_v = gravimetric solution content, = volume of carryover solution/soil wt. (L kg⁻¹),

E_i = equivalent fraction of ion in solution; E_{Na} = [Na]/[Na] + [Ca], and E_{Ca} = [Ca]/[Na] + [Ca],

ESR = NaX/CaX, and

CEC = is in mmol_c kg⁻¹.

Method A, from Bolt et al. (1978), assumes that Cl is the only anion in the equilibrating solution and that the equivalent fractions of Na and Ca in the carryover solution are equal to the equivalent fractions of those same ions in the equilibrating solution. Anion exclusion is accounted for by considering only cations associated with anions in the carryover solution to be soluble. All other cations are considered exchangeable.

METHOD A:

NaX = $T_{Na} - T_{Cl}E_{Na}$
CaX = $T_{Ca} - T_{Cl}E_{Ca}$
ESR = NaX/CaX or NaX/(CEC − NaX)
CEC = NaX + CaX

Method B assumes that the concentrations of cations in the carryover solution are equal to the concentrations in the final decantate, and that Na, Ca, and Cl are the only ions in the system. Anion exclusion is accounted for by calculating an excess Cl value. This term (ClX) is generally negative, indicating that the carryover solution is deficient in Cl, compared with the bulk-solution Cl concentration.

METHOD B:

NaX = $T_{Na} - \theta_v[Na]$
CaX = $T_{Ca} - \theta_v[Ca]$
ClX = $T_{Cl} - \theta_v[Cl]$
ESR = NaX/CaX or NaX/(CEC − NaX + ClX)
CEC = NaX + CaX − ClX

In soils containing CaCO₃ and gypsum, mineral weathering can affect the composition of both the equilibrating rinse (soil solution) and the extracting solution. Specifically, the anions SO₄ and HCO₃ will be present in the soil solution as well as Cl, and the amount of exchangeable Ca can be in error due to extensive mineral dissolution during the extraction step.

Following are the additions we have made to the Bolt et al. (1978) methods. First, in order to determine the concentration of SO₄ and HCO₃ in the carryover solution (Method A), we assumed that the fraction of HCO₃ and SO₄ that was excluded from the carryover solution (due to anion exclusion) was the same as for Cl. This approximation is good for HCO₃ and is probably reasonable for SO₄, even though SO₄ exclusion is probably greater than Cl exclusion, it is counter-balanced by higher SO₄ adsorption. Exact calculation of excluded HCO₃ and SO₄ is not possible, due to mineral weathering during the extraction step. In the systems studied, Cl was the dominant anion, particularly at high concentrations. Since the quantity of salt involved in anion exclusion was significant only at concentrations >100 mmol_c L⁻¹ (Jurinak et al., 1984), the assumption of equal exclusion seems reasonable. Assuming that all of the extracted Cl was from the carryover solution, then T_{Cl} = carryover Cl. Therefore, the fraction of Cl excluded from the carryover solution is equal to 1 − $T_{Cl}/\theta_v[Cl]$. Assuming that the fraction of HCO₃ excluded is equal to the fraction of Cl excluded yields

$$\frac{\text{Carryover HCO}_3}{\theta_v[HCO_3]} = \frac{T_{Cl}}{\theta_v[Cl]}$$

Solving for carryover HCO₃ (C_{HCO_3}) simplifies this expression to

$$C_{HCO_3} = [HCO_3]T_{Cl}/[Cl]$$

By analogy, the carryover SO₄ (C_{SO_4}) can be estimated by

$$C_{SO_4} = [SO_4]T_{Cl}/[Cl]$$

The correction for CaCO₃ and gypsum dissolution is based on the assumption that any HCO₃ and SO₄ found in the extracting solution, in excess of that which should be present from the carryover solution, is due to calcite and gypsum dissolution, respectively. Thus, the amount of Ca in the extracting solution is partitioned into contributions from the exchanger phase, the solution phase, and dissolving mineral phases.

The amount of Ca added to the $Mg(NO_3)_2$ extract as a result of weathering was calculated as follows:

Ca derived from $CaCO_3$ dissolution $= Ca_{calcite} = T_{HCO_3} - C_{HCO_3}$

Ca derived from gypsum dissolution $= Ca_{gypsum} = T_{SO_4} - C_{SO_4}$

The calculations for exchangeable cations, CEC, and anion exclusion were then performed as follows:

CORRECTED METHOD A:

$NaX = T_{Na} - (T_{Cl} + C_{SO_4} + C_{HCO_3})E_{Na}$

$CaX = T_{Ca} - (T_{Cl} + C_{SO_4} + C_{HCO_3})E_{Ca} - Ca_{calcite} - Ca_{gypsum}$

$ESR = NaX/CaX$

$CEC = NaX + CaX$

CORRECTED METHOD B:

$NaX = T_{Na} - \theta_v[Na]$

$CaX = T_{Ca} - T_{HCO_3} - T_{SO_4} + \theta_v([HCO_3] + [SO_4] - [Ca])$

$ClX = T_{Cl} - \theta_v[Cl]$

$HCO_3X = \dfrac{[HCO_3]ClX}{[Cl]}$

$SO_4X = \dfrac{[SO_4]ClX}{[Cl]}$

$CEC = NaX + CaX - ClX - SO_4X - HCO_3X$

$ESR = NaX/CaX$ or $NaX/(CEC - NaX + ClX + SO_4X + HCO_3X)$

The example in Table 2 is given to clarify and compare the calculations. The soil, in this case, was calcareous and slightly gypsiferous, and the initial equilibrating solution had a total concentration of 25 $mmol_c$ L^{-1} and an SAR of 5. Since the total solution concentration was low, the correction for

anion exclusion was minimal (ClX, HCO_3X, and SO_4X are close to zero). However, the correction for mineral weathering was significant, as can be seen by comparing CaX and CEC values.

Failure to correct for mineral weathering resulted in a 28% error in the CEC (too large) and a 15% error in the ESR (too low), so the mineral-weathering correction is important. In this instance, the K_G value was too low by 15% and 27%, respectively, using Method A and B without mineral-weathering corrections. Using Method B for estimating the ESR may be invalid because the exchangeable cations do not necessarily sum to the CEC (Helmy, 1963a,b). The term *total adsorbed metal charge* has been used by Sposito et al. (1983) for the sum of exchangeable cations calculated using Method B. If anion exclusion is insignificant, the CEC will be equal to the total adsorbed metal charge. In soils or clays where anion exclusion is important, the ESR values determined by the two methods can be significantly different (see below).

The determination of cation selectivity in soils equilibrated at high salt concentrations requires particularly accurate determination of the solution composition. In this procedure (and in all other procedures where there is no removal of soluble salts prior to extraction, including the Polemio and Rhoades [1977] CEC method), there is the potential for error magnification. This problem can be attributed to the likely error when one large number is subtracted from another large number to obtain a small number (in this instance the exchangeable-cation concentration). For example, the carryover Na (from the original equilibrating solution or from initial soluble salts) can be a significant proportion of the total extracted Na. The difference between the total extracted Na and the carryover Na is taken as the exchangeable Na.

A sensitivity analysis of the potential error in this procedure was done by assuming the exchanger to be Na saturated and that NaCl was the only soluble salt (Table 3). This analysis assumed a 5% error in the determination of both Na (5% too high) and Cl (5% too low) in the extracting solution. Such assumptions yield a maximum possible error for this situation. The carryover-solution-volume/soil-weight ratios in Table 3 are actual measured values for soils and clays after centrifugation and decantation. Table 3 shows that the potential error increases with increasing solution concentration. The Polemio and Rhoades (1977) CEC method recommends equilibrating the soil with 0.5 M Na, so potential errors for this particular procedure would range from 18 to 55%. Decreasing the equilibrating solution concentration to 0.050 M would reduce the error to acceptable levels at the assumed 5% error levels for Na and Cl. Unfortunately, as shown later, 0.05 M solutions may be insufficient to achieve Na saturation.

The determination of exchangeable cations in calcareous and gypsiferous soils of low CEC requires replication and careful, accurate analyses. This is especially true when such samples are equilibrated with saline solutions.

Table 2a. Composition of the final equilibrium solution and the soil-solution content (θ_v) prior to extraction.

Na	12.67 $mmol_c$ L^{-1}
Ca	14.56 $mmol_c$ L^{-1}
Cl	25.03 $mmol_c$ L^{-1}
HCO_3	0.27 $mmol_c$ L^{-1}
SO_4	1.95 $mmol_c$ L^{-1}
θ_v	0.562 L kg^{-1}

Table 2b. Amount of cations and anions in the $Mg(NO_3)_2$ extracting solution.

	$mmol_c$ kg^{-1}
Total Na	13.2
Total Ca	158.5
Total Cl	13.9
Total HCO_3	25.1
Total SO_4	10.0

Table 2c. Calculated values for exchangeable cations and anion exclusion using Methods A† and B‡.

	Corrected for mineral weathering		Not corrected for mineral weathering	
	Method A	Method B	Method A	Method B
		$mmol_c$ kg^{-1}		
SO_4 in carryover solution	1.1	–	–	–
HCO_3 in carryover solution	0.2	–	–	–
Exchangeable Na	6.1	6.1	6.7	6.1
Exchangeable Ca	116.6	116.1	151.1	150.3
Cl exclusion	–	−0.17	–	−0.17
HCO_3 exclusion	–	−0.002	–	–
SO_4 exclusion	–	−0.013	–	–
Cation-exchange capacity	122.7	122.8	157.8	156.6
Exchangeable Na ratio	0.052	0.052	0.044	0.041
Gapon selectivity coefficient (K_G)	0.0111	0.0111	0.00943	0.00863

† Method A uses the anion concentration in the extracting solution to calculate the concentration of soluble cations carried over from the equilibrating step to the extracting step.

‡ Method B uses the volume of the equilibrating solution carried over to the extracting step to calculate the concentration of soluble cations present in the extracting solution.

Table 3. Potential error in calculation of cation-exchange capacity (CEC) assuming a Na-saturated soil and that both Na and Cl concentrations are in error by 5%.

Actual CEC	Carryover-solution volume to soil-weight ratio	Measured CEC at three solution concentrations		
		0.050 M	0.50 M	1.0 M
$mmol_c \cdot kg^{-1}$	$L \cdot kg^{-1}$		$mmol_c$ kg^{-1}	
50	0.50	54	78	103
100	0.50	110	130	155
300	0.75	321	354	390
700	2.80	770	875	1015

RESULTS AND DISCUSSION

The solubility of Na salts in ethanol and the solubilities of $CaCO_3$ and gypsum in various extracting solutions are reported in Table 4. The use of ethanol to remove soluble salts from soils is ineffective, due to the low solubility of Na_2SO_4 and Na_2CO_3. In fact, the high ESP values reported by Nadler and Magaritz (1981) and Gupta et al. (1985) can be attributed to incomplete removal of Na salts from their soils. Gupta et al. (1985) washed sodic, high pH soils with 90% ethanol until the electrical conductivity of the solution was less than 0.010 dS/m. According to the solubility data of Table 4, significant amounts of Na_2SO_4 may still be present under such conditions. Subsequent extraction with NH_4OAc would then dissolve the Na_2SO_4, which would be reported as exchangeable Na.

Workers often adjust NH_4OAc solutions to pH 8.6 in order to suppress $CaCO_3$ solubility. The data in Table 4 demonstrate that this is only partially effective in reducing $CaCO_3$ dissolution. The data also further demonstrate the problem of using NH_4OAc to measure exchangeable-Ca levels.

Due to the solubility of $CaCO_3$ and gypsum in the 0.25 M $Mg(NO_3)_2$ extracting solution, the weathering correction for exchangeable Ca was significant in our study, but varied depending on contact time with the extracting solution. For gypsiferous systems without weathering corrections, exchangeable Ca would have been overestimated by 30 to 500% with resultant errors in K_G of comparable magnitude. In the calcareous system, the weathering correction reduced the apparent-exchangeable-Ca values by 3 to 20% and increased the K_G values by the same percentage. The correction for mineral dissolution in the pure mineral systems varied from 0 to 20%, apparently depending on the amount of impurities in the mineral specimen. We knew from earlier work that the Wyoming bentonite sample had a trace of $CaCO_3$ (Amrhein, 1987, unpublished data).

Representative values for the various corrections to ESR as a function of SAR at two different total concentrations are presented in Fig. 1. The points marked A (solid circles) are the ESR values determined by modified Method A, which includes mineral weathering and anion exclusion. This is considered the best estimate of the ESR and, thus, of K_G. The points marked B (open circles) are the ESR values determined by modified Method B, which includes the weathering corrections but assumes no anion exclusion. The differences between points A and B are due to anion exclusion. The points marked C (open triangles) are the ESR values determined by the old Method B without the mineral-weathering or anion-exclusion corrections. Since the slope of the ESR–SAR plot is K_G, an accurate determination of the ESR is required in order to observe differences in the selectivity coefficient due to total solution composition, pH, or exchanger-phase composition.

For the Shiprock soil, and for the Many Farms soil at low concentrations, anion exclusion was not an important phenomenon. For the Wyoming bentonite and the Many Farms soil at higher concentration, however, anion exclusion was important. This suggests that ESR calculations using Method B will not be accurate. The

Table 4a. Solubility of Na salts in ethanol/water (v/v) mixtures.

Salt	Electrical conductivity of saturated solution	
	95% ethanol	90% ethanol
	dS m⁻¹	
Na_2SO_4	0.0025	0.0050
Na_2CO_3	0.019	0.029
$NaHCO_3$	0.075	0.122
NaCl	0.87	0.93
NaOAc	2.44	2.46

Table 4b. Calcium carbonate and gypsum solubility in water and salt solutions.

	$CaCO_3$	Gypsum
	mmol$_c$ L⁻¹	
Water	0.3	30
1.0 M NH_4OAc, pH 8.6	9.1	133
1.0 M NH_4OAc, pH 7.0	20.5	135
0.25 M $Mg(NO_3)_2$, pH 7.0	2.7	101

data uncorrected for mineral weathering (open triangles) always underestimate the ESR values, especially in the gypsiferous system (Fig. 1, Shiprock soil).

One advantage of this new procedure is that it allows the determination of cation selectivity and CEC at any exchanger-phase composition. Figure 2 shows the relationship between modified Method A and modified Method B for calculating cation-exchange capacity. Plotted on Fig. 2 are 150 points, each point representing the average of four replications determined on three soils and three clay minerals of concentrations from 25 to 1000 mmol$_c$ L⁻¹, SAR values from 0 to 50, and pH values from 6.5 to 8.5. Figure 2 shows that either calculation method will yield the same CEC value when anion exclusion and mineral weathering are properly taken into account.

Table 5 compares the CEC as measured by the Polemio and Rhoades (1977) method, a modified Polemio and Rhoades method in which the saturating solution was made to several different concentrations (at SAR = ∞), and the proposed procedure at concentrations 25, 50, 125, 500, and 1000 mmol$_c$ L⁻¹ and SAR values of 0, 5, 15, 25, and 50 (mmol L⁻¹)$^{1/2}$. The Polemio and Rhoades (P&R) method, when modified to low saturating-solution concentrations, gives low CEC values (Table 5). This is attributed to incomplete saturation of the exchanger with Na as a result of Ca release during weathering. This demonstrates that, in calcareous soils, it is nearly impossible to saturate a soil with Na at solution concentrations <0.5 M. This explains the low CEC values measured by Gupta et al. (1984) using 0.1 M NaCl. The recommended Na concentration for CEC determinations by the P&R method is 0.5 M.

There was no trend in the CEC with either total electrolyte concentration or ESP for the soils or minerals equilibrated with various salt solutions (Table 5). This is in contrast to the reported increases in CEC with increasing ionic strength for soils high in variable-charge materials (Chan et al., 1979; Gillman, 1981; Kalisz, 1986). Thus, for soils low in kaolinite, Fe–Al oxides, and organic matter, the assumption of constant
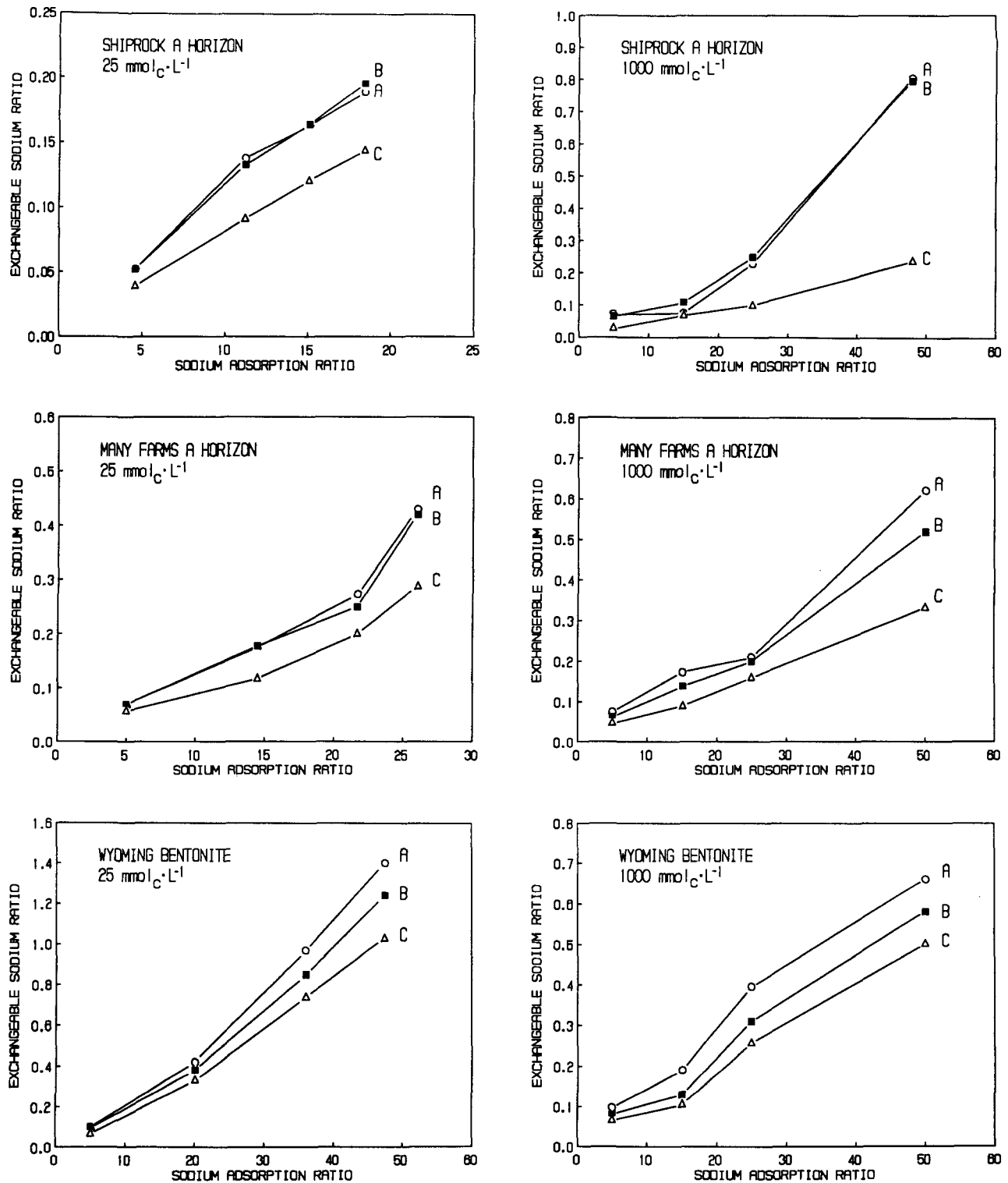
Fig. 1. The relationship between ESR and SAR as calculated by three methods at two concentrations. Line A corresponds to modified method A, which corrects for both mineral weathering and anion exclusion. Line B corresponds to modified method B, which corrects for mineral weathering but not anion exclusion. Line C corresponds to unmodified method B, which does not correct for either mineral weathering or anion exclusion.

CEC at a given pH seems reasonable. Determinations of K and Mg in the equilibrating solutions and K in the extracting solutions showed that release of these cations during extraction was negligible. The CEC determined by the new procedure agreed quite well with that from the P&R method (at 500 mmol$_c$ L^{-1}) for all of the samples except illite. The CEC of illite was strongly dependent on ionic strength in the 60% ethanol solution but not in the water suspensions. Mineral weathering cannot explain such results.

Table 5. Cation-exchange capacity determined at various equilibrating solution concentrations.

Soil or mineral	Concentration, mmol$_c$ L^{-1}						
	20†	50†	125†	500†	760†	1000†	25–1000‡
	cmol$_c$ kg^{-1}						
Imperial Valley clay	13.6 ± 0.1	17.8 ± 0.2	22.8 ± 0.4	30.2 ± 0.7	31.1 ± 1.0	29.4 ± 1.2	28.1 ± 2.3
Shiprock soil, A horizon	6.4 ± 0.1	9.4 ± 0.0	10.5 ± 0.2	12.1 ± 0.3	12.1 ± 0.5	12.7 ± 1.5	11.7 ± 1.0
Many Farms soil, A horizon	13.4 ± 0.2	13.2 ± 0.2	13.4 ± 0.4	13.5 ± 0.6	13.8 ± 0.7	14.0 ± 0.7	13.0 ± 0.7
Wyoming bentonite	56.2 ± 0.8	60.3 ± 1.8	68.1 ± 0.9	68.2 ± 1.4	70.0 ± 2.3	68.5 ± 0.9	66.4 ± 4.4
Utah vermiculite	70.0 ± 0.5	73.1 ± 1.4	73.0 ± 1.5	71.8 ± 1.8	ND§	70.7 ± 2.1	71.2 ± 6.7
Silver Hill illite	11.5 ± 0.1	12.6 ± 0.3	13.5 ± 0.1	17.1 ± 1.5	ND	24.0 ± 2.2	13.6 ± 1.5

† Modified Polemio and Rhoades (1977) method, uncorrected for mineral dissolution, SAR = ∞.
‡ Proposed procedure, corrected for anion exclusion and mineral weathering. Mean of all samples equilibrated with 25, 50, 125, 500, 1000 mmol$_c$ L^{-1} and SAR values 5, 15, 25, and 50 (mmol L^{-1})$^{1/2}$ and SAR = 0 at 100 mmol$_c$ L^{-1}.
§ Not determined.

Table 6. Measured anion exclusion ± standard deviation as a function of equilibrium solution concentration and sodium adsorption ratio (SAR).

Equilibrium solution concentration	Wyoming bentonite				Utah vermiculite			
	SAR 5	SAR 15	SAR 25	SAR 50	SAR 5	SAR 15	SAR 25	SAR 50
mmol$_c$ L^{-1}	cmol$_c$ kg^{-1}							
25	−1.3 ± 0.3	−2.5 ± 0.1	−3.6 ± 0.3	−4.3 ± 0.5	−0.09 ± 0.06	0.04 ± 0.09	−0.07 ± 0.05	0.14 ± 0.08
50	−1.7 ± 0.1	−2.4 ± 0.8	−3.5 ± 0.5	−6.1 ± 1.7	−0.21 ± 0.04	−0.06 ± 0.03	−0.22 ± 0.02	−0.88 ± 0.40
125	−3.3 ± 0.3	−2.7 ± 0.2	−4.4 ± 0.3	−6.3 ± 0.1	−0.85 ± 0.21	−0.64 ± 0.60	−0.25 ± 0.10	−1.2 ± 0.2
500	−11.7 ± 0.4	−16.9 ± 1.7	−11.9 ± 0.9	−9.5 ± 0.2	−3.9 ± 0.2	−1.0 ± 2.5	−0.9 ± 1.7	−2.7 ± 1.1
1000	−19.4 ± 1.5	−19.4 ± 2.9	−18.9 ± 1.2	−13.9 ± 1.0	−3.2 ± 0.7	−4.7 ± 2.4	−5.5 ± 2.6	−3.9 ± 1.7

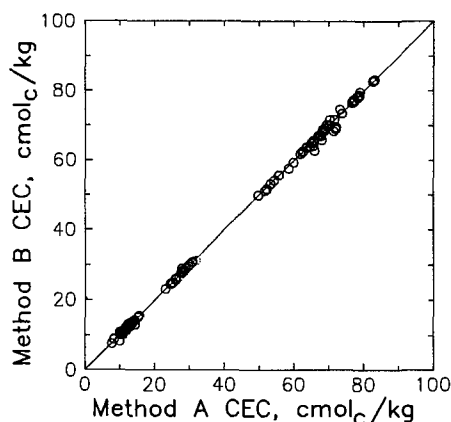| Equilibrium solution concentration	Many Farms soil, A horizon			
	SAR 5	SAR 15	SAR 25	SAR 50
mmol$_c$ L^{-1}	cmol$_c$ kg^{-1}			
25	−0.06 ± 0.05	−0.03 ± 0.01	−0.29 ± 0.07	−0.06 ± 0.01
50	−0.13 ± 0.07	−0.23 ± 0.05	−0.15 ± 0.01	−0.27 ± 0.05
125	−0.39 ± 0.13	−0.38 ± 0.03	−0.37 ± 0.03	−0.56 ± 0.09
500	−0.73 ± 0.65	−1.3 ± 0.2	−1.3 ± 0.5	−0.72 ± 0.22
1000	−0.19 ± 0.86	−1.8 ± 0.6	−0.65 ± 0.24	−1.1 ± 0.05

Fig. 2. Cation-exchange capacities (CEC) as determined by the modified Methods A and B when mineral weathering and anion exclusion are taken into account. See text for description of Methods A and B.

Calculation by Method B allows quantification of anion exclusion at various salt concentrations and exchanger compositions. Table 6 gives the anion-exclusion values for the bentonite, vermiculite, and Many Farms samples, and shows that anion exclusion was a significant fraction of the total CEC for bentonite (as much as 28% at 1.0 mol$_c$ L^{-1}). Thus, determination of exchangeable cations by Method B without accounting

for anion exclusion could result in an error in the CEC. Based on the extent of exclusion on SWy-1 bentonite at 50 mmol$_c$ L^{-1}, the observation of decreasing total adsorbed metal charge with increasing exchangeable Na, as reported by Sposito et al. (1983), may be explained by anion exclusion.

The surface-charge density of vermiculite was 4.5 times larger than that of the bentonite. Thus, according to diffuse-double-layer theory, vermiculite should exhibit more anion exclusion and a lower K_G value. Measured anion exclusion, however, was substantially lower for the vermiculite system, and its average K_G value was more than double that of the bentonite system. The quantity of salt involved in anion exclusion tended to increase (predictably) with increasing concentration, but was largely unaffected by exchanger composition. El-Swaify et al. (1967) found anion exclusion on vermiculite to be independent of both ionic strength and exchanger composition. However, Jacobs (1966) found a trend of increasing anion exclusion with increasing salt concentration for hydrobiotite, similar to our results.

The Imperial Valley soil has a high CEC and its clay mineralogy is dominated by smectite. Even though anion exclusion was expected in this system, it was not significant (mean = 0.2 ± 0.8 cmol kg^{-1}). It seems likely that anion exclusion occurs, but is being balanced by anion adsorption. The exclusion calculation

actually yields net anion exclusion (exclusion minus adsorption). A similar conclusion can be made for the illite and for the Shiprock soil, which also had no net anion exclusion (mean values of 0.1 ± 1.2 and 0.3 ± 0.7 cmol kg^{-1}, respectively). The Many Farms soil exhibited some anion exclusion with increasing salt concentration; however, the amount was low, generally less than 10% of the CEC (Table 6).

CONCLUSIONS

Exchanger-phase composition and Na–Ca selectivity of calcareous and gypsiferous soils were accurately determined by accounting for mineral dissolution during the equilibration and extracting steps. This offers an alternative to the currently accepted procedure of calculating exchangeable Ca by difference. Thus, it allows for the determination of exchangeable cations, CEC, anion exclusion, and Na–Ca selectivity at any solution composition, concentration, and pH. This is in contrast to other methods, which require as many as three different soil samples for individual determinations of CEC, exchangeable cations, and soluble cations. The use of ethanol to remove soluble salts prior to extraction for exchangeable cations is not recommended, due to the low solubility of Na salts in ethanol/water mixtures.

Anion exclusion was accounted for, and mineral weathering was determined, by measuring the CO$_3$ + HCO$_3$ alkalinity and the SO$_4$ in equilibrating and extracting solutions. Weathering corrections were significant when determining exchangeable Ca, which would have been overestimated by 30 to 500% in the gypsiferous soils and 3 to 20% in the calcareous soils with similar errors in the K_G values.

No trends in CEC with ionic strength (.025–1.45 M) or exchangeable Na were observed for the three soils and three minerals studied, when anion exclusion and mineral weathering were properly accounted for. Anion exclusion was significant in the Wyoming bentonite system but was generally <10% of the CEC for all other systems. Apparently, anion exclusion was partly balanced by anion adsorption on the soils and the illite sample.

With the exception of the illite data, there was good agreement between the P&R CEC method and our proposed method. Two methods for partitioning the total extracted cations into soluble and adsorbed phases were compared. The method using anion analysis to calculate soluble cations (Method A) was preferred over the gravimetric method to determine the volume of entrained solution (Method B), because the sum of the exchangeable cations is consistently equal to the CEC in Method A. In Method B, a portion of the CEC is accounted for via an anion-exclusion term. Thus, the sum of exchangeable cations may not necessarily equal the CEC.

ACKNOWLEDGMENTS

REFERENCES

Amrhein, C., and D.L. Suarez. 1987. Calcite supersaturation in soils as a result of organic matter mineralization. Soil Sci. Soc. Am. J. 51:932–937.
Begheyn, L.Th. 1987. A rapid method to determine cation exchange capacity and exchangeable bases in calcareous, gypsiferous, saline and sodic soils. Commun. Soil Sci. Plant Anal. 18:911–932.
Bolt, G.H., M.G.M. Bruggenwert, and A. Kamphorst. 1978. Adsorption of cations by soil. p. 54–90 In G.H. Bolt and M.G.M. Bruggenwert (ed.) Soil chemistry. A. Basic elements. Elsevier Scientific Publ. Co., New York.
Bower, C.A., and J.T. Hatcher. 1962. Characterization of salt-affected soils with respect to sodium. Soil Sci. 93:275–280.
Bower, C.A., R.F. Reitemeier, and M. Fireman. 1952. Exchangeable cation analysis of saline and alkali soils. Soil Sci. 73:251–261.
Carpena, O., A. Lax, and K. Vahtras 1972. Determination of exchangeable cations in calcareous soils. Soil Sci. 113:194–199.
Chan, K.Y., B.G. Davey, and H.R. Geering. 1979. Adsorption of magnesium and calcium by a soil with variable charge. Soil Sci. Soc. Am. J. 43:301–304.
Cruanas, R., and J. Cardus. 1987. Cation exchange capacity determination in soils: Study of a new potentiometric method for calcareous, gypsiferous, and saline soils. Soil Sci. 144:311–318.
El-Nahal, M.A., and L.D. Whittig. 1973. Cation exchange behavior of a geolitic sodic soil. Soil Sci. Soc. Am. Proc. 37:956–958.
El-Swaify, S., N.T. Coleman, G. Bredell, and M. Arca. 1967. Negative adsorption by vermiculite: Salt exclusion from interlayer volumes. Soil Sci. Soc. Am. Proc. 31:464–466.
Frenkel, H., Z. Gerstl, and J.R. Vandeveen. 1986. Determination of gypsum and cation exchange capacity in arid soils by a resin method. Geoderma 39:67–77.
Gillman, G.P. 1981. Effects of pH and ionic strength on the cation exchange capacity of soils with variable charge. Aust. J. Soil Res. 19:93–96.
Gupta, R.K., D.K. Bhumbla, and I.P. Abrol. 1984. Sodium–calcium exchange equilibria in soils as affected by calcium carbonate and organic matter. Soil Sci. 138:109–114.
Gupta, R.K., C.P. Singh, and I.P. Abrol. 1985. Determining cation exchange capacity and exchangeable sodium in alkali soils. Soil Sci. 139:326–332.
Jacobs, D.G. 1966. Use of negative sorption in studies of ion fixation by hydrobiotite. Clays Clay Miner. 13:341–350.
Helmy, A.K. 1963a. On cation-exchange stoichiometry. Soil Sci. 95:204–205.
Helmy, A.K. 1963b. Calculation of negative and positive adsorption in some clay electrolyte systems. J. Soil Sci. 14:217–224.
Jurinak, J.J., C. Amrhein, and R.J. Wagenet. 1984. Sodic hazard: The effect of SAR and salinity in soils and overburden materials. Soil Sci. 137:152–159.
Kalisz, P.G. 1986. Effect of ionic strength on the cation exchange capacity of some forest soils. Commun. Soil Sci. Plant Anal. 17:999–1007.
Misopolinos, N.D., and I.M. Kalovoulos. 1984. Determination of CEC and exchangeable Ca and Mg in non-saline calcareous soils. J. Soil Sci. 35:93–98.
Nadler, A., and M. Magaritz. 1981. Expected deviation from the ESP–SAR empirical relationships in calcium and sodium carbonate containing arid soils: Field evidence. Soil Sci. 131:220–225.
Okazaki, R., H.W. Smith, and C.D. Moodie. 1963. Hydrolysis and salt retention errors in conventional cation exchange capacity procedures. Soil Sci. 96:205–209.
Papanicolaou, E.P. 1976. Determination of cation exchange capacity of calcareous soils and their percent base saturation. Soil Sci. 121:65–71.
Polemio, M., and J.D. Rhoades. 1977. Determining cation exchange capacity: A new procedure for calcareous and gypsiferous soils. Soil Sci. Soc. Am. J. 41:524–527.
Pratt, P.F. 1961. Effect of pH on the cation exchange capacity of surface soils. Soil Sci. Soc. Am. Proc. 25:96–98.
Pratt, P.F., L.D. Whittig, and B.L. Grover. 1962. Effect of pH on the sodium-calcium exchange equilibria in soils. Soil Sci. Soc. Am. Proc. 26:227–230.
Rhoades, J.D. 1967. Cation exchange reactions of soil and specimen vermiculites. Soil Sci. Soc. Am. Proc. 31:361–365.
Rhoades, J.D. 1982. Cation exchange capacity. p. 149–157. In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. ASA and SSSA, Madison, WI.
Rhoades, J.D., and D.B. Krueger. 1968. Extraction of cations from silicate minerals during the determination of exchangeable cations in soils. Soil Sci. Soc. Am. Proc. 32:488–492.
Sposito, G., K.M. Holtzclaw, L. Charlet, C. Jouany, and A.L. Page.

1983. Sodium–calcium and sodium–magnesium exchange on Wyoming bentonite in perchlorate and chloride background ionic media. Soil Sci. Soc. Am. J. 47:51–56.

Thomas, G.W. 1982. Exchangeable cations. p. 159–165. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. ASA and SSSA, Madison, WI.

Tucker, B.M. 1985. A proposed new reagent for the measurement of cation exchange properties of carbonate soils. Aust. J. Soil Res. 23:633–642.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. USDA Agric. Handb. 60. U.S. Gov. Print. Office, Washington, DC.