Sonderdruck aus

Zeitschrift für Pflanzenernährung und Bodenkunde

144. Band, Heft 1, Seite 87—100

Verlag Chemie GmbH, Weinheim (Bergstr.)

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Z. Pflanzenernaehr. Bodenkd. *143,* 87–100 (1980)

The cation- and anion exchange characteristics of soils with a large sesquioxide surface area

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Eingegangen am: 7.7.1980 Angenommen am: 28.11.1980

Summary – Zusammenfassung

The theory on colloids with a pH-dependent surface potential indicates that the anion exchange capacity of soils containing hematite or similar oxides depends on pH, electrolyte concentration and valency of counterions.

These relationships were tested for the salinity- and pH-range of importance to agriculture, using a percolation technique. $MgSO_4$ was chosen as impregnating salt to minimize the overall error caused by salt exclusion.

The assumptions on the anion exchange behaviour proved to be correct; moreover they applied also to a considerable fraction of the cation exchange. The results were formulated in terms of multiple linear regression equations relating the exchange capacities to pH and the square root of the electrolyte concentration.

Consequently, the adsorption behaviour of ferruginous soils can not be characterized by the determination of CEC and AEC at one level of pH- and salt concentration in solution.

Due to the inefficiency of the ethanol washing step, two standard methods overestimated CEC by a factor 2 to 4.

Das Kationen- und Anionen-Austauschverhalten von Böden mit großer Sesquioxid-Oberfläche

Nach der Theorie über Kolloide mit pH-bedingtem Oberflächenpotential hängt die Anionenaustauschkapazität von Böden, die Hämatit und verwandte Oxide enthalten, vom pH, der Elektrolytkonzentration und der Wertigkeit der Gegenionen ab.

Diese Beziehungen wurden für den landwirtschaftlich wichtigen Bereich der Salzgehalte und pH-Werte mittels einer Perkolationsmethode geprüft. Aufgrund seiner im Durchschnitt geringsten Dicke der salzfreien Wasserhaut wurde als Sättigungslösung eine $MgSO_4$-Lösung gewählt.

Die Annahmen über das Anionenaustauschverhalten wurden bestätigt, sie trafen außerdem auf einen bedeutenden Teil der Kationenadsorption zu.

Die Resultate wurden als multiple lineare Regressionsgleichungen formuliert, diese erklären die Austauschkapazitäten aus dem pH-Wert und der Quadratwurzel der Elektrolytkonzentration.

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Dies zeigt, daß die Austauschkapazitäten eisenhaltiger Böden offensichtlich nicht durch Bestimmung an nur einem Punkt des pH- und Konzentrationsbereichs charakterisiert werden können.

Wegen der Ineffizienz der Äthanolauswaschung ergaben zwei Standardmethoden 2–4mal zu hohe Werte für die Kationenaustausch-Kapazität.

Theoretical background

Since *Schofield* (1949) papers on the simultaneous determination of cation- and anion adsorption of soils have been numerous, as shown by the literature reviews by *Morais et al.* (1976) and *Tucker* (1960).

The aim of the present work was to develop a method less laborious than *Schofield*'s, to apply this method to a number of soils, and to develop a model or formula by which the results can be interpreted easily.

Anion adsorption is usually caused by Fe- and Al-oxides. The theory of adsorption was treated in a general way by *Kruyt* (1949) and *van Olphen* (1963); *Breeuwsma* (1973) and *Arnold* (1977) gave specific information.

In most soils of the temperate zones the negative surface charge, caused by ionic substitution in clay minerals, is nearly pH independent, while the charge caused by dissociation of acid groups on soil organic matter depends on pH. In the case of iron and aluminium oxides, however, the surface *potential* depends on pH. With respect to the mechanism of this process the following aspects may be mentioned:

a. The oxides of Fe and Al can acquire a surface charge σ as a result of a proton association-dissociation equilibrium of the surface oxygen atoms. Such a surface charge is balanced by an equal amount of oppositely charged ions, the counterions. The electrical potential of the protons on the surface, ψ_s, varies with the chemical potential of the H-ions, the pH, in solution.

b. There exists a particular pH at which the oxide surface is uncharged. This point of zero charge (p.z.c. or pH_0) has a characteristic value for a particular oxide. When acid is added to an oxide at p.z.c., the $\triangle pH = pH - pH_0$ will become negative and protons are adsorbed to the surface until the correspondingly rising positive surface potential ψ_s is again in equilibrium with the ambient pH; thus $\psi_s = f(\triangle pH)$. Together with the protons anions are adsorbed as counterions, forming the diffuse and exchangeable part of the double layer. Since the amounts of protons and anions are nearly equivalent (*Breeuwsma*, 1973, p. 81), the system behaves as if acid had been adsorbed.

When base is added on the alkaline side of p.z.c., where $\triangle pH > 0$, protons are released from the surface and neutralized. The negative charge thus originated is balanced by the adsorption of cations. So the system behaves as if base had been adsorbed.

c. The capacity of the double layer, C, is related to the charge σ and the surface potential ψ_s by $\sigma = C \cdot \psi_s$. As a first approximation C may be taken inversely proportional to the Debye-Hückel characteristic length $1/\varkappa$ which, in turn, is inversely proportional to the square root of the ionic strength. Accordingly, one may conclude that the surface charge is likely to be roughly proportional to, or at least a function of, $\triangle$pH, z and $c_o^{1/2}$. Here z indicates the valency of the counterions, and c_o is the molar concentration of the ions in solution. Using data given by *Breeuwsma* (1973), this functional dependance is depicted in Fig. 1 for a hematite system.

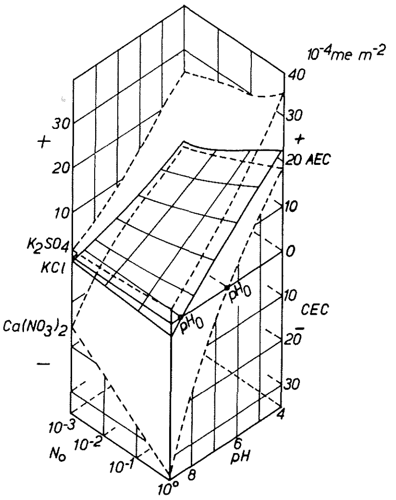

Figure 1: Surface charge of hematite as a function of pH and salt concentration for different types of salts; constructed from data of *Breeuwsma* (1973).

Abbildung 1: Oberflächenladung des Hämatits als Funktion von pH und Salzkonzentration für verschiedene Salze; konstruiert nach *Breeuwsma* (1973).

d. A further complication is that certain ions like Ca^{2+} and SO_4^{2-} become specifically adsorbed, causing a shift in p.z.c. As shown in Fig. 1 the pH_0 of hematite shifts from pH 8.5 for KCl to pH 6.5 for $Ca(NO_3)_2$ and (not shown) to pH 9.5 for K_2SO_4. It is obvious that, when only one salt is used to determine the exchange properties of an oxide, it should be a symmetrical monovalent or divalent salt. With a salt of the type $C_2^+ \cdot R^{2-}$ the anion exchange capacity will be overrated, with $C^{2+} \cdot R_2^-$ underrated.

The consequence of the above mentioned aspects is that the adsorption behaviour of soils rich in sesquioxides is influenced by the pH and salt concentration of the soil solution. In the field pH and salt concentrations vary with the seasons, and thus the adsorption behaviour of these soils can not be represented properly by a determination at just one level of pH and salt concentration as is standard practice. The new method and model sought after enables one to describe cation- and anion exchange capacities over the range of salt concentrations and pH values of importance to agriculture. The salt concentrations of 0.1, 0.01 and 0.001 N, representing the concentrations in the topsoil just after fertilization, during crop growth and after harvest and elution of salts, respectively, were considered to cover this range. With respect to pH, the original soil pH and the value at which Al is no longer toxic were regarded to meet the demands of agricultural practice.

Apart from the appropriate ranges, the following theoretical aspects were considered in the presently proposed new method for the simultaneous determination of CEC and AEC:

a. Co-ion exclusion. This exclusion is important since it influences the calculation of the adsorption capacities. Charged surfaces repel ions of the same sign, thus causing a zone where the salt concentration increases from zero at the surface to the concentration in the free solution. This zone of gradual transition can be described as a salt free layer of thickness $q/(\beta N_o)^{1/2}$, where q is a known constant for any combination of counter- and co-ionic valencies prevailing in the free solution, β equals $1.08 \cdot 10^{15}$ cm. mmol^{-1} at about 15 °C, and N_o is the concentration in the free solution (me.cm^{-3}) (*de Haan & Bolt*, 1963; *Schofield*, 1947). The repulsion of cations and anions by surfaces having the same sign of charge contributes to the total exclusion volume in proportion to their respective areas.

b. Calculation of adsorption capacities. With systems containing only one type of cations and anions, CEC and AEC are calculated according to $\text{CEC} = T_{cat} - S$ and $\text{AEC} = T_{an} - S$, where T is the total amount of cations or anions in the system and S is the amount of neutral salt in solution ($S = S_{cat} = S_{an}$, *Schofield*, 1949). S is calculated by multiplying the volume of solution retained in the system with the salt concentration as measured in the free solution. In this way, however, S is overestimated because the volume of the salt free layer is not subtracted from the total volume of the retained solution.

c. Choice of impregnating ions. To calculate CEC and AEC properly an ion combination that causes the smallest exclusion volume should be chosen as impregnating salt. Differences in exclusion distances for various ion combinations may be represented as differences in q. For asymmetrical salts a mean factor $\overline{q\ \text{salt}}$ may be calculated, depending on proportion of the positively and negatively charged surface areas.

For instance, $\overline{q\ \text{salt}}$ will be small for $MgCl_2$ with 100 % negative area, since the divalent positive ions will be attracted strongly and the monovalent negative ions repelled weakly. In contrast at 100 % positive area, $\overline{q\ \text{salt}}$ of $MgCl_2$ will be large, monovalent negative ions being weakly attracted and divalent positive ions strongly repelled. The relationship between $\overline{q\ \text{salt}}$ and the proportion of the positively and negatively charged surface areas is depicted in Fig. 2 for the salts KCL, K_2SO_4, $MgCl_2$ and $MgSO_4$, using data of *de Haan*

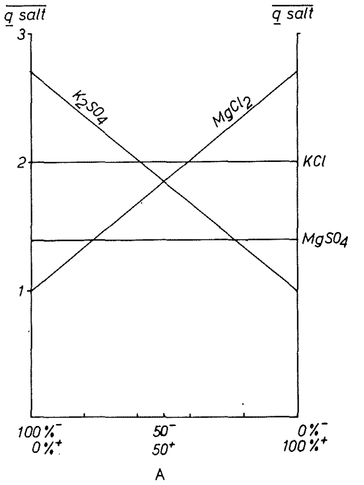

Figure 2: Overall salt exclusion factor, $\overline{q\ \text{salt}}$, as a function of the proportion of the positively and negatively charged surface areas.

Abbildung 2: Allgemeiner Salzausschluss-Faktor, $\overline{q\ \text{Salt}}$, in Abhängigkeit des Anteils positiv oder negativ geladener Fläche an der Gesamtoberfläche.

(1965). On the average $MgSO_4$ will give the smallest number and was therefore chosen as the impregnating salt, expecting that the shift in pH_0, caused by Mg^{2+} on the one hand and SO_4^{2-} on the other would cancel each other. This view is supported by the results of *van Ray & Peech* (1972, Table 2). Because Cs will compress the negative double layer completely (*Greenland*, 1974), CsCl will give the smallest value of $\overline{\text{q salt}}$, up to 80 % positive surface area. For lack of determination facilities, however, Cs could not be employed.

Materials and Methods

The present method, further referred to as dilution method, was designed to meet two important demands, i.e. preservation of the granular structure of aggregates and minimizing the amount of solution retained. The granular structure must be maintained to insure permeability and to contain the expansion of the double layer. These requirements are met by the set-up depicted in Fig. 3. A funnel with a fritted glass filter (hardness 3) is used to drain the sample with a suction of 0.1 bar without sucking through air. The soil is covered by glass beads to obtain a homogeneous distribution of the percolating liquid and to prevent slaking of the granules by drop impact. Slaking by air explosion is prevented by slowly moistening the soil by means of capillary action. For this purpose a strip of tissue paper is pushed against the lower side of the filter disc, while the other end is kept in the impregnating solution for about 16 hours. The percolation steps following thereafter were stretched to last at least 3 hours. Adjustment of the pH of the solutions was effected prior to use.

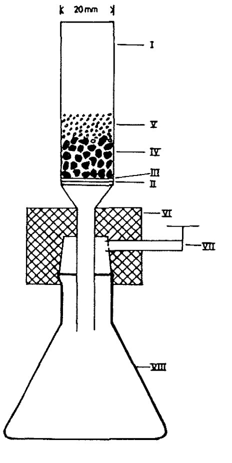

Figure 3: Percolation set up.
I-percolation funnel, II-fritted glass filter, III-glass fiber paper, IV-soil sample, V-glass beads, VI-rubber joint, VII-tap to bubble tube and exhaust, VIII-collection vessel.
Abbildung 3: Perkolationsapparat.
I-Perkolationsrohr, II-Glasfritte, III-Glasfaserpapier, IV-Bodenprobe, V-Glasperlen, VI-Gummiverbindung, VII-Hahn zum Durchperlrohr und Vakuum, VIII-Sammelgefäß.

In the present study most CEC and AEC determinations were done at pH values measured in suspensions of 1 part of soil in 2.5 parts of impregnating solution; this pH value is referred to as the soil pH. To obtain measurements at other pH-values, the soil was percolated with acetate buffer of the desired pH before impregnation with the desired salt solution. Further details of the procedure are described below:

a. Preparation. The filter disc of the tube is protected from contamination by a glass filter paper on which 5 g of soil aggregates (1-2 mm) are placed and covered with 10 g of glass beads. The dry weight is determined (G_1), whereafter the soil is slowly moistened. The solutions are applied from a burette or inverted bottle. Air bubbles between the aggregates are not removed as they may improve exchange efficiency. In case of the andepts, field moist soil was used, in a quantity equivalent to 5 g dry soil.

b. Impregnation step. The tube is placed into the suction arrangement and 50 ml of the 1 N (monovalent) or 0.5 N (divalent) impregnating solution is percolated through the sample.

c. Dilution steps. After impregnation the salt level is lowered by percolating 100 ml solution of the desired concentration (in the present study: 0.1, 0.01 and 0.001 N). In the last 5 ml of this percolate, the concentration of the impregnating cation and/or anion, N_o, is determined. N_o is assumed to represent the equilibrium concentration and is used in further calculations. After percolation the suction is maintained at 0.1 bar for half an hour and the tube is weighed to obtain the wet weight (G_2). The average amount of retained solution amounted to about 1 ml per gram of soil as compared to 2 ml per gram of soil after centrifugation (*Schofield*, 1949).

d. Stripping step. The total amount, T, of cations or anions present in the system is removed by stripping with 50 ml 1 N NH_4NO_3.

e. Chemical analysis. The standard series for N_o was prepared in water, that for the sum of ions in 1 N NH_4NO_3; Mg^{2+} was determined by atomic absorption spectrophotometry, SO_4^{2-} by turbidimetry according to *Lachica Garrido* (1964).

f. Calculation.

$$CEC = \{T_{cations} - (G_2 - G_1) \times N_o\} \times 100/5 \text{ me per 100 g soil.}$$
$$AEC = \{T_{anions} - (G_2 - G_1) \times N_o\} \times 100/5 \text{ me per 100 g soil.}$$

Remark: The above procedure b to d can be repeated without impairing the permeability of the sample. Therefore the determinations at various salt levels and pH values can be done either simultaneously (3 salt levels in duplicate : 6 tubes) or one salt level after the other using the same two tubes (duplicate).

The results of the present method were compared with those obtained with two standard methods (*Peech* et al., 1947; *Richards*, 1969). Because of the discrepancy between the CEC values obtained with the present method and the standard methods (see Results and Discussion) the following additional investigations were carried out, using the same experimental set-up:

Experiment 1. The influence of the pH of the impregnating salt solution of *Peech*'s method on CEC was investigated using NH_4OAc of pH 6.8 or 5.0 in step b and c of the dilution method.

Experiment 2. The influence of the contact time between the washing solution and the soil sample on CEC was studied using NH_4OAc-pH 6.8 in step b and 70 or 96 % ethanol in step c.

Experiment 3. The influence of the type of impregnating salt solution and the washing solution on CEC was studied using either NH_4OAc-pH 6.8, NH_4OAc-pH 5.0, $(NH_4)_2SO_4$-pH 5.4 or $MgSO_4$-pH 5.1 in step b and diluted solutions of these salts or 70 % ethanol in step c. In case of $MgSO_4$ the influence of the washing solution on AEC was also studied. For stripping (step d) 50 ml of a 10 % NaCl solution acidified to pH 2 was used in case NH_4^+ was the impregnating cation, whereas 1 N NH_4NO_3 was used when Mg^{2+} was the impregnating cation. NH_4^+ was determined by microdestillation, Mg^{2+} and SO_4^{2-} as described. Corrections for free salts were made only when working with diluted solutions in step c. Further details with respect to the treatments are presented in Table 4. For these three experiments only Bogor soil was used.

For the main investigations (CEC and AEC determinations with the dilution method and CEC determinations with standard methods) material was used from B-horizons of soils rich in free sesquioxides from various continents (Table 1).

Table 1: Locality, classification and CEC values of the soil samples.
Tabelle 1: Herkunft, Klassifizierung und KAK Werte der Bodenproben.

Locality	Country	Classification	CEC (me per 100 g soil)			
			Peech	Richards	Dilution method	
			pH 7 NH_4OAc	pH 8.2 NaOAc	10^{-3}N $MgSO_4$	pH
Ragunan	Indonesia	Typic Paleudult	25.3	27.2	5.7	4.7
Depok	Indonesia	Typic Tropudult	21.4	17.3	5.4	4.7
Semplak	Indonesia	Antraquic Dystropept	n.d.	n.d.	12.4	6.0
Bogor	Indonesia	Antraquic Dystropept	30.8	22.8	9.4	5.1
Punçak	Indonesia	Andept	38.7	28.4	6.3	5.8
Campinas	Brazil	Terra Roxa Ligitima	5.0	5.3	1.7	6.0
Kindaruma	Kenya	Rhodic Ferralsol	12.8	12.5	5.2	5.2
Molokai	Hawaii USA	Typic Torrox	13.5	11.8	5.1	6.0
Hilo	Hawaii USA	Typic Hydrandept	n.d.,	n.d.	2.6	5.8

Results and Discussion

The effect of salt concentration and pH on CEC and AEC, as evaluated with the dilution method, is shown in Table 2. It is evident that with increasing pH CEC increases and AEC decreases, whereas both adsorption capacities increase with concentration. The relationships of AEC and CEC with concentration are curvilinear as shown in Fig. 4a for Molokai soil, a soil typical for the soils studied. However, plotting AEC and CEC versus $N_0^{1/2}$ yields a linear relationship (Fig. 4b).

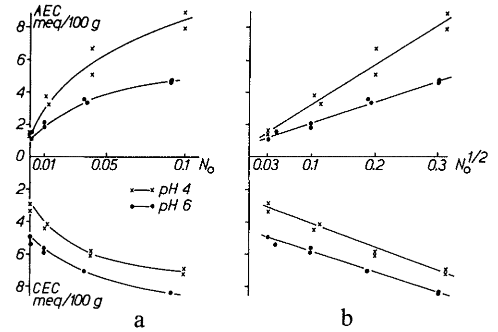

Figure 4: CEC and AEC of the Molokai soil as a function of $MgSO_4$-concentration at pH values of 4 and 6.
Abbildung 4: Der Einfluß der $MgSO_4$-Konzentration bei pH 4 und 6 auf KAK und AAK des Bodens „Molokai".

The linear relationship of AEC with the square root of the salt concentration at a given pH is in accordance with theoretical considerations for iron oxides (*van Olphen*, 1963). A considerable part of the CEC follows the same pattern; beside negatively charged clays with constant charge, other colloids with pH dependent potential and a pH_0 well below 4 may be present. The presence of aluminium silicates would be an obvious assumption.

Table 2: CEC and AEC (me per 100 g soil), determined with the dilution method at different salt concentrations and pH-values.

Tabelle 2: Einfluß von Salzkonzentration und pH auf die Kationen- und Anionen-Austauschkapazität nach der Verdünnungsmethode. (AK in mval/100 g Boden).

Soil	pH of impregnating solution	CEC			AEC		
		approximate normality of diluted solutions					
		0.001–0.004	0.01–0.03	0.09–0.10	0.001–0.004	0.01–0.03	0.09–0.1
Ragunan	4.7	5.7	6.7	8.8	3.9	4.8	7.4
	6.0	5.0	6.3*	12.8	2.2	3.7*	7.9
Semplak	4.6	7.2	9.0	12.2	3.6	5.2	7.9
	6.0	12.4	13.7	16.5	1.3	2.5	4.9
Bogor	4.3	n.d.	7.6*	11.8	n.d.	3.6*	6.6
	5.1	9.4	10.7	12.9	2.3	3.2	5.6
Molokai	4.0	3.1	4.2	7.0	1.5	3.6	8.4
	6.0	5.1	5.8	8.4	1.4	2.0	4.7
Hilo	4.7	1.3	9.6	35.1	17.8	27.6	54.2
	5.8	2.6	16.2	41.9	17.6	30.3	57.3

*Determined at 0.005 N.

Correlation- and regression coefficients of the relationships between AEC or CEC and N_0 and $N_0^{1/2}$ have been calculated for all soils investigated (*Breimer & Leffelaar,* 1976). This revealed that most correlation coefficients were higher for the relationships of CEC and AEC with $N_0^{1/2}$, than with N_0.

It may be expected that the regression coefficient of the relationship of AEC vs. $N_0^{1/2}$ at soil pH, is related to the Fe_2O_3 content of the soil. However, Fig. 5 shows the correlation to be rather poor, probably due to differences in degree of crystallization of the iron oxides or the presence of other oxides with a positive surface charge. The andepts containing iron hydroxides exibit the largest regression coefficients, as high as 146 for Hilo at a Fe_2O_3 percentage of 39.5.

On the other hand CEC and AEC vary with pH. To see whether these relationships may be regarded as linear, data were taken from the literature (*Morais* et al., 1976; *van Ray & Peech,* 1972) and correlation coefficients calculated. Since most correlation coefficients were highly significant it was concluded that the relationship between CEC or AEC and pH is linear for most ferruginous soils. This linearity was assumed to apply also to the soils in the present study, the more so because only a small range of pH values is covered.

To obtain a better insight in the dependency of CEC and AEC on both $N_0^{1/2}$ and pH, three dimensional plots were constructed.

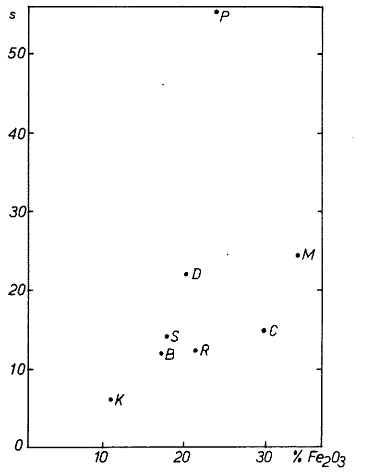

Figure 5: The regression coefficient (s) of the relationship between AEC and $N_o^{1/2}$ at soil pH as a function of the Fe_2O_3 content for different soils. Capitals denote first letter of the soil name as given in Table 1. Analysis of Fe_2O_3 by *L. Th. Begheyn,* Dept. of Soil Science and Geology, Duivendaal 10. Wageningen, The Netherlands.

Abbildung 5: Der Regressionskoeffizient (s) aus der Beziehung zwischen AAK und $N_o^{1/2}$ bei Boden-pH im Verhältnis zum Fe_2O_3-Gehalt. (Kennzeichnung der Böden aus Tabelle 1 durch Großbuchstaben).

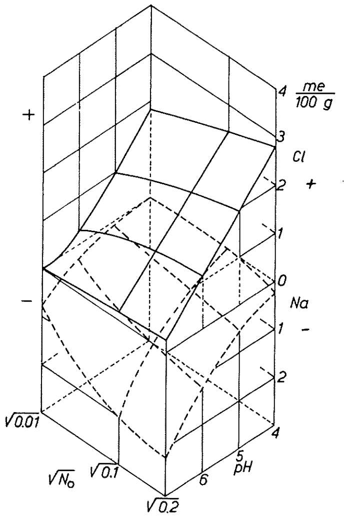

Figure 6: CEC and AEC of the Acrorthox-B_2 as a function of pH and NaCl concentration ($N_o^{1/2}$); constructed from data of *van Ray & Peech* (1972).

Abbildung 6: KAK und AAK des Acrorthox-B_2 in Abhängigkeit von pH und NaCl-Konzentration ($N_o^{1/2}$); konstruiert nach Daten von *van Ray & Peech* (1972).

A typical example of such a plot is given in Fig. 6, showing that CEC and AEC are represented by slanting warped planes. These slanting warped planes may be approximated by a regression model of the type

$$EC = a\, N_o^{1/2} + b\, pH + c\, N_o^{1/2}\, pH + d \tag{1}$$

However, taking into account the linearities found above, also equations of the type

$$CEC = a_c N_o^{1/2} + b_c pH + c_c \tag{2a}$$

$$AEC = a_a N_o^{1/2} + b_a pH + c_a \tag{2b}$$

representing slanting flat planes, should give a fair approximation. The regression coefficients of Eqs. 1 and 2 were calculated by the method of least squares for the soils of Table 2, and the data of *Gallez et al.* (1976) and *van Ray & Peech* (1972).

The overall correlation coefficients for Eq. 1 were slightly higher than those for Eq. 2, nevertheless the latter coefficients were also significant at the 1 % level two sided. Therefore, the approximation of the slanting warped planes by a slanted flat plane as described by Eq. 2 was adopted and some regression equations obtained herewith are presented in Table 3. The most remarkable feature of the $MgSO_4$-adsorption characteri-

Table 3: Regression equations relating CEC and AEC to $N_o^{1/2}$ and pH.
Tabelle 3: Regressionsgleichungen zwischen KAK bzw. AAK und $N_o^{1/2}$ sowie pH.

Soil: Impregnated with:	
Ragunan	CEC = $20\,N_o^{1/2} + 1.2\,pH - 1.6$
$MgSO_4$	AEC = $15\,N_o^{1/2} - 0.6\,pH + 5.8$
Semplak	CEC = $15\,N_o^{1/2} + 2.9\,pH - 6.6$
$MgSO_4$	AEC = $13\,N_o^{1/2} - 1.7\,pH + 11.4$
Bogor	CEC = $15\,N_o^{1/2} + 2.0\,pH - 3.3$
$MgSO_4$	AEC = $12\,N_o^{1/2} - 1.1\,pH + 8.6$
Molokai	CEC = $13\,N_o^{1/2} + 0.8\,pH - 0.4$
$MgSO_4$	AEC = $19\,N_o^{1/2} - 0.9\,pH + 5.4$
Hilo	CEC = $138\,N_o^{1/2} + 3.7\,pH - 25.3$
$MgSO_4$	AEC = $143\,N_o^{1/2} + 0.9\,pH + 5.1$
Egbeda, B_{2t}*	CEC = $11\,N_o^{1/2} + 1.2\,pH - 4.8$
NaCl	
Acrorthox, B_2**	CEC = $2\,N_o^{1/2} + 0.4\,pH - 2.2$
NaCl	AEC = $2\,N_o^{1/2} - 0.8\,pH + 4.9$

For interpolation limits see Table 2.
* Data from Gallez et al., 1976: Fig. 5b.
** Data from van Ray & Peech, 1972; Table 3.

stics is that the regression coefficients of $N_o^{1/2}$ of the Hilo soil are 7 to 10 times higher than those of the other soils, whereas its regression coefficients of pH are not excessive. For the NaCl impregnated soils, the Egbeda shows a stronger variation with $N_o^{1/2}$ than the Acrorthox.

The factors a_c and a_a denote the proportional increase of the exchange capacity with salt concentration, in case of CEC by adsorption of base and in case of AEC by adsorption of acid. Neglecting the effect of the permanent charge, the soil pH will decrease with increasing salt concentration if $a_c > a_a$ and increase when $a_c < a_a$. On dilution the reverse applies. For some soils these coefficients are nearly equal; then the adsorption with increasing salt concentration is termed „salt adsorption". The factors b_c and b_a can be used to calculate the lime requirement, as far as it is due to the colloids with pH dependent potential. Per unit increase of pH, b_c denotes the amount of base adsorbed and b_a the amount of acid released.

The differences between CEC values obtained with the dilution method and two standard methods are demonstrated in Table 1. Obviously standard methods overestimate CEC values by a factor 2 to 4 in soils rich in sesquioxides. At first glance these differences may be attributed to the different pH values of the impregnating solutions. However, results obtained by the dilution method using $MgSO_4$ as impregnating salt show at best an increase in CEC of 5 me/100 g when pH is raised from 4 to 6 (Table 2). Therefore, experiment 1 with Bogor soil was carried out to investigate whether the influence of pH was the same when e.g. NH_4OAc was used as impregnating salt.

CEC values only show a small decrease, from 12.3 to 9.7 me/100 g, upon changing the pH from 6.8 to 5.0 (Table 4). It was concluded, therefore, that beside pH other factors must influence the amount of cations retained in the sample after washing, but prior to stripping. These factors, such as the ethanol percentage of the washing solution and the contact time during washing (experiment 2) and the possible interaction of ethanol with the impregnating salt (experiment 3) are discussed below.

In Fig. 7 it is demonstrated that CEC stabilizes after contact times of 3 and 6 hours at 14 and 28 me/100 g for 70 and 96 % ethanol, respectively. The CEC value obtained with 96 %

Table 4: CEC and AEC of the Bogor soil as influenced by type of impregnating salt and washing solution.

Tabelle 4: Der Einfluß der Zusammensetzung der Sättigungslösung und der Auswaschungslösung auf KAK and AAK des Bodens "Bogor".

Impregnating salt (100 ml)	NH_4OAc				$(NH_4)_2SO_4$		$MgSO_4$	
Concentration	1.0				1.0		0.5	
pH value	6.8		5.0		5.4		5.1	
Washing solution	NH_4OAc	ethanol	NH_4OAc	ethanol	$(NH_4)_2SO_4$	ethanol	$MgSO_4$	ethanol
(100 ml/5 g)	0.01 N	70 %	0.01 N	70 %	0.01 N	70 %	0.01 N	70 %
Contact time (h)	6	6	6	6	6	14	3	1.5
CEC (me/100 g)	12.3	13.6	9.7	11.6	12.0	20.8	10.7	20.6
AEC (me/100 g)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.2	13.7

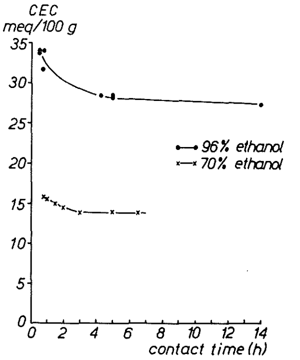

Figure 7: CEC of the Bogor soil as a function of the contact time during elution with 70 and 96 % ethanol. (Impregnating salt: 1 N NH_4OAc, pH 6.8).

Abbildung 7: Der Einfluß der Kontaktzeit bei der Salzauswaschung mit 70 % und 96 % Aethanol auf die KAK des Bodens „Bogor". (Sättigungslösung 1 N NH_4OAc, pH 6.8).

ethanol is seen to be about the same as the value obtained with *Peech*'s method for the Bogor soil (Table 1), though the ratio of ethanol to soil (v/w) was 20 to 1 in this experiment, and only 4 to 1 in *Peech*'s method.Furthermore, the CEC value obtained with 70 % ethanol is about the same as the one found with the dilution method using 0.01 N NH_4OAc, pH 6.8 (Table 4). In conclusion, removing excess salt with ethanol 96 % is not effective, even when the contact time is prolonged and the ratio of ethanol to soil is high. These findings are in accordance with *Leonard & Jackson* (1975), who reported specific adsorption effects on charged surfaces with ethanol percentages above 80. The above reported agreement of the CEC values obtained by washing with 70 % ethanol and those obtained by washing with 0.01 N of the impregnating salt was not found for $(NH_4)_2SO_4$ or $MgSO_4$ (Table 4). The CEC data for these impregnating salts using 70 % ethanol as washing solution are about 10 me/100 g higher than those obtained by washing with a diluted solution of the impregnating salt; the latter values are in accordance with the values obtained with NH_4OAc (Table 4). Since both CEC and AEC are about 10 me/100 g higher when 70 % ethanol is used instead of 0.01 N $MgSO_4$, neutral salts seem to be retained. These results indicate that there is an interaction between $(NH_4)_2SO_4$ and $MgSO_4$ as impregnating salts and 70 % ethanol, resulting in ineffective removal of excess salts. The experimental evidence for the Bogor soil supports the view that in ferruginous soils removal of excess salts with a diluted salt solution is to be preferred over the use of ethanol in CEC determinations.

Besides the experimentally derived objections against the CEC determination of ferruginous soils with the methods of *Peech* et al. (1947) and *Richards* (1969), we also like to give some theoretical comments on the procedures of other methods. In the methods of *Kappen* (1928) and *Soil Survey Staff* (1973), the CEC is determined by the sum of exchangeable bases plus the exchange acidity at pH 7 and 8. Thus the adsorbed protons and their counterions, constituting the AEC, will be released and this acid is subsequently titrated and interpreted as part of the CEC. This view is supported by *Juo* et al. (1976) and results in an overestimation of CEC. Another method, (*Ulrich*, 1966; *Coleman & Thomas*, 1967) determines the so-called effective CEC, which is the sum of the exchangeable bases plus KCl replaceable acid. Here the raised salt concentration increases the double layer capacity resulting in proton adsorption at the positively charged surfaces. Thus protons exchanged at the negatively charged sites will, at least partly, be bound as HCl at the positive sites. This results in underestimation of the exchange acidity and thus of the CEC. Recently *Gillman* (1979) proposed an extension of *Bascomb*'s method to determine CEC and AEC simultaneously, suggesting one determination of each. The major drawback of this method is the use of $BaCl_2$ as impregnating salt, resulting in a decrease of pH_0 similar to $Ca(NO_3)_2$ in Fig. 1, see also *Breeuwsma* (1973, p. 63). This implies that AEC is underestimated. Considering the objections raised against the above methods, we believe that the dilution method is a valuable alternative to characterize exchange behaviour of ferruginous soils.

To decide whether it is warranted to examine the exchange behaviour of an unknown ferruginous soil in more detail, it is suggested to determine first CEC and AEC at 0.05 N $MgSO_4$ at soil pH. When AEC is appreciable, the regression coefficients a_a and b_a in Eq. 2 b will no longer be negligible. Then, for calculation of Eq. 2, data on two more points are needed, e.g. at 0.001 N and soil pH (giving a span of 0.2 units of $N_o^{1/2}$) and at 0.05 N and another pH-value, e.g. where Al is no longer toxic, (if the soil pH has a value of 5.5 or more, the second pH should be 1–2 units lower, but not below pH 4). In this way, three points of CEC and AEC are acquired and the regression coefficients of Eq. 2 can be calculated. It should be remembered that use of the equations can only be permitted within the limits of the determinations of pH- and salt concentration-values. These limits should be provided together with the equations.

Finally, if one is interested in the adsorption of monovalent ions, a symmetrical salt like KCl should be used. Because of the near identical behaviour of Cl^- and NO_3^- as to adsorption, such a determination would give a measure of the adsorption of the most important nutrients. The agricultural importance of an AEC derived from a pH dependent surface potential is difficult to assess accurately. On the one hand the capacity decreases with the concentration to low values (an AEC of 1 me/100 g over a layer of 10 cm is equivalent to about 200 kg $ha^{-1} NO_3$–N), on the other hand the presence of this AEC will firstly help to buffer the salinity at fertilization, secondly it will retard the elution of nitrate and sulphate. The importance of this retardation needs quantitative investigation.

Conclusion

The experimental data presented in this paper and those taken from the literature, proved that AEC and CEC of ferruginous soils depend strongly on the pH-value and concentration. This is in accordance with theory. As these factors are subject to changes, the characterization of adsorption capacity of soils by a single determination is insufficient, even if AEC is included. Both exchange characteristics of soils rich in sesquioxides should be determined over ranges encountered in agricultural practice and the results be approximated by an equation such as proposed in this paper.

Acknowledgement

The valuable help of *J. van der Maarl, Th. Vens, F. X. K. Alimu* and *Raj Pal Sharma* is gratefully recognized.

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