

A NEW METHOD FOR THE DETERMINATION OF EXCHANGEABLE ALUMINIUM IN ACID SOILS*

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Introduction

In addition to Al in the crystal lattice of clay minerals, Al in soils can be divided into two major groups viz., exchangeable and non-exchangeable. The Al equilibrium in soils is controlled by the solubility of the solid phase Al compounds on the one hand and the adsorption characteristics of the adsorption phase on the other. Thus for a given soil the amount of exchangeable Al will depend on the relationship between the type and quantity of Al compounds present and the cation exchange capacity of the soil.

The importance of exchangeable Al in acid soils has often been mentioned, but no satisfactory quantitative method for its determination has yet been presented. This may well be due to the paucity of knowledge regarding the chemistry of the non-exchangeable forms of Al present in these soils.

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The quantity of Al released under standard experimental conditions may exceed the CEC of the soil so that some way must be found to distinguish between the exchangeable and non-exchangeable components. A technique for estimating this latter function is proposed here.

Principle

The proposed method is based on controlling the amount of non-exchangeable Al removed so that it can be readily measured. Subsequently a correction factor can then be applied to the total Al extracted — the difference representing exchangeable Al.

Exchangeable Al is displaced with difficulty by other cations but it can effectively be removed by a long series of successive extractions. If experimental conditions with respect to soil to solution ratio, and period of contact are kept constant during extraction then the amount of non-exchangeable Al dissolved

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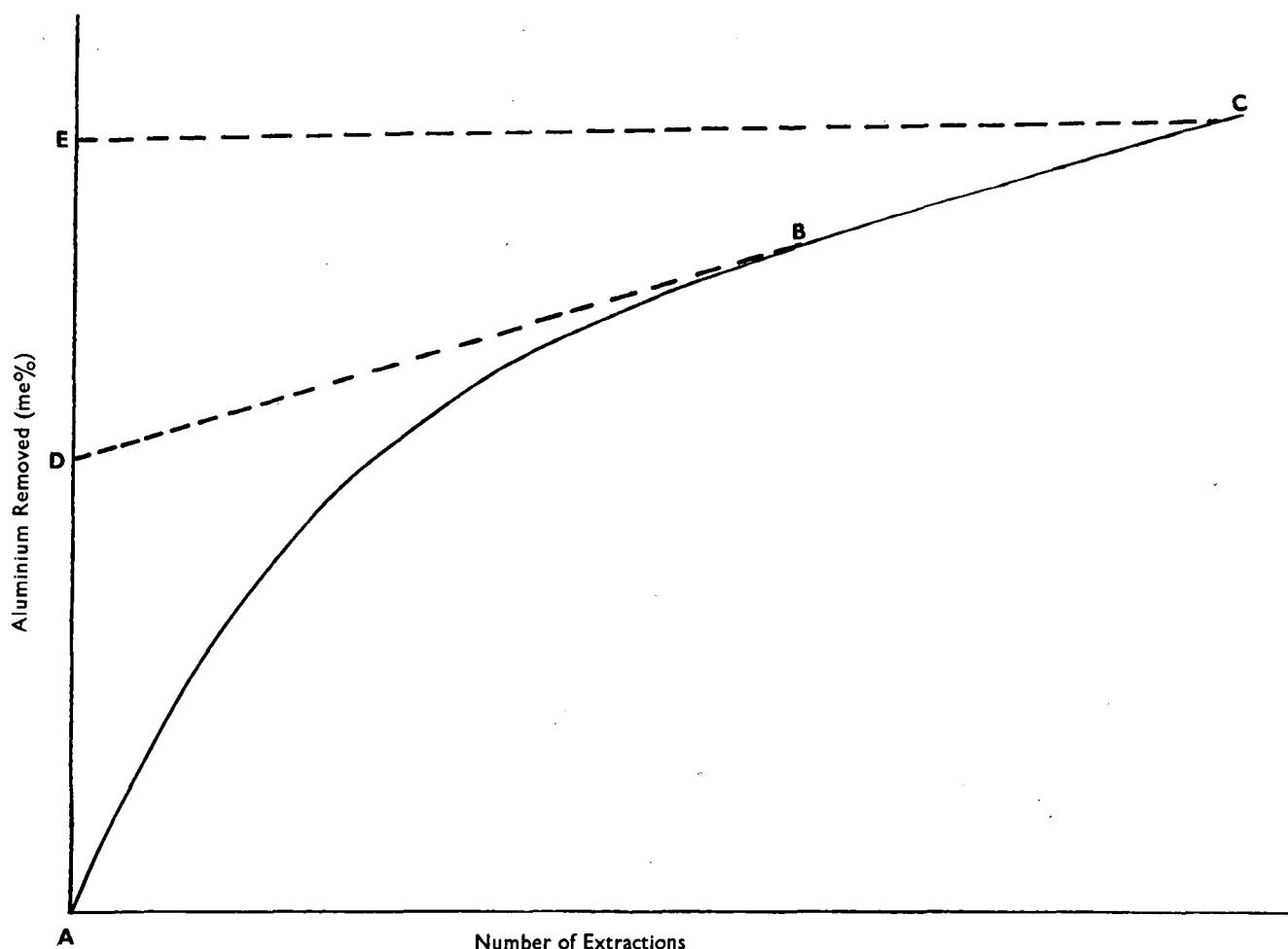


Figure 1 — Characteristic curve for the progressive extraction of aluminium from acid soils

during each extraction in the series should be constant. The sum of the contributions from this source can then be subtracted from the total extractable Al to give an estimate of exchangeable Al.

With each successive extraction a steadily decreasing amount of exchangeable Al will be released together with a constant quantity of non-exchangeable Al. When plotted as a cumulative function of the number of extractions, the resulting Nernst type curve should become linear if continued beyond the point at which all exchangeable Al has been removed.

In figure 1 the curve AB represents the progressive removal of both forms of Al and BC, that of non-exchangeable Al only. When BC is extrapolated to zero number of extractions, i.e., zero shaking time, AD will represent exchangeable and DE non-exchangeable Al.

Materials and Methods

The samples used were from the A₁ horizons of four highly weathered acid ferrallitic soils. These soils have been depleted of bases such as Ca, Mg, K and Na, leaving a residue consisting mainly of highly weathered clay and large amounts of Al oxides and hydroxides in an ill-defined form. X-ray evidence suggests the presence of a 14Å mineral in all four soils. These peaks represent vermiculite which according to Jackson (1963) is stabilised by interlayer Al. The natural occurrence of such interlayers is well established. The interlayered product referred to as chloritized vermiculite is equivalent to what has been called dioctahedral vermiculite by Rich and Cook (1961) and intergradational vermiculite-chlorite by Jackson (1959).

Some properties of the soils studied are presented in table 1.

TABLE 1
Charge distribution, pH value and exchangeable bases of some Natal soils

SOIL SERIES	pH VALUE		*CHARGE (me%)			EXCHANGEABLE BASES (me%)				
	H ₂ O	NKCl	Pos.	Neg.	Net	Ca	Mg	Na	K	†BS%
Kranskop (1) . . .	4.5	3.9	2.2	8.6	6.4	0.6	0.8	0.2	0.8	28.1
Clovelly (2) . . .	4.6	3.8	1.0	7.0	6.0	0.2	0.6	0.1	0.6	20.0
Clovelly (3) . . .	4.6	3.7	1.0	6.2	5.2	0.4	0.6	0.1	0.6	28.8
Clovelly (4) . . .	4.5	3.6	1.3	11.6	10.3	1.2	1.9	0.2	1.9	34.0

* Determined at field pH (4.0).

† Defined as the total exchangeable bases expressed as a percentage of the net charge.

pH values were determined in a 1:2.5 soil to solution ratio. Electric charges carried by the soils at field pH were determined by a modification of the method proposed by Schofield (1949). Exchangeable bases were extracted by leaching the soils with 0.2N NH₄OAc. The experimental procedure for the extraction of Al was as follows:

Place 5g air dry soil in a tared 100 ml centrifuge tube and add 50 ml extracting solution adjusted to the field pH value of the soil; shake for exactly two minutes in a reciprocating shaker centrifuge and decant. Reweigh the tube so as to obtain the weight of the occluded solution; add a further 50 ml of extractant, shake, centrifuge and decant. This procedure is repeated 24 times decanting into a separate container each time. Determine the Al present in each extract and correct for the occluded solution. Plot the cumulative data as shown in figure 1.

Aluminium was determined colorimetrically using the aluminon reagent by a modification of the method proposed by Frink and Peech (1962).

Extractions were carried out with various solutions to illustrate the effect of (i) different cations, (ii) different anions and (iii) concentration on the extraction of both forms of Al.

Results and Discussion

(i) The effect of cation species

The quantities of Al displaced by various salt solutions are presented in table 2.

TABLE 2
The effect of cations on the extraction of aluminium from acid soils.

SOIL NUMBER	TOTAL Al EXTRACTED (me%)				
	0.2N KCl	0.2N NH ₄ Cl	0.2N MgCl ₂	0.2N CaCl ₂	N NaCl
1	5.1	5.5	5.0	4.7	4.5
2	5.7	6.0	5.6	5.4	6.0
3	4.9	5.6	5.6	4.9	6.1
4	6.6	7.9	7.8	7.5	8.3
	NON-EXCHANGEABLE Al PER EXTRACTION (me%)				
1	0.084	0.084	0.080	0.072	0.059
2	0.075	0.079	0.084	0.074	0.090
3	0.070	0.079	0.090	0.070	0.092
4	0.075	0.100	0.120	0.095	0.121
	EXCHANGEABLE Al (me%)				
1	3.2	3.5	3.1	3.0	3.1
2	3.9	4.0	3.6	3.6	3.8
3	3.3	3.7	3.4	3.3	3.9
4	4.9	5.5	5.0	5.2	5.4

Soil 1 contains least exchangeable Al followed by soils 3, 2 and 4 in increasing order. Apart from the Na⁺ ion which was used as a normal solution, there appears to be little variation in the total amounts of Al extracted by the remaining four cations.

Although individual values of successive extracts are not presented here, the effect of cation species on the rate of Al release follows the order NH₄⁺ > K⁺ > Ca²⁺ > Mg²⁺ > Na⁺. The inference here is that the valency of the cation is not the main factor controlling the release of Al. Rather it appears that the hydrated radius of the extracting cation governs its relative replacing power. For temperatures near 18° C, the extent of hydration is calculated to be as follows (expressed in Å³):

Ion:	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺
Size:	5.37	5.4	9.6	10.8	8.4

It would appear that when cations are hydrated to the same degree, valency once more assumes domi-

nance. The most suitable cations for the extraction of exchangeable Al thus appear to be NH₄⁺ and K⁺. These ions are probably capable of replacing the adsorbed Al ions more efficiently hence their greater rate of exchange.

(ii) *The effect of anion species*

Aluminium interlayers are presumably olated compounds in which the Al atoms are linked through bridging OH⁻ groups. Penetration of anions into such compounds causes deolation resulting in the release of Al which is not exchangeable. The extent of this process depends partly on the relative co-ordinating tendencies of the replacing anion as well as on its degree of hydration. A salt containing an anion which effectively minimises the process of deolation will obviously be the most suitable for the extraction of exchangeable Al from acid soils. The quantities of Al extracted using eight different salt solutions are presented in table 3.

TABLE 3
The effect of anions on the extraction of aluminium from acid soils*

SOIL NUMBER	TOTAL Al EXTRACTED (me%)							
	Mg(NO ₃) ₂	MgCl ₂	MgSO ₄	Mg(OAc) ₂	NH ₄ NO ₃	NH ₄ Cl	(NH ₄) ₂ SO ₄	NH ₄ OAc
1	4.6	5.0	5.5	12.5	5.6	5.5	8.0	8.0
2	5.1	5.6	6.0	11.8	6.0	6.0	7.8	8.2
3	5.1	5.6	5.7	10.6	5.7	5.6	8.1	7.4
4	7.1	7.8	8.3	13.8	7.6	7.9	10.7	9.5

SOIL NUMBER	NON-EXCHANGEABLE Al PER EXTRACTION (me%)							
	Mg(NO ₃) ₂	MgCl ₂	MgSO ₄	Mg(OAc) ₂	NH ₄ NO ₃	NH ₄ Cl	(NH ₄) ₂ SO ₄	NH ₄ OAc
1	0.074	0.080	0.109	0.231	0.093	0.084	0.170	0.136
2	0.066	0.084	0.095	0.183	0.087	0.079	0.140	0.121
3	0.072	0.090	0.094	0.158	0.090	0.079	0.134	0.115
4	0.100	0.120	0.135	0.250	0.105	0.100	0.220	0.153

SOIL NUMBER	EXCHANGEABLE Al (me%)							
	Mg(NO ₃) ₂	MgCl ₂	MgSO ₄	Mg(OAc) ₂	NH ₄ NO ₃	NH ₄ Cl	(NH ₄) ₂ SO ₄	NH ₄ OAc
1	3.0	3.1	3.1	(6.9)	3.3	3.5	(3.9)	(4.7)
2	3.5	3.6	3.7	(7.3)	3.8	4.0	4.1	(5.2)
3	3.4	3.4	3.5	(6.8)	3.5	3.7	(4.8)	(4.6)
4	4.7	5.0	5.0	(7.7)	5.1	5.5	5.4	(5.7)

* All solutions are 0.2 N.

Apart from the acetates and (NH₄)₂SO₄, the remaining salts all appear to extract comparable quantities of exchangeable Al.

The use of NH₄OAc as an extractant for Al has given rise to controversy. McLean, Heddleson and Post (1959) and Pawluk and Carson (1963) favoured extraction with NH₄OAc buffered at pH 4.8. Pratt and Bair (1961) believe that there is reason to suspect that the lowering of the pH to 4.8 dissolves Al from otherwise

insoluble compounds. This view is supported by Lin and Coleman (1960) who are of the opinion that extraction with buffered solutions cannot help in distinguishing between Al on exchange sites and the other forms in which it may exist. Because of the controlling effect of a buffered solution on the soil, the quantity of Al removed will not truly reflect the amount of exchangeable Al existing under field conditions.

Anion penetration into the polymeric Al complexes decreases in the order acetate, sulphate, chloride and nitrate (Bailar (1956)). This is the order of the 'lyotropic series' which is the order of decreasing hydration. The chloride and nitrate ions which are less hydrated than most and which possess relatively low co-ordinating tendencies, as shown by the amount of non-exchangeable Al they remove, are the most suitable anion species for the extraction of Al from soils. Of the salts used, NH_4Cl probably offers the best combination, i.e., a rapid release of exchangeable Al together with a relatively low level of non-exchangeable Al.

(iii) The effect of concentration

While it is known that the extent of anion penetration is determined in part by the co-ordinating tendency of the anion, it would be interesting to note what effect a change in concentration of the extracting solution would have on the removal of both exchangeable and non-exchangeable Al. Since NH_4Cl has been decided upon as the most suitable salt for the extraction of exchangeable Al, solutions at three additional concentration levels were employed in this investigation. The results are presented in table 4.

TABLE 4
The effect of concentration on the extraction of aluminium from acid soils.

SOIL NUMBER	TOTAL Al EXTRACTED (me %)			
	0.1N NH_4Cl	0.2N NH_4Cl	0.5N NH_4Cl	N NH_4Cl
1	3.8	5.5	6.6	7.2
2	4.1	6.0	6.9	6.8
3	3.6	5.6	6.5	6.6
4	5.5	7.9	9.2	10.0
	NON-EXCHANGEABLE Al PER EXTRACTION (me %)			
1	0.048	0.084	0.090	0.091
2	0.045	0.079	0.085	0.078
3	0.045	0.079	0.085	0.080
4	0.069	0.100	0.110	0.105
	EXCHANGEABLE Al (me %)			
1	2.6	3.5	4.3	4.9
2	3.1	4.0	4.8	4.9
3	2.7	3.7	4.4	4.7
4	3.8	5.5	6.5	7.5

There appears to be a general increase in the total amount of Al extracted with increase in concentration. This increase occurs mainly in the exchangeable fraction.

Two possibilities arise. Firstly, the increase may be due to the exposure of new exchange sites otherwise blocked to ion exchange by 'fixed Al'. Secondly, it

may be due to the removal of more strongly adsorbed Al which is electrostatically unavailable at a certain concentration.

Obviously if an increase in exchangeable Al is caused by the exposure of new exchange sites, then the non-exchangeable Al removed should increase markedly with increase in concentration of the extracting solution. However, if the increase in exchangeable Al is only due to a greater exchange arising from the increase in concentration then the difference in exchangeable Al measured between any two concentrations should correspond closely to the difference in the total amount of Al extracted.

By studying the increase in non-exchangeable Al with concentration one can decide which of the above two theories is correct.

The data in table 4 show that non-exchangeable Al contributes to only a small fraction of the increase in total Al extracted. Shen and Rich (1962) found that the exposure of 1 me required the removal of 1 mole of 'fixed Al'. The results show that this is not the case here.

Barshad (1960) believes that exchangeable Al tends to become hydroxylated and thus rarely remains in the trivalent state. Furthermore, he showed that Al ions are preferentially adsorbed the higher their degree of hydroxylation. This may offer an explanation for the observed increase in exchangeable Al, i.e., that certain ions are more strongly adsorbed than others. It is difficult to conceive that below a pH value of 5.0 (the pK value of the hydrolysis reaction of Al in solution), that the majority of Al ions are not trivalent. It is possible however that a certain degree of hydroxylation does take place which would account for the observed preferential adsorption.

These results indicate that an 0.2N solution is the most suitable. Extractions at this concentration will minimise the removal of any 'hydroxylated' exchangeable Al which may or may not exist in the trivalent state. The exchange sites electrostatically blocked by preferentially adsorbed Al ions are probably to all intents and purposes not available for ion exchange under natural field conditions.

Summary

A method for the determination of exchangeable Al in soils is proposed. This involves a long series of successive extractions during which experimental conditions with respect to soil to solution ratio and period of contact are kept constant. By plotting the cumulative data for the amount of Al removed against the number of extractions, the amount of non-exchangeable Al removed can be calculated from the resultant Nernst type curve.

Different salts remove similar amounts of exchangeable Al. The cation effect on the rate of Al release follows the order $\text{NH}_4 > \text{K} > \text{Ca} > \text{Mg} > \text{Na}$ when in the form of chlorides. Chlorides and nitrates appear to be the most effective in minimising the release of non-exchangeable Al. Increasing concentration of the extractant from 0.1N to N results in an increase in exchangeable Al which can probably be ascribed to a certain amount of preferential adsorption of Al ions on the exchange complex.

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Professor Orchard: Soils scientists have long argued whether the presence of exchangeable aluminium in acid soil is harmful or whether it is of no consequence; no one has yet said it is beneficial.

There is this suspicion about aluminium for two reasons. Plant physiologists have shown in culture solutions that free aluminium ions can be very toxic to plants. Also, the highly leached acid soils which

contain exchangeable aluminium are often infertile, this infertility being attributed to the aluminium. We have only now, however, for the first time found a sound method for determination of available aluminium.

The method is rather laborious, but is an important new tool in assessing the role of aluminium in soils. It will also now be possible to study the practical application of aluminium in soils. Why are soils rich in exchangeable aluminium infertile and suitable for certain crops only? Is it that the large amount of aluminium present occupies the exchange positions and in this way prevents more useful cations being held by the negative charges of the colloids, or is it that the large amount of exchangeable aluminium gives rise to a high concentration of aluminium in the soil solution?

An adsorbed aluminium ion on a colloidal surface is not the same as a free aluminium ion in the soil solution, and their toxicities towards plants are quite different. This can now be studied.

We can find out how to treat such soils to reduce the amount of active aluminium and so increase soil productivity.

What would be the effect of raising the pH value, or the concentration of competing ions, e.g., calcium, on the exchangeable aluminium?

We often regard our acid soils as being very unsaturated, i.e. many of the exchange positions are occupied by hydrogen. Mr. le Roux, working at the University of Natal, has found that many acid soils in Natal are saturated at their field pH value, which is sometimes very acid, if one counts in the aluminium together with calcium, magnesium, sodium and potassium. The problem then in liming the soil is not to replace hydrogen, as was thought, but aluminium, and this is a much tougher proposition, because non-exchangeable aluminium present in the soil from other sources can get back onto the colloid and the position may remain unchanged.