Potentiometric Titration of Acid Soils From Peninsular Malaysia

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Key words: **Potentiometric titration; acid soils;** Peninsular Malaysia.

RINGKASAN

Kajian ini menunjukkan bahawa Al memainkan peranan yang penting dalam mengawal keasidan tanah-tanah asid di Semenanjung Malaysia. Tindakan tampanan tanah-tanah ini dikawal oleh Al apabila pH kurang dari 5.5 dan oleh mineral-mineral lempung apabila pH lebih dari 5.5. Kadar pengekstrakan Al dari tanah bergantung kepada kepekatan larutan penekstrak. Keperluan kapur tanah-tanah boleh didapati dengan mendarap bes untuk meninggikan pH tanah ke 5.5 oleh faktor 1.3.

SUMMARY

The study indicates the dominance of Al in controlling the acidity of acid Peninsular Malaysian soils. The buffering action of the soils is dominated by Al below pH 5.5 and by the clay minerals, mainly kaolinite, at pH above pH 5.5. The rate of extraction of Al from the soils depends on the concentration of the extracting solution. Lime requirement of the soils can be obtained by multiplying the base needed to raise the pH of the soil to 5.5 by a factor 1.3.

INTRODUCTION

An important component of humid tropical soils is Al, which is either present in the solution or chemically adsorbed on the clay surfaces. The behaviour of this Al can be studied by potentiometric titration. This study attempts to explain the behaviour of soils on adding bases and to estimate lime requirement of these soils.

MATERIALS AND METHODS

Soils for this study were sampled from various sites throughout Peninsular Malaysia. The soils are Nangka, Bt. Tuku, Kerayong, Lintang, Sg. Buloh, Napai, Awang and Holyrood Series. They are alluvial soils of Holocene age, which have been described by Paramananthan (1981) as the T2 terrace soils. The taxonomic classification of these soils is given in Table 1. The morphology, physico-chemical characteristics and genesis of these soils will be published elsewhere.

The titration procedure is as follows: 1 g air-dried sample was equilibrated in 10 ml KCl solution for a period of two days, with occasional shaking. The soil was then titrated with 0.05 N NaOH solution to pH 9.0, using an automatic titrator coupled to an autoburette and a titrigraph. The change in pH with the amount of base added was recorded on a paper sheet. Two KCl concentrations, *viz.* 1 N and 0.1 N, were used. For each soil series, potentiometric titrations were carried out for both Ap and B horizons.

RESULTS AND DISCUSSION

General Consideration

The existence of partially hydrolysed Al ions on the surface of acid soils and clays was demonstrated by potentiometric titration of extracts with various salt solutions (Cabrera and Talibudeen, 1979).

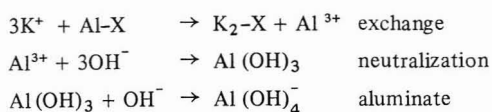It is well known that the titration curve of Al depends on Al concentration, ionic strength and titration speed.

An example of a titration curve of Al is given in *Figure 1,* where data from the work of Cabrera and Talibudeen (1979) are presented. From the diagram, it is seen that there are three buffering zones. The first zone marks the neutralization of

Table 1
Taxonomic classification of the studied soils.

SERIES	SUBGROUP	FAMILY
Nangka	Oxic Dystropept	Coarse loamy, siliceous, non-acid, isohyperthermic
Bt Tuku	Plinthaquic Dystropept	Fine loamy, mixed, acid, isohyperthermic
Kerayong	Aquic Dystropept	Fine clayey, kaolinitic, non-acid, isohyperthermic
Lintang	Oxic Dystropept	Coarse loamy, siliceous, acid, isohyperthermic
Sg Buloh	Orthoxic Quartzipsamment	Coated, acid, isohyperthermic
Napai	Typic Paleudult	Coarse loamy over clayey-skeletal, kaolinitic, acid, isohyperthermic
Awang	Aquic Dystropept	Coarse loamy, siliceous, acid, isohyperthermic
Holyrood	Typic Paleudult	Fine loamy, mixed, acid, isohyperthermic

excess H^+ present. The second zone marks the neutralization of Al, while the third zone indicates the formation of aluminate. The arrows in the diagram indicate the point of inflection. It has, however, been found also that aluminium hydroxide particles formed during titration are positively charged up to pH of 10.

Titration of exchangeable Al in soil can be schematized as follows:

$$3K^+ + Al\text{-}X \rightarrow K_2\text{-}X + Al^{3+} \quad \text{exchange}$$
$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad \text{neutralization}$$
$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \quad \text{aluminate}$$

The first reaction takes place before the titration in which K replaces Al into the solution. Al in the solution is partly hydrolysed and H^+ is thus released:

$$Al^{3+}(H_2O)_6 \rightarrow [Al.OH(H_2O)_5]^{2+} + H^+$$

Thus, when OH^- is added for neutralization part of the added OH^- is being used for the neutralization of H^+ released by the hydrolysis of Al. At high pH, gibbsite may be formed. Further addition of OH^- will raise the pH, and at the same time aluminate is slowly being formed.

The reaction of the added OH^- with the soil chemical component is not limited to Al only, but some reaction with Fe is also possible. Although it is not likely that K will replace much Fe on the clay surface (Dewan and Rich, 1970), reaction may be possible with Fe, Fe oxides and/or hydroxides already present either on the surface or in the solution. This reaction may be viewed as follows:

$$Fe^{2+}.H_2O + OH^- \rightarrow Fe^+.OH + H_2O$$
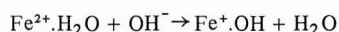
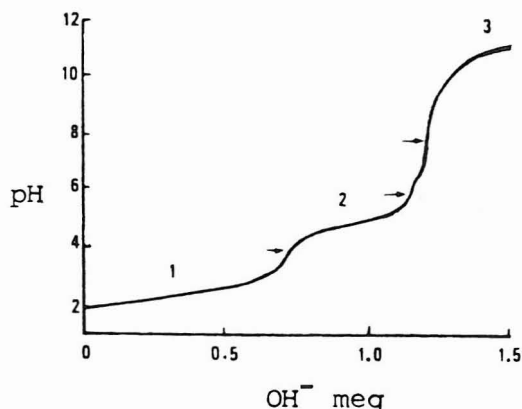It is possible that this reaction, together with that of Al provides a strong buffer at a pH level

Fig. 1. *Base titration curve of acidified 2.9 × 10^{-3} M Al $(NO_3)_3$ in 10^{-2} M $NaNO_3$ (after Cabrera and Talibdeen, 1979).*

above 7. As the pH increases, H^+ from the organic functional groups, especially the carboxyl, is released. This H^+ will be neutralized by the added OH^- as well.

Buffering Action of Al

A potentiometric titration was carried out for the Ap and B horizons of all the soils under study. The resultant titration curves were studied in detail. Practically, the change in pH with OH^- follows the same pattern. Only the points of inflection are different. This implies the existence of some kind of relationship between the shape of the curves and the chemical and mineralogical composition of the soils.

Two distinct parts where the soils show strongest buffering are noted in all cases. These are around pH 5 and above pH 8. On this basis, the two parts are discussed separately. To illustrate the significance of this fact, a titration curve of the Holyrood series is plotted, which is given in *Figure 2*. The two parts referred to in this study are the part of the curve between the pH of the soil up to pH 5.5 and the part between pH 5.5 and 9.0. The reason why the pH of 5.5 is taken as the dividing point is that if one refers to *Figure 1*, one will immediately see that the second point of inflection is at the pH between 5 and 6 and this probably marks the end of the significance of Al in the solution. In fact the buffering zone ends somewhere around pH 5.3.
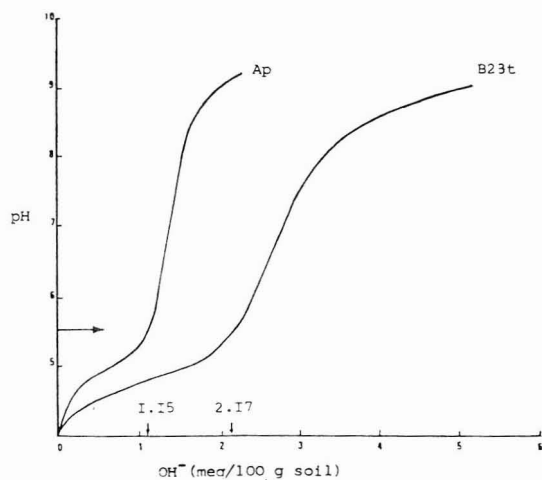

Fig. 2. Potentiometric titration curves of soils of Holyrood Series.

In part 1, the following reactions may have taken place:

1. Neutralization of H^+ in the solution

2. Neutralization of Al^{3+}
3. Neutralization of organic functional groups.

The amount of base needed to raise the pH to 5.5 is estimated from the buffer curves (Table 2). From this, it is possible to determine the relationship between the base and Al. The regression equation is given by:

$$OH^- = 0.232 + 0.829 \, (Al), \; r = 0.93^{**}$$

(pH 5.5)

The plot of the base against Al is given in *Figure 3*. It is thus confirmed that Al plays an important role in the buffering of the soil below pH 5.5. The reaction with Fe is not expected as pKa of Fe (III) is 3.0 and Fe (II) is 9.5.
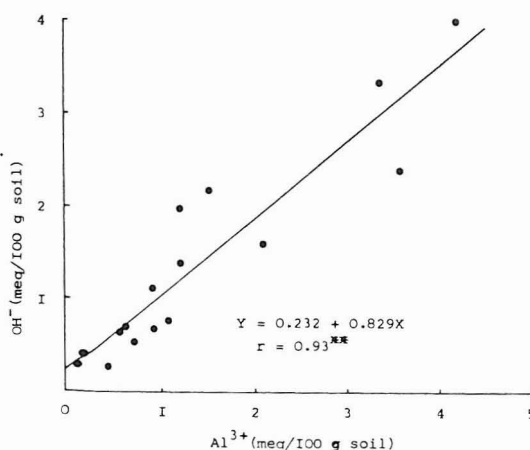

Fig. 3. The relationship between the base needed to raise the pH to 5.5 and the Al^{3+} present in the soils.

Buffering Action of Clays

In part 2, one or more of the following reactions may have taken place:

1. Reactions with broken edges of colloids
2. $Al\,(OH)_3 + OH^- \rightarrow Al\,(OH)_4^-$
3. $Fe^{2+}.H_2O + OH^- \rightarrow Fe^+.OH + H_2O$
4. $RCOOH + OH^- \rightarrow RCOO^- + H_2O$

The four mentioned reactions can provide some buffering action in the pH range of 5.5–8.0. To find out which one of them plays a dominant role, the amount of base needed to change the pH from 5.5 to 9.0 were estimated from the buffer curves (Table 2). The base needed was then compared to the amount of clay content, iron oxide, organic matter and Al present in the soil.

Table 2
The amount of OH⁻ needed to raise the pH of the soils to 5.5, 9.0 and
between pH 5.5 and 9.0 for samples equilibrated in 1N KCl

| SERIES | HOR | OH^- meq/100 g soil | | | CLAY % | Fe_2O_3 % | O.C % | Al meq/100 g |
		pH 5.5	9.0	5.5-9.0				
Nangka (I)	Ap	0.28	1.00	0.72	8.5	0.21	1.27	0.43
	B22	0.65	1.27	0.62	12.1	0.29	0.12	0.90
Bt Tuku (3)	Ap	1.58	3.21	1.63	17.9	0.36	0.81	2.14
	B22	2.43	3.53	1.10	31.5	1.04	0.06	3.60
Kerayong (4)	Ap	0.30	6.62	6.32	53.5	1.77	1.74	0.11
	B22	4.03	8.01	3.98	54.4	2.29	0.09	4.21
Lintang (9)	Ap	0.70	3.28	2.58	14.9	0.57	0.85	0.58
	B23	0.68	2.50	1.82	23.1	0.93	0.19	0.55
Sg. Buloh (II)	Ap	0.75	1.34	0.59	5.9	0.52	1.64	1.08
	AC3	0.55	1.61	1.06	9.3	9.52	0.08	0.71
Napai (18)	All	1.40	4.38	2.98	12.2	1.25	1.68	1.17
	B23tcn	3.35	10.59	7.24	53.1	4.89	0.32	3.36
Awang (20)	Ap	0.38	1.01	0.63	4.2	0.13	0.42	0.11
	B3/BC	2.00	4.06	2.06	25.2	0.50	0.03	1.17
Holyrood (21)	Ap	1.15	2.35	1.20	21.2	0.88	1.92	0.94
	B23t	2.17	5.23	3.06	34.6	1.44	0.15	1.50

The regression equation for the relationship was determined and is given by:

$$OH^- (pH\ 5.5\text{-}9.0) = -0.28 + 0.116\ (\%\ Clay) - 0.068\ (\%\ Fe_2O_3) + 0.396\ (\%OC) - 0.217\ (\%\ Al)$$

$$F_{4;11} = 9.76^{**}\ R^2 = 0.77,$$

The best relationship is obtained for the % of clay, with $r = 0.85^{**}$. The r values for the rest in order of decreasing importance are OC > Al > Fe_2O_3. The relationship between bases and clay % is given by:

$$OH^- (pH\ 5.5\text{-}9.0) = -0.016 + 0.099\ (\%\ clay)$$

$$F_{1;14} = 35.26^{**},\ r = 0.85$$

This relationship is illustrated in *Figure 4a.*

It is thus known that clay minerals play a dominant role in the adsorption of base above pH 5.5. In order to know which of the minerals determines the reaction, the base was compared to the amount of kaolinite, mica/chlorite, gibbsite and iron oxide (represents mainly goethite) present in the soil. The regression equation is given by:

$$OH^- = 0.114 + 0.055\ (\%\ Kaol) + 0.015\ (\%\ Mica/Chlo) + 0.449\ (\%\ Gibb) + 1.09\ (\%\ Fe_2O_3)$$

$$F_{4;9} = 11.23^{**},\ R^2 = 0.81$$

The highest r is obtained for kaolinite with $r = 0.83^{**}$. The relation between the base and the % of kaolinite *(Figure 4b)* is given by the equation:

$$OH^- (pH\ 5.5\text{-}9.0) = -0.067 + 0.186\ (\%\ Kaol),\ r = 0.83^{**}$$

The reaction with kaolinite is taking place at the broken edges. Kaolinite develops a small amount of positive charges at low pH, around the edges of the crystal (shown below), due to proton acceptance by the aluminol group (Greenland and
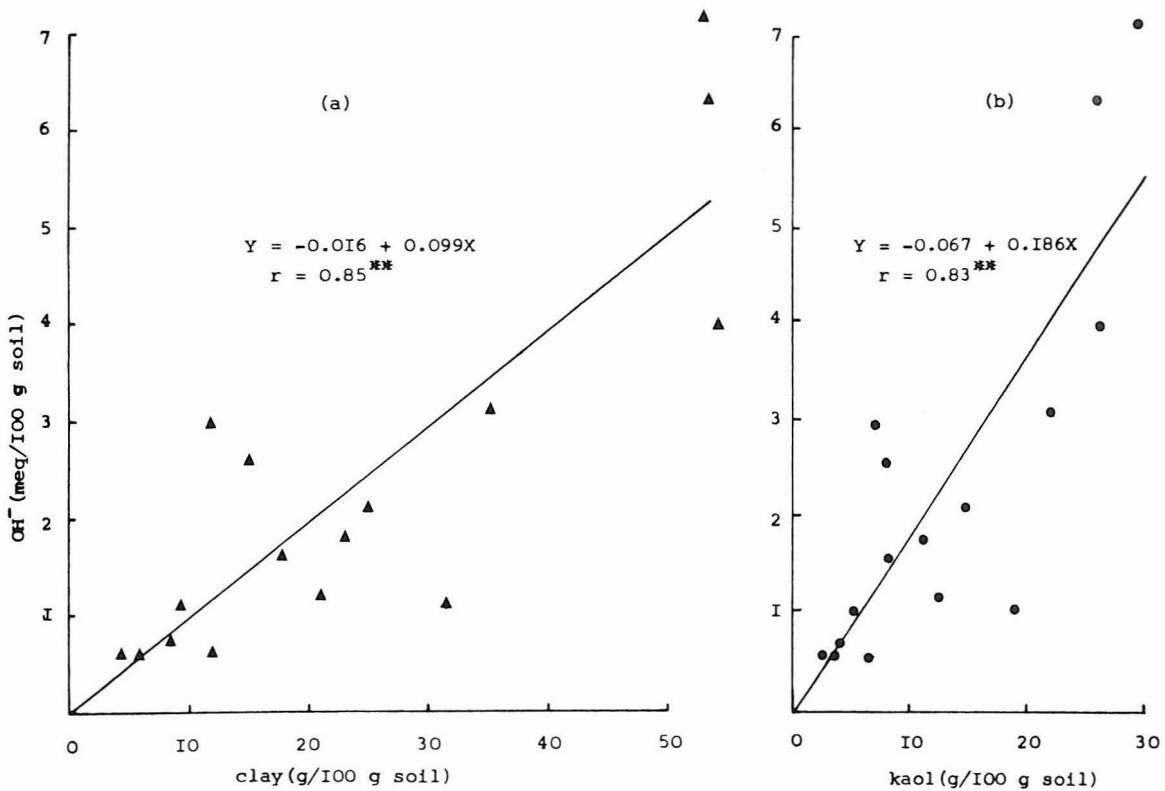
Fig. 4. The relationship between the base needed to raise the pH from 5.5 to 9.0 and clay(a) and between the base and kaolinite present in the soils(b).

Mott. 1978) Note that below the edge pH_0 there is no negative charge present on the edges.

The pH at which the net charge of the edges is zero (pH_0) is 7.3 (Rand and Melton, 1975). Note that the pH_0 of the whole kaolinite crystal is much lower, i.e., between 4 and 5 (Dixon, 1977).
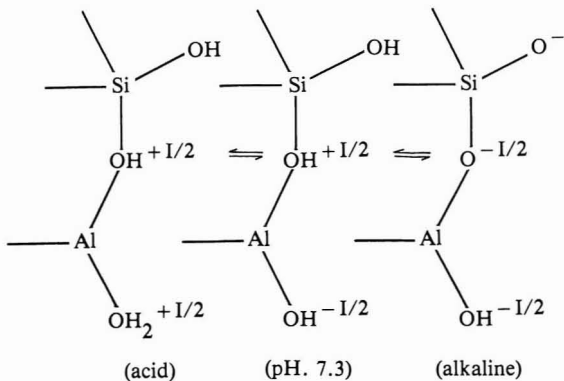
The more kaolinite present in the soil, the greater the buffering action it will give to the soil. This probably explains why in *Figure 2* the titration curve of the Ap horizon of Holyrood Series is steeper than that of the B23t around pH 5.5-8.0. More kaolinite is present in the B23t than in the Ap (resp. 21.86% and 12.64%). This phenomenon has also been noticed in other soils.

Extraction of Al by KCl solution
In this study, the samples were equilibrated in either 1 N KCl or in 0.1 N KCl before they were titrated. It is found that for 1 N KCl equilibrating agent, the amount of OH^- needed to raise the pH to 5.5, 7.0 and 9.0 is slightly higher than the values obtained by using 0.1 N KCl. This is similar to the findings of Dewan and Rich (1970) (Table 3).

This difference arises as a result of the different rate of extraction of Al by the different concentration of KCl solution (Amedee and Peech, 1976).

Table 3

Comparison between titration curves of soils equilibrated in 1N KCl and those equilibrated in 0.1 N KCl solution.

SERIES	HOR	1N KCl			0.1 N KCl		
		pH 5.5	7.0	9.0	5.5	7.0	9.0
		OH^- (meq/100 g soil)			(meq/100 g soil)		
Kerayong	B^{22}	4.03	5.40	8.01	4.00	5.25	7.45
Lintang	Ap	0.70	0.93	3.28	0.50	0.80	3.20
Sg. Buloh	AC3	0.55	0.85	1.61	0.50	0.80	1.60
Awang	Ap	0.38	0.55	1.01	0.18	0.38	0.90
Holyrood	B2 3t	2.17	2.75	5.23	2.10	2.73	5.15

Table 4

Lime requirement (ton/ha) of the studied soils by the methods of Sanchez (1976), (Lathwell, 1979) and the buffer curves.

SERIES	Alx1.65 (Sanchez, 1976)	Alx2 (Lathwell, 1979)	OHx1.3
Nangka	0.71	0.86	0.37
Bt Tuku	3.53	4.28	2.05
Kerayong	0.18	0.22	0.39
Lintang	0.96	1.16	0.91
Sg. Buloh	1.78	2.16	0.97
Napai	1.93	2.34	1.82
Awang	0.18	0.22	0.50
Holyrood	1.55	1.88	1.50

Estimation of Lime Requirement

One important practical application of the titration curves obtained in this study is the estimation of the lime requirement. Liming is a common agronomic practice in tropical soils, which are usually limed to the pH of 5.5 on the basis that the effect of Al toxicity is minimal above this pH.

The theoretical calculation of the lime requirement is done in the following way. The weight of 1 ha of soil to a depth of 20 cm with an average density of 1.3 g/cm^3, is 2.6×10^9 g. Taking the case of Ap horizon of Holyrood Series, the amount of OH^- needed to raise the pH to 5.5 is 1.15 meq/100 g soil (Figure 2). 1 meq of OH^- is equivalent to 1 meq of carbonate (1 meq of $CaCO_3$ O 50 mg). Therefore, the lime requirement is:

100 g soil need 1.15×50 mg $CaCO_3$

$$2.6 \times 10^9 \text{ g soil need } \frac{1.15 \times 50 \times 2.6 \times 10^9}{100 \times 10^9} \text{ ton/ha}$$

$$= 1.5 \text{ ton/ha}$$

For simplicity, a factor of 1.3 can be derived from the above calculation. To calculate the lime requirement (ton/ha), one can just multiply 1.3 with the base. The amount of the base (OH^-) can be obtained directly from the titration curves. In this way, a simple method to estimate lime requirement of soil is thus proposed.

Soils with variable charge colloids often have pH values of 5 or less. Under this conditions, Al is present in significant amounts and Al toxicity is a common cause of infertility in this soils. Liming soils with variable charge colloids leads to an increase of negative charges, hence the soils can retain more K, Ca and Mg.

Theoretically, it is possible to lime the soil to any pH value, depending on the physiological requirement of the crop. One of the reasons for the choice of pH 5.5 is that at higher pH, the effect of Al is considered minimal. A comparison of the lime requirement obtained by this method with those of other methods is shown in *Table 4*.

Q t-rest on paired observations shows that for the comparison between Sanchez method and the present one, the $t_{cal} = 1.378$, to be compared with $t_{7;0.2} = 7.415$. For the comparison with the Lathwell method the $t_{cal} = 2.02$, to be compared with $t_{7;0.05} = 2.365$.

It is thus seen that the lime requirement of the studied soils obtained by potentiometric titration is comparable to that obtained by the method of Sanchez (1976) and by the method of Lathwell (1979).

CONCLUSIONS

Potentiometric titration provides evidence on Al as a dominant component of acidity in acid tropical soils below pH 5.5. Above pH 5.5, kaolinite proivdes a strong buffering action to the soils. The lime requirement of these soils can be obtained by multiplying the amount of base needed to raise the pH of the soil to 5.5 by a factor 1.3.

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