Mineralogy and Surface Charge Properties of two Acid Sulfate Soils from Peninsular Malaysia

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ABSTRAK

Dua siri tanah asid sulfat yang diambil dari ladang kelapa sawit di Perak, Semenanjung Malaysia telah dikaji. Tanah-tanah ini dicirikan oleh pH yang rendah dan kehadiran motel kuning, yang dikenalpasti sebagai jarosit dan/atau natrojarosit. Mineral lain yang turut ada ialah kaolinit, mika, mika-smektit dan smektit. Cas negatif di atas permukaan tanah didapati bertambah dengan bererti dengan kenaikan pH. Kenaikan pH itu tidak bergantung kepada kehadiran oksida dan/atau hidroksida kerana bahan-bahan tersebut terlalu sedikit di dalam tanah. Di atas kenaikan pH itu, adalah disyorkan bahawa KPK tanah asid sulfat sepatutnya ditentukan di pH tanah untuk menggambarkan keadaan yang sebenarnya. Di samping itu juga, tanah-tanah itu menampan dengan kuat di pH 3 – 5. Penampanan di pH itu bersangkutan dengan kehadiran aluminium yang tinggi.

ABSTRACT

Two acid sulfate soils sampled from an oil palm estate in Perak, Peninsular Malaysia, were studied. The soils were characterized by a low pH and the presence of yellowish mottles, which were identified as jarosite and/or natrojarosite. Other minerals present were kaolinite, mica, mica-smectite and smectite. The negative charges on the soil surface were found to increase significantly with an increase in pH. This increase was not related to the presence of oxides and/or hydroxides as these materials were present in very small amounts in the soils. On account of the increase in the negative charges with an increase in pH, it is suggested that CEC of acid sulfate soils be determined at soil pH to give a better reflection of the soil properties. Further, it was found that the soils were highly buffered at pH 3-5. The strong buffering at this pH range was related to the presence of high amounts of aluminium in the soil.

INTRODUCTION

In Malaysia, acid sulfate soils usually undergo an amelioration programme before they are used to grow oil palm, coconut and paddy (rice). These soils are characterized in the field by the presence of yellowish mottles, with a hue of 2.5Y or yellower and a chroma of 6 or more. The pH of most of the acid sulfate soil samples below 50 cm depth, is reported to be around 3 - 4 (Bloomfield and Coulter, 1973). Van Breemen (1982) and Carson *et al.* (1982) attribute the soil buffering at that pH range to the action of jarosite, $Fe(OH)_{a}$ and kaolinite.

Acid sulfate soils are widespread, occupying about 110 000 ha, along the west coast of Peninsular Malaysia (Kanapathy, 1973). Under natural conditions, the soils are occupied by mangrove (*Rhizosphere macronata*) and/or nipah palm (*Nipa frutescens*). On draining, pyrite in the potential acid sulfate soils is oxidized and extreme acidity is subsequently produced. The high acidity attacks the phyllosilicates in the soils particularly the 2 : 1 minerals; 1 : 1 minerals like kaolinite are more resistant to acid attack (Van Breemen, 1973).

Bloomfield and Powlson (1977) estimate that about 200 tonnes of CaCO₃ are needed to neutralize the potential acidity in 1 ha of soil, containing 1% pyrite-S to a depth of 100 cm. Considering that some acid sulfate soils in Malaysia are known to contain 5% or more pyrite-S (Bloomfield *et al.*, 1968), it is obviously impractical to reclaim the soil by liming alone.

In this experiment, some of the physicochemical processes taking place in some common acid sulfate soils are explained in terms of their mineralogical and surface charge properties. The data available from this study should be useful for the reclamation of acid sulfate soils for crop production.

MATERIALS AND METHODS

Two soil series sampled from an oil palm estate, in Teluk Intan, Perak, Peninsular Malaysia, were selected for the study. These soils are characterized in the field by the presence of yellowish mottles at 50 - 100 cm depth. They belong to the Tongkang and Jawa Series and are classified as Sulfic Tropaquepts (Paramananthan, 1983). The soils, which were sampled according to horizons, were air-dried, ground and sieved (<2 mm). Routine chemical analysis was carried out_on the samples and the results of the analysis are given in Table 1.

The clay fraction, from the textural analysis, was kept for mineralogical studies. Minerals in the clay fraction were identified by X-ray diffraction (XRD) and their amounts were subsequently estimated by Thermogravimetric Analysis (TGA) or by Differential Scanning Calorimetry (DSC). Complementary identification of minerals was also carried out by Scanning Electron Microscope (SEM) and transmission electron microscope (TEM). The yellowish materials scraped from the ped faces and/or voids were subjected to X-ray diffraction analysis.

Titration curves were prepared by titrating 5 g of soil, equilibrated overnight in 50 ml 1N KCl, by 1N KOH or 0.1N HCl, using an autotitrator. The bases needed to raise the soil pH to 5.5 and from 5.5 to 9.0 were estimated from the curves. The negative and positive charges on the soil surfaces at pH 3, 4, 5 and 6 were determined by the method of Gillman and Uehara (1980). Fe³⁺ titration curve was prepared by titrating 50 ml 0.01N FeCl₃ with 0.1N KOH while the Al³⁺ titration curve was prepared by titrating 2 mg Al³⁺ in 50 ml 1N KCl by 0.1N KOH.

RESULTS AND DISCUSSION

Mineralogy

The X-ray diffractogram of the yellowish mottles is shown in *Fig. 1;* clear peaks at 6.0Å, 5.1Å, 4.25Å, 3.35Å, 3.11Å and 3.08Å are present. XRD peaks at 6.0Å, 5.1Å, 3.11Å and 3.08Å indicate the presence of natrojarosite (NaFe₃ (SO₄)₂ (OH)₆) and/or jarosite (KFe₃ (SO₄)₂ (OH)₆) in the sample (De Coninck, 1978). The 4.25Å and 3.35Å XRD peaks are the peaks of quartz, which are present together with the yellowish mottles.



Fig. 1: X-ray diffractogram of untreated yellowish mottles scraped from ped faces and voids.

Series	Hor	Depth (cm)	Bases				App. CEC	0.C.	Fe O 3	pH (H <u>2</u> O)	
		(011)	Na	K	Ca neq/100 g so	Mg oil	Al	clay)	70	70	
Jawa	Ap	0-20	0.16	1.13	40.42	3.90	0.24	37.95	40.5	0.02	7.0
	B 21	20 - 60	0.18	0.42	0.72	1.30	6.41	30.63	1.58	0.03	3.8
	B 22	60 - 101	0.47	0.49	1.86	4.16	17.83	33.19	0.99	0.02	3.5
	С	+ 101	0.12	0.11	0.26	6.90	49.46	37 75	1.41	0.02	2.3
Tongkang	Ap	0-8	0.46	0.73	3.88	6.93	3.00	40.38	1.12	0.01	4.3
	B 21	8 - 80	0.52	0.37	2.37	5.20	6.57	38.20	0.54	0.01	3.6
	B 22	80 - 120	0.34	0.26	2.10	4.95	6.74	39.66	1.28	0.05	3.2
	С	+ 120	0.27	0.07	3.86	11.26	18.73	38.69	1.54	0.02	3.0

TABLE 1 Chemical properties of Jawa and Tongkang Series

Under the scanning electron microscope (Plate 1), jarosite and natrojarosite appear as cubes. These cubes are usually found in voids or old root channels and occur as clustered crystals. A similar kind of occurrence has been reported in Canada (Mermut et al., 1985). It is not possible to distinguish the two forms of jarosites just by their morphology. From the point of view of morphology and crystal system, it has been suggested that jarosite (natrojarosite) is a pseudomorph of pyrite (cubic). This view has been rejected by Mermut et al. (1985) who found natrojarosite to be smaller than pyrite. They suggested that natrojarosite was formed by recrystallization from the solution. In nature, jarosite (natrojarosite) is believed to have been formed by the oxidation of pyrite in the presence of K⁺ and Na⁺. The oxidation of pyrite (Van Breemen, 1982) is given by the equation: -

$$\text{FeS}_{9} + 15/40_{9} \rightarrow \text{Fe(OH)}_{8} + 2\text{H}_{9}\text{SO}_{4}$$



Plate 1: SEM micrographs (A and B) of octahedral shaped jarosite crystals in C horizon of Jawa Series; jarosite crystals are clustered in voids.

In the presence of K⁺, jarosite (KFe_s (SO₄)₂ (OH)) is formed, while natrojarosite (NaFe₃ (SO₄)₂(OH)) is formed if Na⁺ is present. Some of the potassium and sodium needed for the reaction can be supplied by soil minerals released from weathering (acid attack) under very acid conditions.

Fig. 2 is a XRD diffractogram of deferrified (dithionite) clay fraction from the Ap horizon of Tongkang Series. This diffractogram (Mgsaturated) shows the presence of mica (10\AA , 5\AA , 3.35A), kaolinite (7.2\AA , 3.57\AA), gibbsite (4.85\AA) and quartz (4.25\AA). Some halloysites are also present in the sample as shown by the transmission electron microscope (*Plate 2*). Under TEM, halloysite is normally tubular, while kaolinite is hexagonal in shape. Goethite is absent as indicated by the very low amount of free iron oxide present in the soil (Table 1).

When the Mg-saturated sample was saturated with glycol, the 15Å peaks completely expanded to 17.5Å (*Fig. 2*). The expansion of the 15Å peaks to 17.5Å points to the presence of smectite. No mica mixed layer is present in soils of this horizon, but mica mixed layers were



Fig. 2: X-ray diffractogram of the treated clay sample from the Ap horizon of Tongkang Series.

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Plate 2: TEM micrographs showing kaolinite (hexagonal) and halloysite (tubular) from the soils of Jawa (A) and Tongkang Series (B).

present in the C horizon (not given). This is indicated by the presence of a 13Å peak in the Mg-saturated sample. The 13Å peak completely expanded to 14.5Å on glycolation, pointing to the presence of mica-smectite. There is only a slight mineralogical difference between the Ap horizon and the C horizon.

After the sample was saturated with K ⁺, part of the 14 - 15Å peaks collapsed and when it was heated to 550°C, the whole peaks collapsed to 10Å. These and the absence of a 16Å peak in the glycolated sample show that the soils do not contain chlorite and/or chlorite mixed layers.

The clays of Jawa Series gave a more or less similar XRD pattern, pointing to a similar kind of mineralogy. This study indicates that some of the mica in the Ap horizon have been completely transformed into smectite. Whereas, in the C horizon, under anaerobic conditions, the mica is partly converted to mica-smectite and partly to smectite.

Fig. 3 gives the TGA thermograms of the studied soils. The weight loss at 291°C and 513°C show the presence of gibbsite and kaolinite respectively. The amount of kaolinite was estimated from the thermogram and is given in Table 2. The amount of gibbsite was too low for estimation by the TGA. The DSC, which is more sensitive than TGA, was therefore used to estimate the gibbsite; the estimated amount of gibbsite in the clay fraction was small (<1%).

By X-ray diffraction and thermal analysis, it was found that the dominant minerals in the clay fraction of the studied soils were kaolinite, smectite, mica and mica-smectite. Knowing the percentage of kaolinite and considering that the



Fig. 3: TGA thermograms of clay samples from Jawa and Tongkang Series.

sand and silt fractions are entirely made of quartz, it is possible then to estimate the combined percentage of mica, mica-smectite and smectite (together). The data in Table 2, shows that the combined percentage of mica, micasmectite and smectite exceeds that of kaolinite. Mica, mica-smectite and smectite are usually referred to as permanent charge minerals (Uehara and Gillman, 1980; 1981), meaning that the charges on these minerals do not change significantly with the change in pH. Their properties are considered different from the oxides in Oxisols which tend to change with the change in pH (Tessens and Shamshuddin, 1982; 1983).

Surface Charge

The active part of the soil, that is the clay fraction, was composed almost entirely of phyllo-



Fig. 4: The change of negative charges on the soil surfaces with increasing pH.

TABLE 2								
Mineralogical	composition	of soils	of Jawa	and	Tongkang	Series (per	100	g soil)
in the Ap and C horizons								

Series	Horizon	Silt sand	Kaolinite	Smectite mica mica-smectite
Jawa	Ap	45.2	26.1	27.7
	C	31.5	30.8	37.7
Tongkang	Ap	47.9	24.6	27.5
	C	39.6	27.9	32.5

silicates, namely kaolinite, mica, mica-smectite and smectite. Oxides and hydroxides, which are variable charge minerals, were present in very small amounts. In spite of the dominance of the permanent charge minerals, the negative charges on the soil surface were found to increase with pH. This is illustrated clearly by the soils of Tongkang and Jawa series (*Fig. 4*).

The negative charge at pH 6 is about double (Fig. 4) that of pH 3 (Table 3). This is not in agreement with the current thinking on the charge properties of phyllosilicate (Uehara and Gillman, 1980). The increase in negative charge with increasing pH is not due to oxides, as in the case of oxisols (Tessens and Shamshuddin, 1982; 1983). It is therefore assumed that the charges on the mica, mica-smectite and smectite are not completely permanent. Some of the charges on these minerals are variable, possibly those located at the broken edges of the minerals. This explanation is consistent with the work of Hendershot and Lavkulich (1983), who showed that when the pH was increased from 3 to 7, the CEC of mica was increased by twice while that of kaolinite increased by four times.

The CEC (meq/100 g soil) of acid sulfate soils is usually measured at pH 7. For the soils studied, the CEC was also determined at pH 7. The apparent CEC (meq/100 g clay) value at pH 7 for the soils studied is more than 30 meq/100 g clay (Table 1). The apparent CEC at the soil pH (around pH 3) could be much lower. So base saturation calculated on the basis of CEC at pH 7 underestimates the true value. Fertilizer recommendations based on this base saturation therefore leaves much to be desired. For acid sulfate soils, it may be better to determine the CEC by unbuffered NH₄ Cl, which is the CEC close to the soil pH.

Following the low oxides/hydroxides content, the positive charges in the soils are very low, with less than 1 meq/100 g soil (Table 4). The values decrease gradually with increasing pH. The low oxides/hydroxides and high phyllosilicate content are reflected by the low pH_{o} ; the

Series	Horizon	- VE Charges		Increase
		3	6	
			meq/100 g soi	1
awa	Ap	5.55	10.28	4.73
	С	9.77	19.10	9.93
Tongkang	Ap	10.93	15.59	4.66
	С	11.52	20.26	8.74

TABLE 3 The differences in negative charges in acid sulfate soils at pH 3 and 6

TABLE 4

pH_o and positive charges on the soil at pH 3, 4, 5 and 6 of two acid sulfate soils

Sories	Horizon	+ VE Charges (meq/100 g soil)						
	110112011	3	4	5	6	pH _o		
Jawa	Ар	0.67	0.66	0.55	0.27	4.4		
	С	0.42	0.41	0.21	0.09	2.7		
Tongkang	Ар	0.81	0.71	0.69	0.48	2.2		
	С	0.65	0.44	.24	0.21	2.6		

value of pH_o is less than 3 in the lower horizons (Table 4). Soils with high amounts of oxides/ hydroxides register much higher pH_o values (Uehara and Gillman, 1981; Hendershot and Lavkulich, 1983).

Comparing the negative charges (Fig. 4) and the positive charges (Table 4) at pH 3, 4, 5 and 6, we see that the amount of negative charges exceed that of positive. Even at pH close to 0, negative charges are higher than positive charges. Hence, it is not possible to determine the PZNC of these soils. PZNC, as defined by Gillman and Uehara (1980), is the pH at which the amounts of negative and positive charges of the soil systems are equal.

An interesting feature of these soils is that the soils are strongly buffered at pH 3-5 (Fig. 5; buffering curves of Tongkang Series are not shown here). Strong buffering at this pH range could be due to the action of jarosite, kaolinite and Fe(OH)₃ as suggested by Carson *et al.* (1982). For the weathered, non-acid sulfate soils in Malaysia, it has been shown (Shamshuddin and Tessens, 1983) that aluminium controls buffering action occuring below pH 5.5.

The titration curves for the samples were compared to the standard curves of Al^{3+} (Fig. 6). The titration curves of the soil samples follow closely that of Al^{3+} , but not that of Fe³⁺. The





Fig. 6: Standard titration curves of Fe³⁺ and Al³⁺

effect of Fe³⁺ is probably minimal as the amount of iron in the soil is low (Table 1).

The bases (ml) needed to raise the soil pH to 5.5 were estimated from the curves and the results were compared to the clay content, organic matter and Al present in the soils. Jarosite was excluded in the regression analysis as it was difficult to determine its amount accurately by X-ray diffraction or thermal analysis.

The relationships between base (ml) and the three factors selected is given by the equation: –

OH
$$^{-}$$
 = 0.68 + 0.19 clay % + 1.14 OM + 0.21 Al
R² = 0.91, F₂ = 10.58*

Thus, it was shown that the base needed to raise soil pH to 5.5 was significantly correlated to the clay content, organic matter and Al. The most important factor controlling buffering action was found to be Al. The regression equation relating OH $^-$ and Al is given by the equation: –

OH $^{-}$ = 5.20 + 0.26 Al R² = 0.88, F_{1.5} = 37.97**

The significance of Al in controlling the soil buffering is shown in *Fig.* 5 where buffering increases with depth following the increase of Al with depth (Table 1).

The bases needed to raise the soil pH from 5.5 to 9.0 were also estimated. The multiple linear regression study showed that there was a poor correlation between bases and the three variable parameters selected. In an earlier study by Shamshuddin and Tessens (1983), for non-acid sulfate soils, it was established that clay content (mainly kaolinite) was highly correlated to the base. Perhaps in acid sulfate soils, other components such as jarosite and pyrite or even $Fe(OH)_3$ might be involved in the buffering action above pH 5.5.

General Discussion

Though the soils are dominated by mica, mica-smectite and smectite, which are traditionally referred to as permanent charge minerals (Uehara and Gillman, 1980), the negative charges in the soils were found to increase significantly when the pH was increased to 6. Negative charges at pH 7 are then considered to be much higher than at soil pH. As such the traditional method of CEC determination on pH 7 does not reflect the true CEC value of the soil.

When the pH is raised, more OH $\overline{}$ are adsorbed onto the surface or H $^+$ are released into the solution, causing an increase in negative charges. These reactions are much more important above pH 5.5. Below pH 5.5, most of the OH $\overline{}$ are used to neutralize Al $^{3+}$ in the soil.

These reactions, most probably, take place at the broken edges of the phyllosilicates. As for kaolinite, the increase in negative charges becomes important only at high pH; the pH of the broken edges of kaolinite is around 7.3(Rand and Melton, 1975). This particular property may have some effects on soil buffering (*Fig. 5*).

When lime is applied, Al^{3+} is initially neutralized by the OH ⁻ produced by the hydrolysis of CO₃⁻. Soil pH will remain below 5 until Al^{3+} is fully neutralized. Luckily, hydrolysis of jarosite is minimal, as it is very insoluble (Carson *et al.*, 1982). Natrojarosite persists even at high pH and in the presence of CaCO₃ (Mermutt *et al.*, 1985). This provides further proof of the low solubility of the mineral. If the mineral is highly soluble, its hydrolysis will cause the pH to remain below 4 until the reaction is complete.

From past experience, neutralizing the total acidity by liming alone is not economical as it requires too much lime. Besides, overliming may be detrimental to plant growth (Van Breemen and Pons, 1978).

CONCLUSION

The dominant clay minerals in the soils studied are kaolinite, mica, mica-smectite and smectite. In increasing the soil pH from 3 to 6, the negative charges on the soil surface increased twice, although the soils are dominated by the so-called permanent charge minerals. The reaction is thought to take place mainly at the broken edges of the phyllosilicates. The increase in charge with increasing pH implies that the traditional CEC determination at pH 7 does not reflect the true CEC under field conditions. The soils are also strongly buffered at pH 3-5. The strong buffering at this pH range is due to the presence of high amounts of Al³⁺ in the soil.

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