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Tho, Huynh-tong

Laboratory of Soil Science, Faculty of Agriculture, Kyushu University

Egashira, Kazuhiko

Laboratory of Soil Science, Faculty of Agriculture, Kyushu University

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Some Chemical, Physical and Mineralogical Properties of Acid Sulfate Soils from the Mekong Delta in Vietnam

Huynh-tong-Tho and Kazuhiko Egashira

Laboratory of Soil Science, Faculty of Agriculture,
Kyushu University, Fukuoka, Japan

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Vietnam acid sulfate soils were analysed on their physico-chemical and mineralogical properties. Effects of submerging on their electrochemical and chemical changes were also investigated.

These acid sulfate soils were characterized by heavy texture, with clay and silt contents of more than 90%. These soils had rather high organic matter and CEC levels but were deficient in exchangeable K and available P. They were also characterized by strong acidity ($\text{pH} < 3.7$). Their strong acidity was ascribed to the presence of aluminum and ferric sulfate. The clay fraction ($< 2\mu\text{m}$) of these soils consisted mainly of illite and kaolinite with lesser amounts of montmorillonite, vermiculite and chlorite. The Vietnam acid sulfate soil sample showed a retarded development of soil reduction, namely, gradual decrease in Eh and gradual increase in Fe^{2+} , during submergence. Its acidity did not change. Addition of starch caused a considerable increase in Fe^{2+} , whereas addition of CaCO_3 caused the precipitation of Fe^{3+} and Al^{3+} .

I. INTRODUCTION

Acid sulfate soils are soils of marine floodplains which upon drainage and aeration show a definite and severe acidification due to the oxidation of sulfides (mainly pyrites, FeS_2) and the formation of sulfuric acid. These soils in their oxidized form show straw-yellow mottlings and streaks of basic ferric sulfate $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. It is to be noted that these soils are not limited to marine floodplains exclusively; other soils that bear FeS_2 deposit in the inland may show the same characteristics. However, the acid sulfate soils outside the recent or fossil marine plains are scarce (Moormann, 1963).

Acid sulfate soils cover large areas in tropical and subtropical regions. The review of Bloomfield and Coulter (1973) gives some indications of their extent: **800,000** ha in Thailand; 2 million ha in Vietnam; **200,000** ha in Malaya; **100,000** ha in Sierra Leone; 2-3 million ha in Kalimantan.

Almost all of acid sulfate soils in Vietnam are located in the Mekong delta that is comprised of 7.5 million hectares of alluvial deposits of the Mekong river and that is typified by its extreme flatness especially in the lower part. These soils are developed in clayey alluvial sediments rich in sulfides, especially pyrites, and are often flooded by sea or fresh water in rainy season. Nearly half of these areas are so acid as to be uncultivable under the present economic condition. The less acid soils are cultivated as paddy soil but with poor produc-

tion because of low pH *per se*, and toxicity of excess aluminum, iron and hydrogen sulfide.

Various investigations have been done on acid sulfate soils. The genesis and management of these soils was recently reviewed by Bloomfield and Coulter (1973). Moormann (1963) studied the acid sulfate soils of the tropics and stated that these soils which have a very high potential acidity, with pH value below 2, show an extremely low base saturation in their oxidized form. In these soils with low organic matter contents, tilth is mostly poor from the beginning. The surface layers dry up in very hard clods, whereas the deeper layers stay or become highly compact and impervious. Post and Sloane (1971) investigated the nature of clay soils from the Mekong delta, An-giang province, South Vietnam and reported that the delta soil samples consist mainly of quartz, kaolinite and illite with lesser amounts of smectite and vermiculite and traces of a large variety of soil minerals. Tanaka and Navasero (1966) studied the growth of the rice plant on acid sulfate soils from Vietnam and Malaya and concluded that the poor growth of low-land rice on acid sulfate soils is not caused by aluminum toxicity but by iron toxicity. Mai-thi-my-Nhung and Ponnampertuma (1965) studied the effects of CaCO_3 and prolonged flooding on the chemical and electrochemical changes in a flooded acid sulfate soil and proposed some provisional reclamation measures.

The reclamation and improvement of acid sulfate soils are urgent need for agriculture in the tropics. For this reason, this investigation was carried out to understand the characteristics of acid sulfate soils and to consider further investigations for the satisfactory reclamation processes of these soils.

II. PHYSICO-CHEMICAL PROPERTIES OF VIETNAM ACID SULFATE SOILS

Objective

To characterize the physico-chemical properties of Vietnam acid sulfate soils.

Materials and methods

1) *Soil samples*

Acid sulfate soil samples were collected from 2 sites of a paddy field at the experimental campus of Cantho University in the Mekong delta (Fig. 1). Monthly rainfall and monthly average temperature of Cantho province are shown in Figs. 2 and 3, respectively.

Soil samples were air-dried and passed through a 2-mm sieve after grinding with a wooden pestle. They were stored in glass bottles.

2) *Physico-chemical analyses*

Following analytical procedures were used (Aomine and Harada, 1973) :

- (1) Particle-size analysis by pipette method
- (2) pH of 1 : 2.5 soil-water suspension, potentiometrically
- (3) Exchange acidity by Daikubara method
- (4) Cation exchange capacity (CEC) with the $\text{Ca}(\text{CH}_3\text{COO})_2$ method

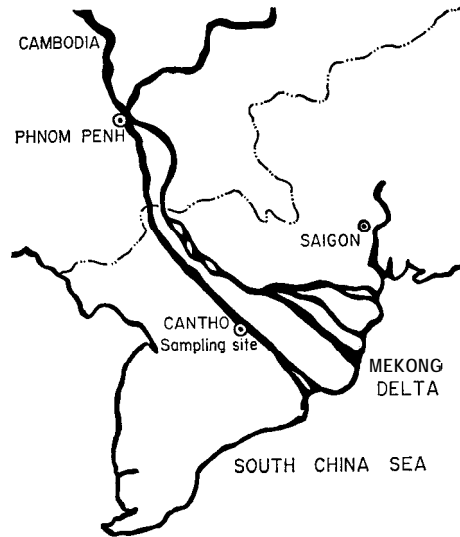


Fig. 1. Location of sampling site of Vietnam acid sulfate soils.

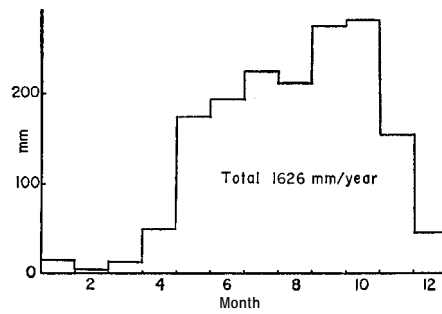


Fig. 2. Monthly rainfall in Cantho province, Mekong delta, average of 53 years. (Mekong Committee, Saigon)

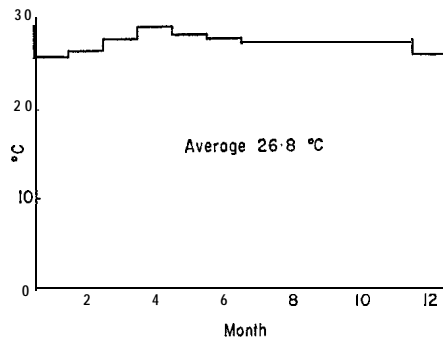


Fig. 3. Monthly temperature in Cantho province, Mekong delta, average of 1937-1940 and 1962-1970. (Directorates of meteorology in Saigon and Phnom Penh, Saigon)

- (5) Exchangeable Ca, Mg, Na, and K in the 1N $\text{NH}_4\text{CH}_3\text{COO}$ extract, determined by chelatometric titration with EDTA (Ca and Mg) or flame photometry (Na and K)
- (6) Organic carbon by wet combustion method (Tyurin's method with minor modification) ; organic matter was calculated by multiplication of organic C by 1.724
- (7) Total nitrogen by Kjeldahl method
- (8) Available phosphorus by Bray-I method
- (9) Soluble sulfate in the 1N NH_4Cl extract, determined based on the Versene chelation of the excess Ba remaining after BaSO_4 precipitation by addition of BaCl_2 (Jackson, 1958).

Results and discussion

The particle-size analysis of Vietnam acid sulfate soils is given in Table 1. The clay and silt contents were very high, and their total amounts were more than 90 % for all layers. These soils were classified as heavy clay except the first layer of profile 1. Heavy texture of these soils shows their poor physical properties.

Table 1. Particle-size analysis of Vietnam acid sulfate soils.

Layer	Depth (cm)	Content (%)			T e x t u r e
		Sand	Silt	Clay	
Profile 1					
1					
2	40-80 0-40	46.2.3	48.0	43.2 56.7	SiC
		1.0	38.7		HC
3	80-120	3.3	35.7	63.3	HC
4	120-130		45: 1	51.6	HC
Profile 2					
1					HC
2	40-80 0-40	46.2.9	43.1 51.2	52.3 45.9	HC
3	80-120	1.0	36.3	62.7	HC
4	120-140	2.7	43.9	53.4	HC

SiC, Silty clay; HC, Heavy clay,

Their chemical properties are given in Table 2. Organic matter levels of these soils were not so high in the upper layers but very high in the third layer. This is the peaty layer with dark color which is always completely reduced under field condition and sometimes contains remnants of a swamp vegetation (*Melaleuca leucadendron*). CEC values were rather high through the profile and highest in the third layer, indicating a considerable contribution of organic matter to CEC. These soils contained large amounts of exchangeable Ca and Mg. Because of the low pH of these soils (Table 3), considerable parts of them seem to be present as salt form, maybe as sulfates. Exchangeable K levels were low. The low K content may cause the K deficiency for crops. It is necessary to carry out further experiments on K need for these soils. Total nitrogen levels were low for all layers and C/N ratios increased with depth.

Table 2. Chemical properties of Vietnam acid sulfate soils.

Layer	Depth (cm)	Organic matter (%)	Total nitrogen (%)	C/N	CEC (me/100g)	Exchangeable					Available P (ppm)
						Ca	Mg	Na	K	Total	
Profile 1											
1	40-80	2.6	0.16	18.7	31.1	15.3	16.0	0.2	0.1	31.6	0.9
2		4.5									
3	80-120	15.7	0.35	26.0	52.5	29.6	13.0	0.6	0.1	43.3	0.1
4	120-130	7.1	0.11	37.3	33.3	11.8	6.9	0.1	0.1	18.9	2.3
Profile 2											
1	40-80	4.3	0.14	17.9	28.0	12.0	15.4	1.2	0.5	28.8	1.1
2											
3	120-140	16.56	0.22	43.6	61.9	31.2	12.7	0.1	0.1	44.4	0.4
4											

Table 3. Acid properties of Vietnam acid sulfate soils.

Layer	Depth (cm)	pH (H ₂ O)	Exchange acidity (y ₁)	Contribution to exchange acidity			Soluble SO ₄ ²⁻ (me/100g)
				H ⁺	Al ³⁺	Fe ³⁺	
				(%)			
Profile 1				33	65		
1	40-80 0-40	3.0	68	49	51	2	40
2		3.4	48	20		0	31
3	120-130 80-120	3.1	321	83	26	73	17
4		2.7				57	7
Profile 2				64		4	
1	40-80 0-40	3.7	24	2	100	32	0
2		5.8				0	26
3		5.8	88		70	7	16
4	120-140 80-120	2.52	8	256	23	9	36
						55	89

Available phosphorus levels were very low. This is probably ascribed to the fixation of phosphorus under forms of iron and aluminum phosphates.

Acid sulfate soils are characterized by strong acidity (usually pH<4). These soil samples also had low pH(<3.7) and high exchange acidity (>24) except the second layer of profile 2 (Table 3). The acidity was weakest in the second layer and increased with depth. The contribution of H⁺, Al³⁺ and Fe³⁺ to the exchange acidity varied with layers. The contribution of Al³⁺ and H⁺ was great in the upper three layers, whereas that of Fe³⁺ was great in the fourth layer with the greatest acidity. The soil samples also contained very large amounts of soluble SO₄²⁻ and their amounts varied proportionally to the acidity. This indicates that the presence of aluminum and ferric sulfates is a main cause of the strong acidity of acid sulfate soils (Mai-thi-my-Nhung and Ponnampuruma, 1966; Moormann, 1963).

From the above experimental results, these acid sulfate soils are characterized by heavy texture, deficiency in available K and P, and strong acidity.

These characteristics have been generally detected by many researchers for acid sulfate soils (Bloomfield and Coulter, 1973; Tanaka and Navasero, 1966; Cate and Sukhai, 1964 ; Moormann, 1963; Pham-huu-Anh *et al.*, 1961) and would have serious effects on crop production.

III. CLAY MINERALOGICAL PROPERTIES OF VIETNAM ACID SULFATE SOILS

Objective

To investigate the clay mineral composition of Vietnam acid sulfate soils.

Materials and methods

Clay fractions ($<2\mu\text{m}$) were separated from the soil samples and their mineral composition was determined with deferrated and parallel-oriented specimens by x-ray diffraction method (Wada, 1966).

Results and discussion

The x-ray diffraction patterns of the clay fractions were generally similar for all layers of both profiles. Therefore, the diffraction patterns of the first layer of profile 1 are presented in Fig. 4 to represent the clay mineral composition which appears to be typical for soils in the Mekong delta.

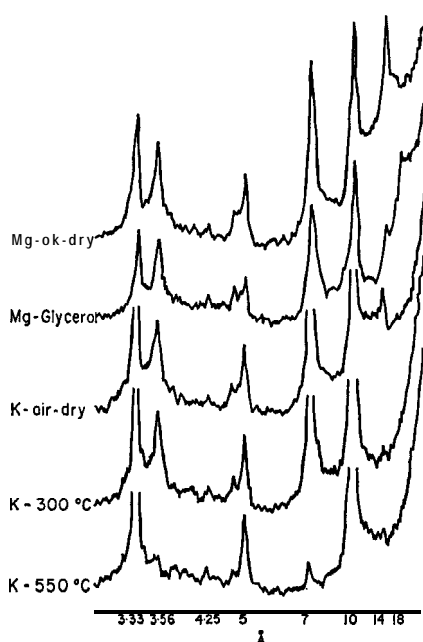


Fig. 4. X-ray diffraction patterns of the clay fraction of the first layer of profile 1.

Illite, identified by the 10 Å, 5 Å and 3.3 Å peaks in the Mg-saturated, air-dried and in all other specimens, existed in the most abundant amounts. In

addition to illite, an abundance of well-crystallized kaolinite was indicated by the very strong sharp peaks at 7.1 Å and 3.56 Å whose intensities were remarkably reduced upon heating to 550°C. There were minor amounts of montmorillonite identified by the 18 Å peak in the Mg-saturated, glycerol-solvated specimen; vermiculite by the enhanced 10 Å peak in the K-saturated, air-dried one; chlorite by the 14 Å peak persisted after heating at 550°C. Intergrade of chlorite-montmorillonite or chlorite-vermiculite was suggested by the 14 Å peak for the K-saturated, air-dried specimen and by the reduction of its intensity after heating at 300°C.

Quartz, identified by the 4.25 Å and 3.33 Å peaks, was present in small amounts for all layers. Estimated clay mineral contents of these soils are given in Table 4.

Table 4. Estimated clay mineral contents of Vietnam acid sulfate soils,

Layer	Depth (cm)	It	Kt	Mt	Vt	Ch	Qr
		(%)					
				Profile 1			
1	0-40	32	32	12	17	7	P
2	40-80	31	36	13	14	6	P
3		28	31	31	7	3	P
4	120-130 80-120	34	38	13*	11*	4	P
				Profile 2			
1	0-40	28	38	14	8	12	P
2	40-80	35	40	10	5		P
3		27	37	11*	10*	10	
4	120-140 80-120	22	36	16*	17*	15.9	P P

It, illite; Kt, kaolinite; Mt, montmorillonite; Vt, vermiculite; Ch, chlorite; Qr, quartz; P, present; * intergrade.

The clay mineral composition of these soils appears to be almost the same as that of acid sulfate soils in An-giang province of South Vietnam (Post and Sloane, 1971) and of some acid sulfate soils on the Guinea coast (Horn and Chapman, 1968). Their clay fractions consist mainly of illite and kaolinite with lesser amounts of montmorillonite, vermiculite and chlorite.

IV. EFFECTS OF SUBMERGING ON ELECTROCHEMICAL AND CHEMICAL CHANGES OF A VIETNAM ACID SULFATE SOIL

Objective

To study the effects of submerging on the electrochemical (pH and Eh) and chemical (Fe^{2+} and Al^{3+}) changes of Vietnam acid sulfate soil. The effects of addition of starch and CaCO_3 were also investigated. The results were compared with those of a Japan paddy soil.

Materials and methods

1) Soil samples

A mixture of the first and second layers of profile 1 was used. Some of its

properties are as follows: initial pH, 3.2; CEC, 31 me/100g; organic matter, 3.5 %; texture, HC. A Japan paddy soil sample was the Ap horizon of the soil collected at Kyushu Agricultural Experimental Station, with the following properties: initial pH, 5.6; CEC, 22 me/100 g; organic matter, 4.4 %; texture, CL.

2) **Treatments**

The treatments of Vietnam acid sulfate soil and Japan paddy soil samples are described in Tables 5 and 6, respectively. Starch was used as organic matter source. In Japan paddy soil, 50 ml of 0.12 N $\text{Al}_2(\text{SO}_4)_3$ was used to make artificial acid sulfate soil, because this quantity of $\text{Al}_2(\text{SO}_4)_3$ decreased its pH to the same level as that of the Vietnam acid sulfate soil sample.

Table 5. Treatments of Vietnam acid sulfate soil sample.

Treatments \ Plot	Original	+ Starch	+ CaCO_3
Air-dried soil (g)	25	25	25
Deionized water (ml)	50	50	50
CaCO_3 (g)	0	0	0.25
Starch (g)	0	0.25	0

Table 6. Treatments of Japan paddy soil sample.

Treatments \ Plot	Original	+ Starch	+ $\text{Al}_2(\text{SO}_4)_3$	+ $\text{Al}_2(\text{SO}_4)_3$ + Starch
Air-dried soil (g)	25	25	25	25
Deionized water (ml)	50	50	0	0
0.12N $\text{Al}_2(\text{SO}_4)_3$ (ml)	0	1	50	50
Starch (g)	0		0	1

3) **Submerging of soil samples and determination of pH, Eh, Fe^{2+} and Al^{3+}**

A soil sample was kept under submerged condition in a 100 ml centrifugal tube which was tightly packed with stopper and incubated at 25°C. Redox potential (Eh) and pH of soil samples were determined every day. In the determination of Eh, a platinum electrode was permanently seated 1 cm below the soil surface during incubation.

Every 5 g of the Vietnam acid sulfate soil samples which were kept submerged in test tubes at the same soil/water ratio was used to determine water-soluble and active Fe^{2+} , and water-soluble and exchangeable Al^{3+} at every 4 days. Every 2g of the Japan paddy soil samples in the same manner was used to determine active Fe^{2+} and exchangeable Al^{3+} at every 3 days. Active Fe^{2+} was extracted with 1N NaCH_3COO of pH 2.8 (Kumada and Asami, 1958) and exchangeable Al^{3+} with 1N KCl. Iron and aluminum were determined by atomic absorption spectroscopy.

Results and discussion

1) **pH**

Figure 5 shows pH changes during submergence. In Vietnam acid sulfate soil, pH of the original sample was very low (pH 3.2) and had almost no change

during submergence, similar to the results of Ponnampetuma et al. (1966), in which pH increased at an almost imperceptible rate from 3.6 to 4.7 after 16 weeks of submergence. Addition of starch had no effect on pH changes. The pH of the soil sample treated with CaCO_3 rapidly increased in the first week of submergence and then gradually decreased to about 5.8. The increase and decrease in pH are ascribed to the dissolution of CaCO_3 and the interaction of dissolved CaCO_3 and soil colloids, respectively (Nielsen, 1957).

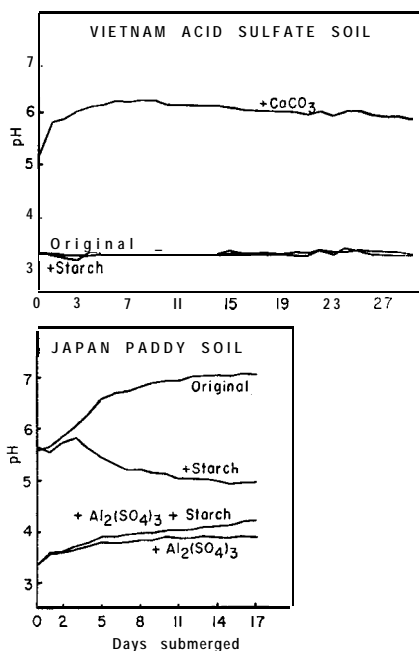


Fig. 5. Changes in pH during submergence.

In Japan paddy soil, pH of the original sample increased to about 7 during submergence, the ultimate pH value reached in submerged soils (Ponnampetuma, 1972). Addition of starch had a great effect on pH changes. The slight decrease in pH during the first day of submergence is probably due to the formation of carbonic acid derived from aerobic respiration of bacteria and its gradual decrease in the later periods due to the formation of organic acids.

The Japan artificial acid sulfate soil samples, made by addition of $\text{Al}_2(\text{SO}_4)_3$, showed a very gradual increase and then almost no change in pH during submergence, similar to that of the original and starch-treated Vietnam acid sulfate soil samples.

2) Eh

Eh changes during submergence are shown in Fig. 6. In Vietnam acid sulfate soil, Eh of the original sample decreased gradually during submergence and was positive (400 mV) even after one month of submergence. Addition of starch slightly decreased Eh of the system. Eh of the soil sample treated with

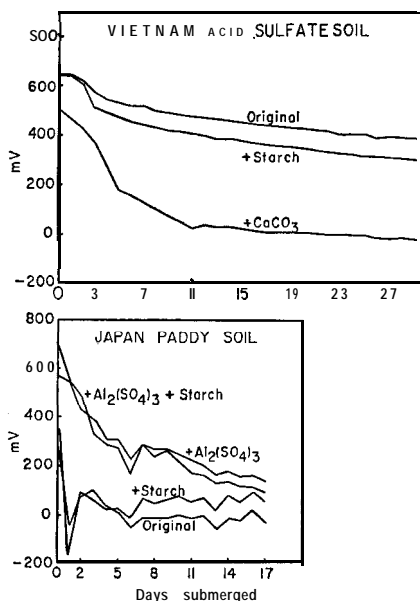


Fig. 6. Changes in Eh during submergence.

CaCO₃ dropped rapidly in the early stage of submergence and appeared to get stabilized in the region of 0 mV. This rapid drop in Eh would be ascribed to the rapid increase in pH rather than the quick development of reduction.

Eh of the original and starch-treated soil samples of Japan paddy soil dropped sharply and rose again within the first two days and then fixed in the region of 0 mV. These Eh changes are a common phenomenon observed in the submergence of aerobic soils (Ponnamperuma, 1972) and the initial rapid drop in Eh has been ascribed to the release of reducing substances accompanying oxygen depletion (Ponnamperuma, 1972) or the production of hydrogen gas occurred by the decomposition of organic matter (Yamane and Sato, 1968). Addition of Al₂(SO₄)₃ caused gradual decrease in Eh, similar to that of the acid sulfate soil samples.

3) Fe²⁺

Changes of water-soluble and active Fe²⁺ of Vietnam acid sulfate soil are shown in Fig. 7. Amounts of water-soluble and active Fe²⁺ of the original soil sample gradually increased during submergence. Addition of starch increased both forms of Fe²⁺. But, active Fe²⁺ of the soil sample treated with CaCO₃ was present in considerable amounts, whereas water-soluble Fe²⁺ was very small. The latter is probably due to the precipitation of water-soluble Fe²⁺ as Fe(OH)₂.

Changes of active Fe²⁺ of Japan paddy soil are shown in Fig. 8. Amounts of active Fe²⁺ of the original soil sample markedly increased during submergence. Addition of starch slightly increased active Fe²⁺. Active Fe²⁺ increase was retarded by addition of Al₂(SO₄)₃ and this retardation was more marked in the soil sample without starch.

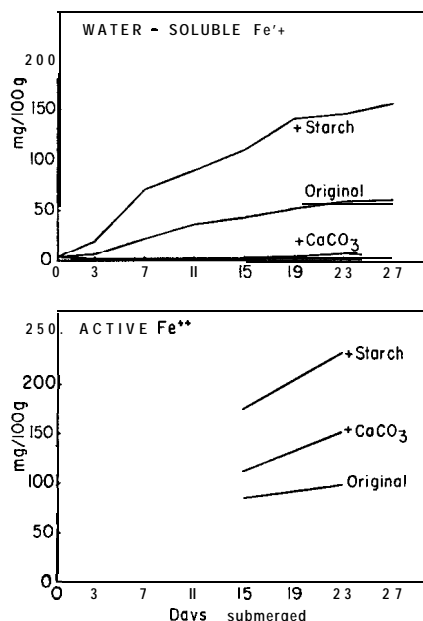


Fig. 7. Changes in Fe²⁺ of Vietnam acid sulfate soil during submergence.

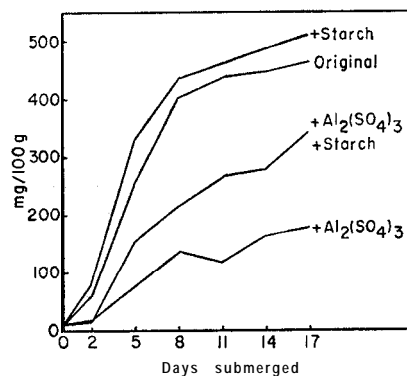


Fig. 8. Changes in active Fe²⁺ of Japan paddy soil during submergence.

4) Al³⁺

In Vietnam acid sulfate soil (Fig. 9), water-soluble and exchangeable Al³⁺ of the original soil sample had no change during submergence. Addition of starch slightly decreased their amounts. Both forms of Al³⁺ were disappeared by addition of CaCO₃.

In Japan paddy soil, exchangeable Al³⁺ was not found in the original and starch-treated soil samples. Aluminum added to make the artificial acid sulfate soil (216 mg/100 g) was not completely extracted with 1N KCl and the extracted amounts gradually decreased during submergence (Fig. 10). This is maybe due

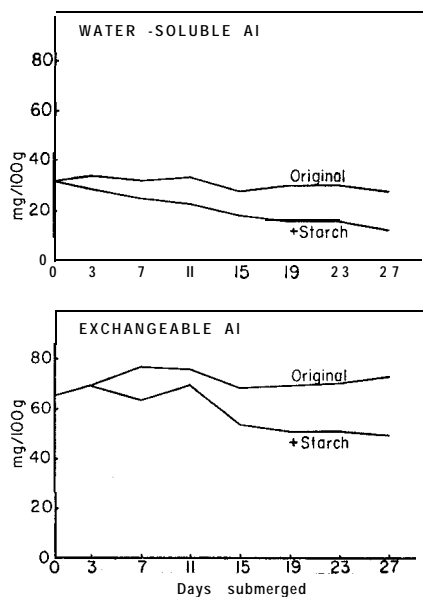


Fig. 9. Changes in Al^{3+} of Vietnam acid sulfate soil during submergence.

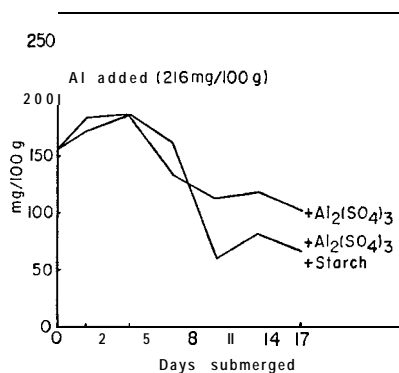


Fig. 10. Changes in exchangeable Al^{3+} of Japan paddy soil during submergence.

to the precipitation of Al^{3+} as $\text{Al}(\text{OH})_3$ or the conversion of Al^{3+} ions to polymerized hydroxy-Al ions.

When an aerobic soil is submerged, its Eh decreases during the first few days and gets stabilized to a value characteristic of the soil, followed by the increase of reduced substances. Comparison of the development of reduction between Vietnam acid sulfate soil and Japan paddy soil indicates that the rate of reduction is slower in Vietnam acid sulfate soil than in Japan paddy soil. This was confirmed by addition of $\text{Al}_2(\text{SO}_4)_3$ to Japan paddy soil. The slow development of reduction in Vietnam acid sulfate soil is maybe ascribed to poor

activity of microorganisms, especially bacteria, due to its strong acidity. Addition of starch caused a quickness of the development of soil reduction and as a result a considerable increase in Fe^{2+} . It had almost no effect on soil acidity. Addition of CaCO_3 decreased the acidity of acid sulfate soil and caused the precipitation of Fe^{2+} and Al^{3+} .

V. CONCLUSION

From the above mentioned data, we can conclude that:

1. Vietnam acid sulfate soils are heavy clayey and extremely acid. They are deficient in nutrients such as K and P.
2. Their clay fraction consists mainly of illite and kaolinite with lesser amounts of montmorillonite, vermiculite and chlorite.
3. They show a retarded development of soil reduction during submergence, as compared with Japan paddy soil.
4. Addition of CaCO_3 is more effective in the decrease of the acidity and the toxicity due to iron and aluminum.

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